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Spectroscopic detection of single  $Pr^{3+}$  ions on the  ${}^{3}H_{4}-{}^{1}D_{2}$  transition

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#### Abstract

Rare earth ions in crystals exhibit narrow spectral features and hyperfine-split ground states with exceptionally long coherence times. These features make them ideal platforms for quantum information processing in the solid state. Recently, we reported on the first high-resolution spectroscopy of single  $Pr^{3+}$  ions in yttrium orthosilicate nanocrystals via the  ${}^{3}H_{4} - {}^{3}P_{0}$  transition at a wavelength of 488 nm. Here we show that individual praseodymium ions can also be detected on the more commonly studied  ${}^{3}H_{4} - {}^{1}D_{2}$  transition at 606 nm. In addition, we present the first measurements of the second-order autocorrelation function, fluorescence lifetime, and emission spectra of single ions in this system as well as their polarization dependencies on both transitions. Furthermore, we demonstrate that by a proper choice of the crystallite, one can obtain narrower spectral lines and, thus, resolve the hyperfine levels of the excited state. We expect our results to make single-ion spectroscopy accessible to a larger scientific community.

#### 1. Introduction

Rare earth ions are ubiquitous in many technologies such as solid-state lasers, amplifiers for optical telecommunication, and magnetic materials. They have also played a central role in the development of high-resolution laser spectroscopy methods such as hole burning and photon echo [1]. Transitions to the lowest lying excited states of an isolated rare earth ion take place within its 4f-shell and are dipole-forbidden. In a solid matrix, however, these transitions become weakly probable with long excited-state lifetimes up to milliseconds. Moreover, because the 4f-intrashell electrons are well shielded by the outer electrons, they are less sensitive against environmental perturbations, resulting in long spin coherence times of the order of hours [2]. In addition, they possess transitions at various wavelengths in the visible and near infrared, where optical detectors are very sensitive. Furthermore, they are optimally photostable even at room temperature and high excitation powers.

The combination of the above-mentioned features makes rare earth ions also very appealing for emerging applications in quantum information processing. Here, one would often like to access quantum states of well-defined spin via optical interactions and have the possibility of storing qubits for long times. In fact, a number of interesting effects have recently been demonstrated in rare earth-doped bulk crystals [3–8]. For the ultimate control of quantum states at the levels of single material and light particles, however, it is desirable to detect and manipulate single rare earth ions. Interestingly, although rare earth ions have been on the wish list of single particle microscopy and spectroscopy since the mid 1980s, this goal was only very recently achieved [9–14].

#### 2. Brief review of our previous results and new narrower spectra in microcrystals

Room-temperature detection of single emitters in the condensed phase requires extremely low concentrations so that neighboring ions are separated by more than the spatial resolution of the imaging system. Under cryogenic conditions, however, one can address individual emitters by tuning the frequency of a narrow-band



**Figure 1.** (a) Fluorescence excitation spectra of ions addressed via the  ${}^{3}H_{4} - {}^{3}P_{0}$  (blue) transition at 488 nm and the energy level scheme. The scan speed was 4 MHz s<sup>-1</sup>. Within our detection spectral range, the  ${}^{3}P_{0}$  state can directly decay into  ${}^{3}H_{6}$  and  ${}^{3}F_{2}$  levels or relax via the  ${}^{1}D_{2}$  state, which decays into the crystal field levels of the  ${}^{3}H_{4}$  ground state. (b) Same as in (a) but with the excitation laser tuned to the  ${}^{3}H_{4} - {}^{1}D_{2}$  transition from the lowest crystal field level at 606 nm. The scan speed was 5 MHz s<sup>-1</sup>. The measured fluorescence is collected at > 608 nm which corresponds to a decay into higher crystal field levels of  ${}^{3}H_{4}$ . The polarization of the excitation light was rotated by 90° with respect to the previous blue excitation. (c) Excitation spectrum of a single ion. The three hyperfine levels of the  ${}^{3}H_{4} - {}^{1}D_{2}$  state separated by 4.6 and 4.8 MHz are not resolved.

laser through the inhomogeneous band of the sample even if the concentration is higher by a few orders of magnitude. In this scheme, every time an emitter becomes resonant with the excitation light, it fluoresces. This signal can be detected on a low background because the other emitters in the excitation volume do not absorb light at that frequency. In our previous work [12], we employed this method pioneered by Moerner and Orrit for the detection of single molecules [15, 16] to detect single Pr<sup>3+</sup> ions in Y<sub>2</sub>SiO<sub>5</sub> yttrium orthosilicate (YSO). As illustrated in the energy level scheme of figure 1(a), we used the <sup>3</sup>H<sub>4</sub>-<sup>3</sup>P<sub>0</sub> transition at a wavelength of 488 nm (blue). The figure shows an example of the excitation spectra of several individual ions over 4 GHz.

Because of a limited access to samples with suitable concentration, in that work we used YSO nanocrystals to keep the background fluorescence to a manageable level. The spectral diffusion caused by the cracks and surface defects in these samples resulted in the broadening of the resonances from the lifetime-limited linewidth of 82 kHz to several MHz [17, 18]. As a result, the hyperfine levels of the excited state could not be resolved. Furthermore, the weak signal of only tens of photon counts per second prevented us from performing various studies, which we now present in this article. In our current work we have increased our signal level beyond 500 counts per second (see figure 1(a)) by using a single photon counting module (SPCM) with a significantly higher quantum efficiency but also a higher dark count rate. This leads to faster measurement times and an overall 1.8-fold improvement of the signal-to-noise ratio.



**Figure 2.** (a) An excitation spectrum of a single ion resolving the three hyperfine levels of the  ${}^{3}P_{0}$  state. This spectrum is the average of the individual spectra shown in (b). The fit (red curve) accounts for a linear background component and yields a linewidth of 1.26 MHz. The splitting ordering of -5.65 and +2.96 MHz confirms our previous assignment [12]. (b) 20 consecutive traces recorded with an integration time of 0.1 s per frequency sample. To arrive at the spectrum in (a), the scans were manually aligned in frequency to compensate for spectral diffusion between scans. The color scale shows the recorded counts per second.

We now provide new spectra recorded in larger YSO crystallites (diameter  $1-5 \mu$ m) with a praseodymium doping level of 0.0001%, which is 50 times lower than that of the nanocrystals used earlier. As sketched in the inset of figure 2(a), the frequencies of three laser beams detuned by the energy differences of the ground-state hyperfine levels are scanned synchronously. The three peaks in figure 2(a) show that the hyperfine levels of the <sup>3</sup>P<sub>0</sub> state of a single ion are resolved. The measured separations of 5.65 and 2.96 MHz are in very good agreement with bulk hole-burning spectra presented in our previous publication [12]. A fit to the spectrum composed of three Lorentzian functions yields a transition linewidth of 1.3 MHz, which is considerably smaller than what we obtained in our former study [12].

Figure 2(b) reveals that although the fast components of the spectral diffusion have been reduced, a certain level of slow diffusion remains on the time scale of minutes. The fact that the dynamics of transitions to all three hyperfine levels are correlated indicates that the diffusion is not caused by spin instabilities. We find it unlikely that the slow resonance frequency variations are caused by temperature changes at the sample because we monitor and maintain the temperature of the cold finger at 4.3 K. In future experiments, we should be able to eliminate spectral diffusion fully by optimizing the YSO crystal size and quality.

#### **3. Detection of single ions on the** ${}^{3}\text{H}_{4}$ – ${}^{1}\text{D}_{2}$ transition

The great majority of bulk studies on Pr:YSO have been reported for the  ${}^{3}H_{4}-{}^{1}D_{2}$  transition (see the level scheme in figure 1(b)) at a wavelength of 606 nm (red) with a natural linewidth of about 1 kHz [3, 4, 7, 19–21]. Our original motivation for working on the  ${}^{3}H_{4}-{}^{3}P_{0}$  transition was the shorter fluorescence lifetime of the  ${}^{3}P_{0}$  state and, thus, a broader transition, which makes the requirements on the laser linewidth less stringent. Considering that our current state of the art in linewidth is limited to about 1 MHz by spectral diffusion, we decided to set up a new dye laser system (without frequency stabilization) to see whether it would also be possible to detect single ions via the  ${}^{3}H_{4}-{}^{1}D_{2}$  transition.

As in the case of [12], sidebands at -10.19 and +17.3 MHz were added to the center excitation laser frequency to prevent shelving of the population in other hyperfine levels of the ground state. Furthermore, we



**Figure 3.** Temporal distribution of the photons arrival times from single ions with a bin size of 100 ns at the excitation wavelength of 488 nm (a) and a bin size of 1  $\mu$ s at the excitation wavelength of 606 nm (b). (c), (d) Display the second-order autocorrelation function  $G^{(2)}$  normalized by the peak height of single ions studied in (a) and (b) integrated for 2.5 (blue) and 4 (red) hours, respectively. Afterpulsing probability was  $\approx 0.1\%$ . The detector deadtime of 42 ns only affects the first bin and was omitted for the analysis. Since all photons in the time tagged photon collection were used to calculate correlation events, the data are symmetric about  $\tau = 0$  ms. The red lines represent fits to the data which are used for normalization and determination of  $g^{(2)}(0)$ .

employed a longpass filter designed for 609 nm with a 4 nm edge to suppress the excitation light. Figure 1(b) shows an example of sharp resonances obtained when sweeping the frequency of the excitation laser over 4 GHz, whereas figure 1(c) displays a zoom of the excitation spectrum of a single ion. These measurements were performed in the very same nanocrystal that was used for our previous work [12]. As a result, the hyperfine levels of the  ${}^{3}\text{H}_{4}$ – ${}^{1}\text{D}_{2}$  state separated by 4.6 and 4.8 MHz are not resolved [22].

#### 4. Antibunching and fluorescence lifetime measurements

A robust proof that the fluorescence signal at each resonance stems from a single emitter can only be provided by the observation of strong antibunching in the second-order autocorrelation function  $G^{(2)}(\tau)$  of the emitted photons. Commonly, the short fluorescence lifetimes of molecules, quantum dots or color centers in the nanosecond regime are comparable with the afterpulsing and deadtimes of SPCMs. To get around this problem, one uses a Hanbury Brown–Twiss configuration and searches for a lack of coincidences on two detectors within short time intervals. The long lifetimes of the excited states in rare earth ions permit, however, to use a single SPCM.

First, we present measurements of the fluorescence lifetime decay. To obtain these data, we tuned the frequency of the excitation laser beam to a narrow resonance (see figure 1) and used an AOM to pulse the excitation light with pulse duration and repetition period of 5  $\mu$ s and 1.5 ms, respectively. The average laser power was set to achieve 10% of the continuous-wave fluorescence. The fluorescence was detected with the SPCM and the photons were time-tagged with a time-correlated single photon counting system. Figure 3(a) displays the fluorescence lifetime curve of the <sup>3</sup>P<sub>0</sub> state from a single ion. The red curve shows a double-exponential fit with 1/*e* times of 2 and 162  $\mu$ s, which can be attributed to the decay directly from the <sup>3</sup>P<sub>0</sub> state and indirectly via the <sup>1</sup>D<sub>2</sub> state, respectively. These findings are in good agreement with the results of bulk studies [19, 23].

Figure 3(b) shows the same measurement as in (a) but for an ion detected on the red transition. This decay curve was also fitted with two exponentials, yielding 1/e times of 25 and 277  $\mu$ s. The long component has a weight of about 96%, which we attribute to the lifetime of the  ${}^{1}D_{2}$  state. Interestingly, 277  $\mu$ s is about 1.7 times longer than the value expected for this state in the bulk. This difference might be caused by the local





inhomogeneities of the environment in a similar fashion that single dye molecules show varying fluorescence lifetimes in dielectrics with disorder [24]. Furthermore, the spontaneous emission rate is also sensitive to the local density of states and can be slowed down in subwavelength dielectric geometries [25, 26]. Access to such variations at the level of individual emitters is one of the fundamental advantages of single-ion spectroscopy. In our current work, we found that the lifetimes do vary from ion to ion in the nanocrystal. However, a proper quantitative investigation of this effect requires further studies. We also note that the weight of the contribution of the shorter lifetime component only amounts to 4%. We could not localize the source of this weak trace of fluorescence.

To generate clean autocorrelation functions, we removed all photons arriving within 7  $\mu$ s of the leading pulse edge and chose time bins of 5 and 25  $\mu$ s for the blue and red transitions, respectively. The center bin at  $\tau = 0$  was discarded to remove the majority of the SPCM afterpulses. Figure 3(c) shows the resulting photon correlation for excitation via the blue transition. The measured histograms were fitted by a piecewise exponential decay and rise function with baseline, overall peak and zero-peak heights as variable parameters. The data were further normalized to set the baseline and the peaks of the fit to 0 and 1, respectively. We note that the data for the blue and the red transitions were not recorded on the same ion (see section 5). The measurement on the red channel is somewhat noisier because of a lower fluorescence collection efficiency since the decay into the lowest crystal field of <sup>3</sup>H<sub>4</sub> is filtered out. The resulting values of  $g^{(2)}(0) = 0.07$  and 0.36 are well below 0.5, confirming that in each case the fluorescence stems from a single ion. More importantly, these measurements show that despite the fact that rare earth ions are orders of magnitude weaker than other emitters such as alkali atoms, molecules, quantum dots or color centers, it is possible to study their photon statistics, which is an important quantity for quantum optical investigations.

#### 5. Polarization dependence

Having demonstrated the feasibility of single-ion spectroscopy on the  ${}^{3}H_{4} - {}^{1}D_{2}$  and  ${}^{3}H_{4} - {}^{3}P_{0}$  transitions, we asked whether it was possible to address the same ion through both channels. Here, one might hope to identify the same spectral landscapes (see figure 1) within the inhomogeneous band of the two transitions. However, after an extended effort, we found no correlation between them. Furthermore, we found that spectral holes burnt in a bulk sample at 488 nm could not be addressed by light at 606 nm and vice versa. We, thus, suspected that each ion experiences different local electromagnetic environments at the two transition wavelengths. Investigations of the polarization behavior of the two excitation channels shed light on this hypothesis.

The blue (top) and red (bottom) maps in figure 4 display the inhomogeneous spectral spread for the transitions  ${}^{3}H_{4} - {}^{3}P_{0}$  and  ${}^{3}H_{4} - {}^{1}D_{2}$  as a function of the excitation polarization. The measurements were performed by focusing the laser beams at a few micrometers below the surface of a bulk crystal without using a solid-immersion lens. We clearly see that the maxima of the two channels are offset by 90°. The orthogonality of the dipole moments associated with the two transitions implies that they are influenced by different components





of the local crystal fields and fluctuations [27]. As a result, one cannot expect any correlation between the details of the spectra within the two inhomogeneous distributions.

#### 6. Emission spectroscopy

Next we turn to the emission spectra of single ions. To record such data, we sent the collected fluorescence to a grating spectrometer equipped with a peltier-cooled EM-CCD camera. The spectra were integrated over 2 s and accumulated 800 times, whereby we occasionally corrected for drifts between the laser frequency and the ion resonance. The fluorescence background was registered by repeating the measurement with the laser frequency detuned from the ion resonance by 50 MHz. Figure 5 shows the single ion spectra for the blue (a) and red (b) transitions. Considering the weak fluorescence rate and the strong dispersion of the emitted photons in a grating spectrometer, such measurements require long integration times and, thus, a high degree of spectral stability.

To identify the origins of the individual peaks, we have also recorded spectra obtained from a bulk sample (0.005% Pr-doping). Figures 5(c), (d) display these spectra recorded with optimum excitation polarization for the respective transitions (see section 5) and detection polarizations along the crystal axes  $D_1$  (cyan) and  $D_2$  (magenta). Each peak is attributed to a transition in agreement with previously published data [19, 28]. We find a clear correspondence between the single-ion and ensemble measurements for each spectral feature although the relative peak heights differ substantially. Here, it is important to note that the emission intensities of different transitions are strongly polarization dependent. In the case of single-ion spectra, the arbitrary orientation of the host crystallite and the strong polarization-dependent coupling of the emission into the solid-immersion lens make it difficult to quantify the relative peak heights.

#### 7. Conclusion

In the present work we have reported on the first detection and spectroscopy of single praseodymium ions via the  ${}^{3}H_{4}-{}^{1}D_{2}$  transition, which has been most widely used in ensemble measurements. In addition, we have demonstrated narrower linewidths than the previous report of single ion spectroscopy [12], allowing us to resolve the hyperfine levels of the  ${}^{3}P_{0}$  state. Furthermore, we have presented several new measurements that are usually desirable at the single-emitter level. These include the measurement of the fluorescence lifetime, autocorellation function and strong photon antibunching as well as emission spectra of single ions. Finally, we have examined the polarization dependence of the excitation and emission channels and have provided evidence that a given ion experiences different local fields and frequency shifts on its various transitions. The findings of this work further fuel the recent emergence of activities on the detection and spectroscopy of rare earth systems at the single-ion level [9–14].

#### References

- [1] Liu G and Jacquier B 2005 Spectroscopic Properties of Rare Earths in Optical Materials (Berlin: Springer)
- [2] Zhong M, Hedges M P, Ahlefeldt R L, Bartholomew J G, Beavan S E, Wittig S M, Longdell J J and Sellars M J 2015 Nature 1517 177-80
- [3] Klein J, Beil F and Halfmann T 2007 Phys. Rev. Lett. 99 113003
- [4] Afzelius M et al 2010 Phys. Rev. Lett. **104** 040503
- [5] Hedges M P, Longdell J J, Li Y and Sellars M J 2010 Nature 465 1052–6
- [6] Sabooni M, Beaudoin F, Walther A, Lin N, Amari A, Huang M and Kröll S 2010 Phys. Rev. Lett. 105 060501
- [7] Heinze G, Hubrich C and Halfmann T 2013 Phys. Rev. Lett. 111 033601
- [8] Riëlander D, Kutluer K, Ledingham P M, Gündoğan M, Fekete J, Mazzera M and de Riedmatten H 2014 Phys. Rev. Lett. 112 040504
- [9] Kolesov R, Xia K, Reuter R, Stöhr R, Zappe A, Meijer J, Hemmer P R and Wrachtrup J 2012 Nat. Commun. 3 1029
- [10] Yin C, Rancic M, de Boo G G, Stavrias N, McCallum J C, Sellars M J and Rogge S 2013 Nature 497 91–94
- [11] Kolesov R, Xia K, Reuter R, Jamali M, Stöhr R, Inal T, Siyushev P and Wrachtrup J 2013 Phys. Rev. Lett. 111 120502
- [12] Utikal T, Eichhammer E, Petersen L, Renn A, Götzinger S and Sandoghdar V 2014 Nat. Commun. 5 3627
- [13] Siyushev P et al 2014 Nat. Commun. 5 3895
- [14] Nakamura I, Yoshihiro T, Inagawa H, Fujiyoshi S and Matsushita M 2014 Sci. Rep. 47364
- [15] Moerner W E and Kador L 1989 Phys. Rev. Lett. 62 2535-8
- [16] Orrit M and Bernard J 1990 Phys. Rev. Lett. 65 2716-9
- [17] Perrot A, Goldner P, Giaume D, Lovrić M, Andriamiadamanana A, Gonçalves R R and Ferrier A 2013 Phys. Rev. Lett. 111 203601
- [18] Meltzer R S and Hong K S 2000 Phys. Rev. B 61 3396
- [19] Equall R W, Cone R L and Macfarlane R M 1995 Phys. Rev. B 52 3963–9
- [20] Nilsson M, Rippe L, Kröll S, Klieber R and Suter D 2004 Phys. Rev. B 70 214116
- [21] Fraval E, Sellars M J and Longdell J J 2005 Phys. Rev. Lett. 95 030506
- [22] Longdell J J, Sellars M J and Manson N B 2002 Phys. Rev. B 66 035101
- [23] Kuleshov N V, Shcherbitsky V G, Lagatsky A A, Mikhailov V P, Minkov B I, Danger T, Sandrock T and Huber G 1997 J. Lumin. 71 27–35
- [24] Donley E A and Plakhotnik T 2001 J. Chem. Phys. 114 9993
- [25] Schniepp H and Sandoghdar V 2002 Phys. Rev. Lett. 89 257403
- [26] Rogobete L, Schniepp H, Sandoghdar V and Henkel C 2003 Opt. Lett. 19 1736–8
- [27] Macfarlane R M and Shelby R M 1987 Spectroscopy of solids containing rare earth ions *Coherent Transient and Holeburning* Spectroscopy of Rare Earth Ions in Solids ed A A Kaplyanskii and R M Macfarlane (Amsterdam: North-Holland)
- [28] Holliday K, Croci M, Vauthey E and Wild U 1993 Phys. Rev. B 47 14741-52