Photophysics of Nitrogen Vacancy centres in Nanodiamonds

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Abstract

NVs are cool because they do cool sciency stuff. All cool stuff comes from NV-. People use 532 excitation to increase charge polarisation so they can optimise cool stuff and neglect NV0. They looked at it with only one excitation wavelength at a time. Clearly charge polarisation depends on wavelength. So clearly quenching must occur with second wavelength. Must understand all of this stuff to intergrate NVs into other systems that use lasers.

INTRODUCTION

The Nitrogen Vacancy (NV) centre is is a point defect consisting of a nitrogen-vacancy lattice pair embedded along the [111] axis of a diamond (???ref1). The NV centre has two stable charge states, the neutral charge state (NV^0) and the negatively charged state (NV^-), with photo-induced interconversion between these two states (???ref2). The NV^- charge state is an intensively studied material that has shown a wide range of applications in both Physics and Biology due to it's high stability and interesting optical properties. Biologists have used them extensively for biolabelling and imaging of internal biological structures (???ref3 and 4). Meanwhile, Physisits have been investigating their use in a wide range of nanoscale sensing and quantum sensing applications(???ref5). By exploiting the quantum mechanical interactions of the defects internal spin state, room temperature quantum effects can be observed in the NV^- centre providing a platform to study a wide variety of quantum manipulation protocols (???ref6). However, these desirable effects rely solely on the properties arising from the NV^- charge state and in most applications the excitation wavelength is chosen to be around 510-540nm, as this region was shown to have the highest charge state polarisation (ref7???). By using a single optimised excitation wavelength the impact of the neutral charge state NV^0 could be neglected despite the optimal charge state polarisation limited at 75%.

In cases where only the single excitation laser is used the NV centre has been long stated to be extremely robust, with no bleaching or blinking under normal conditions(ref8???). However, in many cases once a second probe laser is used in an experiment the fluorescence of the NV centre is dramatically quenched(ref9???), preventing further applications and systems that require additional laser wavelengths. The quenching of fluorescence has been observed and described by numerous potential mechanisms, including (list here???1). In contrast to many of these mechanisms we are collecting the fluorescence of both charge states as well as probing in a non resonant continuous-wave regime of a few 10s of milliwatts eliminating many of the above mechanisms that rely transient mechanisms or high intensities fields.

In this paper we investigate the quenching effects of the NV centre fluorescence in order to provide insight into the charge and spin state photo-dynamics. Our process is to measure the quenching dynamics of the NV centre under steady state illumination and using established physics of the NV centre in order to develop a rate equation model that describes the potential photo-physics of the system. Using this model various assumptions are analysed in order to determine their validity and the most likely model is determined by the Aikike information criteria. We believe this new rate equation model indicates the underlying physics that leads to the quenching of fluorescence that has been observed in the NV centre. By understanding the corresponding rates and processes we aim to apply particular initialisation processes to increase the spin and charge state polarisation of the NV centre. This will lead to direct enhancements of applications such as STED like imaging and for enhancing state preparation for NV based quantum technologies.

★ I should also include some of our conclusions, Don't bury the lede! ★ Should I add examples of further applications and systems that require additional laser wavelengths

Negatively Charge State

The energy level diagram of the negatively charged NV^- centre can be observed in Fig. 3.

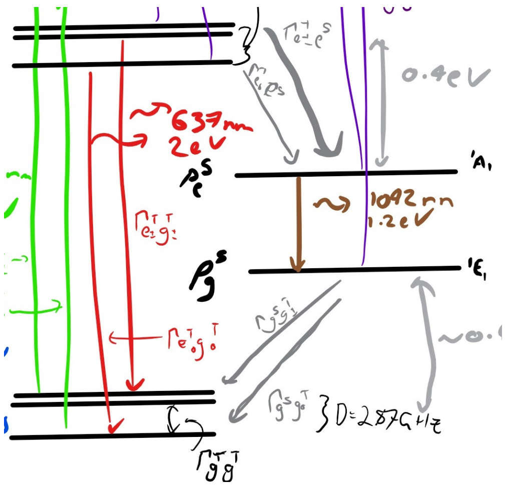

FIG. 1: Energy levels of the NV$^-$ centre.

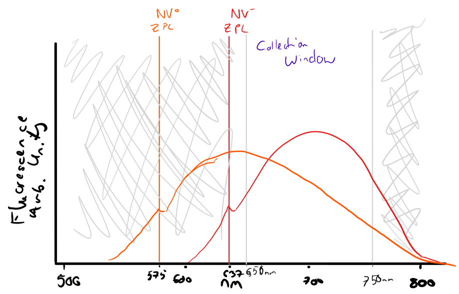

FIG. 2: Fluoresence profiles of NV charge states

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The NV$^-$ consists of a ground triplet state $^3A_2$ and an excited triplet state ^3E, as well as two metastable singlet states $^1E_1$ and $^1A_1$ ref11???. Within the spin triplet states the $m_s = 0$ ans $m_s = \pm 1$ spin states are split in energy at zero magnetic field by $D = 2.87\,\mathrm{GHz}$ for the ground triplet and $D = 1.42\,\mathrm{GHz}$ for the excited triplet (Ref12???). The spin transition rate between the ground $m_s = 0$ ans $m_s = \pm 1$ spin states is given by the spin-lattice relaxation time T_1 and has been measure to be $\approx 6\,\mathrm{ms}$ at room temperature and zero magnetic field (ref13???). This spin mixing rate can be dramatically increased by appling a large magnetic field in the vicinity of the NV centre ref14???.

★ I AM BEING VAGUE ABOUT THE SPIN MIXING RATE BECAUSE BECAUSE I BELIEVE THE CURRENT EXPLANATION OF ZEEMAN SPLITTING THE SPIN SUBLEVELS HAS HOLES IN IT. ASK ME FOR MORE INFO OR LOOK AT COMMENT IN TEX FILE

The principle zero-phonon line between the $^3A_2$ and ^3E is centred at 637nm and can be efficiently excited with spin conservation at most wavelengths below 640nm (ref15???). The radiative lifetime of the excited state is 13 ns for NV centres in bulk diamond (ref16???) and approximately 25 ns for NV centres in nanodiamonds (ref17???). Only a few percent of the Fluorescence is emitted at the ZPL, most fluorescence appears in the phonon side bands between 600 and 800nm as shown in Fig. 2.

The excited triplet states can also decay to the excited singlet state, the rate from the $m_s = \pm 1$ excited triplet state is $2\pi \times 9.4 \times 10^6\mathrm{GHz} = 16.9\,\mathrm{ns}$, whereas the rate from the $m_s = 0$ excited triplet state is almost an order of magnitude smaller at $2\pi \times 1.8 \times 10^6\mathrm{GHz} = 88.4\,\mathrm{ns}$ (ref18???). Whilst it not completely understood why there is a large discrepancy between these decay channels it is noteworthy that this discrepancy is what leads to many of the interesting optical properties of the NV centre. It causes a difference in fluorescence intensity between the two excited spin states which in turn leads to a mechanism for an all optical readout of the centres internal spin state. The excited singlet state has a lifetime of $\approx 1ns$ (ref19???) and populates the longer lived ground singlet state and it has been shown to emit fluorescence at a ZPL of 1042 nm ref20???. The longer lived ground metastable state has a lifetime of 150 ns and decays into the ground the triplet spin state ref21???. It was commonly believed that this population decayed only into the $m_s = 0$ spin state, however a recently this is being challenged and it has been claimed that the decay into the ground triplet has a spin state ratio closer to $\frac{m_s=0}{m_s=\pm 1} = 1.1 - 2$ ref22???.

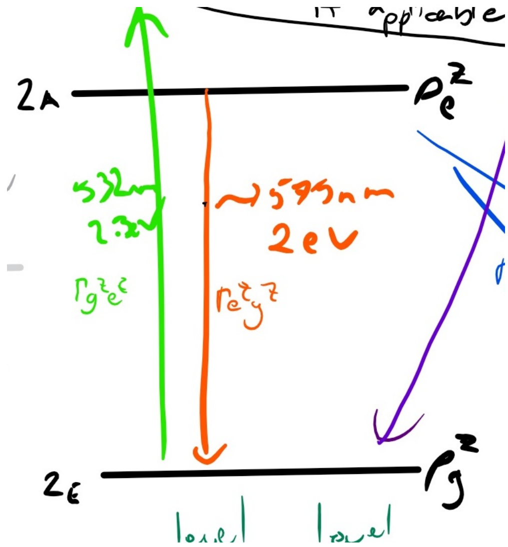

FIG. 3: Energy levels of the NV$^-$ centre.

Neutral Charged State

As opposed to the rigorous study the NV$^-$ charge state has received the NV^0 charge state has often been neglected. However in order to study the NV centre as a whole it must be included. We use the established three level model to describe its intrinsic dynamics. The energy level diagram of the neutral charged NV^0 centre can be observed in Fig. **??**.

The NV^0 charge state consists of of a ground doublet ^2E and an excited doublet ^2A with a ZPL at 575 nm = 2.156 eV. It can be efficiently excited at most wavelengths below 675 nm ref23??? and has a radiative lifetime of $\Gamma_{e^Z g^Z} = 19 \times 2$ns ref26???. The exact excitation cross section is unknown, however, the ratio of excitation cross sections between NV^0 and NV$^-$ can be measured by looking at their relative emission intensities. In addition, since the quantum efficiency of NV^0 and NV$^-$ is ≈ 1 then the ratio of excitation cross sections is given by the ratio of emission cross sections giving $\Gamma_{g^Z e^Z} = \frac{1}{3}\Gamma_{g^T e^T}$ ref25???. Differing from NV$^-$, NV^0 does not have detectable magnetic resonances associated with its degenerate spin doublet ground and excited states ref24???. Only a few percent of the Fluorescence is emitted in the ZPL, whereas most fluorescence appears in the phonon side bands between 550 and 750nm. However, no ODMR or optical readout of this metastable quartet have been measured and it is expected to have negligible impact on the photo-physics of the NV centre and as such has been neglected from our analysis. ★ This statement was true as of February 2013, I need to ensure that this is still true.

★ I think I doubled this value because NV- lifetimes were doubled in ND as compared to bulk and the lifetime I found was in Bulk diamond. Either need to find value for ND's or argue that it should also increase the same way as NV- did...

Ionisation & Recombination

To convert between the two charge states we need to examine both the Ionisation process from NV$^-$ to NV^0 and the recombination process from NV^0 to NV$^-$. The desirable effects of the NV centre rely solely on the properties arising from the NV$^-$ charge state and as a result a standard $\approx$ 532 nm excitation laser used in NV centre applications is chosen so that it produces the highest charge state polarisation in an effort to optimise the effect and allow any effects due to the NV^0 charge state to be neglected (ref7???). However, any additional laser is going to alter this maximised charge state polarisation.

Ionisation Process

Ionisation from NV- to NV0 occurs in a two step process as shown in Fig. 4.

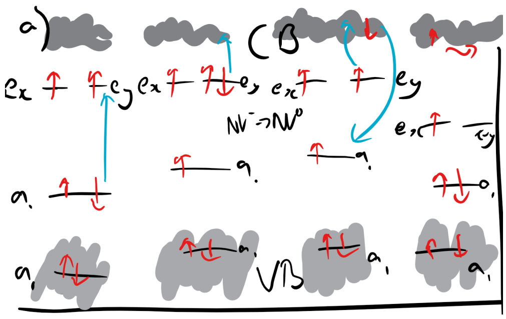

FIG. 4: **Ionsation Processes. a,** Ionisation from NV$^-$ to NV^0 electron view **b,** Ionisation pathways traditional view.

First a photon must excite an electron into the excited ^3E state of the NV$^-$. The electron can then be excited again into the conduction band leading to an Auger ionisation process which strips an electron from the centre converting it into the NV^0 charge state in its ground state configuration (ref28???). This two step process has only been investigated with a single excitation laser which leads to an ionisation rate that is quadratic with excitation power and can no longer occur at wavelength greater than the ZPL of the transition. However, this process can be mediated by two lasers, one that strongly excites the transition and one that strongly ionises the electron leading to the Auger ionisation process.

Recombination Process

The recombination process from NV^0 to NV$^-$ also occurs in a two step process which is shown in Fig. 5.

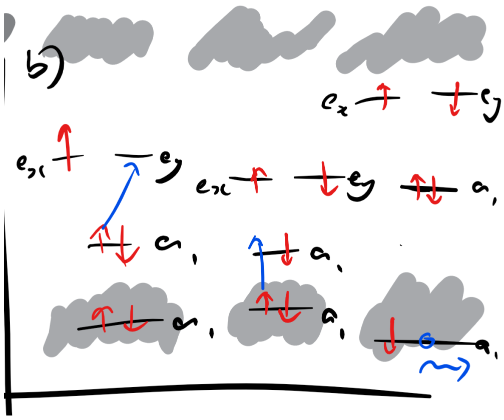

FIG. 5: **Recombination Processes.** **a,** Recombination from NV$^-$ to NV^0 electron view **b,** Recombination pathways traditional view.

First a photon must excite an electron in the NV^0 charge state into the excited ^2A state. A second photon can then be excited from the valence band into the ^2E ground state which provides the extra electron to the centre converting it into the NV$^-$ charge state in its ground state configuration (ref29???). Currently there is no evidence to indicate which spin state the NV$^-$ charge state will now be populated in, however it has recently been observed that the ionisation, recombination process is a spin depolarising process indicating a non negligible component in the $m_s = \pm 1$ spin state ref30???.

Whilst the ionisation and recombination processes have been investigated for single excitation wavelengths we believe however that one can excite the transition with a wavelength < 575 nm satisfying the first stage of the recombination process and then promote electrons from the valance band with a wavelength longer than 575 nm. It has been proposed also that the conversion from NV^0 to NV$^-$ is mediated by ionisation of single substitutional Nitrogen impurities (N_s) in the nanodiamonds providing free electrons to combine with the NV^0 charge state ref32???. Ionisation of N_s impurities requires > 1.7 eV for bulk diamond and slightly lower energy > 1.6 eV for nanodiamonds ref33???. Our nanodiamonds are a highly irradiated sample and therefore contain a high concentration of single substitutional nitrogen N_s. We postulate that the quenching observed in our nanodiamonds could be due to a dramatic increase in the ionisation and recombination rates induced by the NIR lasers and developed a rate equation model to determine the likelihood of this process compared to a STED like mechanism.

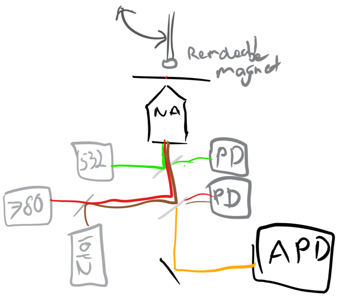

FIG. 6: **Experimental approach.** This is the setup ???

EXPERIMENTAL DETAILS

In our experiment, (???2) type and size nanodiamonds are dispersed on a glass coverslip placed on the sample plane of a custom built scanning confocal microscope. The NV centres are pumped with a 532nm continuous wave laser after focusing through a x.xNA, Brand, type immersion objective lens ???3. The 780nm laser is combined and then superimposed with the 532nm laser before the objective lens. The fluorescence is collected through the same objective and sent to an avalanche photodiode. A permanent neodymium magnet was placed on a moveable arm above the sample plane so that a large non zero magnetic field could be brought in close proximity to the nanodiamond in order to investigate the effect of mixing the spin state of the NV$^-$ ground states. The setup is shown in Fig. 6.

For each nanodiamond We start by collecting a saturation curve of the fluorescence of the NV centre. We then investigate the power dependance of the fluorescence on each of the NIR lasers for ??? powers of the green. We place a neodymium magnet $\tilde{0}$.5mm above the sample plane of the confocal microscope in order to mix the spin state of the NV- charge state as described in §model. Once placed we repeated the above set of measurement. This was repeated for x??? nanodiamonds. The NIR power dependance on the fluorescence of ND??? at ???uW of 532nm is plotted in Fig a. (one with most quenching) and shows that ??mW of NIR laser can suppress fluorescence over ???%.

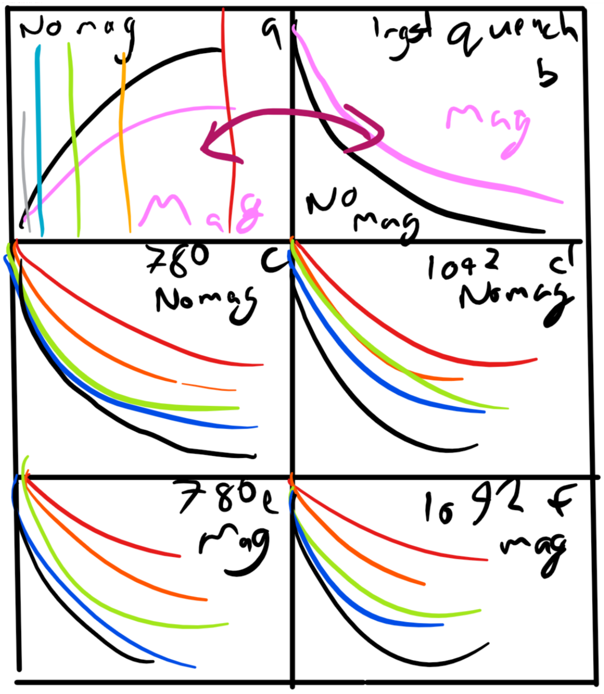

FIG. 7: **Experimental data. a.** This is the data swap a and b???

QUENCHING MODELS

In order to determine the intrinsic photophysics of our nanodiamonds we developed an 8 level rate equation model that incorporates both the ionisation and recombination mechanisms as well as the STED like mechanisms. The free paramaters of the model were varied in order to determine the most likely dynamics of the system. Four approaches were investigated and the most likely model was identified by the Akaike information criteria blah blah

Insert simple diagram of the model and then for each model include separate rates.

Underlying assumptions and unknowns

Blah

'STED' model

Blah

Simple Ionisation and Recombination Model

Where the Ionisation and recombination rates are linearly dependant on laser power indepentant of wavelength.

Wavelength Dependant I&R

Where the Ionisation and recombination rates are linearly dependant on laser power and dependant on wavelenght.

Spin Depenatant I&R

Where the Ionisation and recombination rates are linearly dependant on laser power and dependant on wavelength. In addition there are separate ionisation rates from the $ms = \pm 1$ and $ms = 0$ of the excited NV- charge state to the ground state. However the ratio between these two ionisation channels is held constant for each laser wavelength.

AKAIKE INFORMATION CRITERIA

Blah Blah

Highlight the optimal model, Maybe put table here or in appendix.

DISCUSSION

The optimal model is blah?

Model Parameters

The the values make sense? What are the ionisation rates like? are the close to 10ms/mW. Spin dependancy may occur from different dipolar cross section between the two excited states. Similar with the recombination rates? Link it to singlet nitrogen. Recombination occurs into which ground state of the NV- Singlet recombination between 0.66 and 1 which is consistent.

Charge state

Blah

Spin State

Blah

COMPARISON WITH OTHER WORK

Blah

CONCLUSION

Say that this indicates that this is the channels that are liekly to occur. If you want to use NV with other lasers than only the 532nm these dynamics must be understood. and then provide array of ways that could investigate these affects.

Acknowledgements

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