Photophysics of Nitrogen Vacancy centres in Nanodiamonds

Reece P. Roberts[1,2] and Author2[1,2]

[1] *Department of Physics & Astronomy, Macquarie University, NSW 2109, Australia and*
[2] *ARC Centre for Engineered Quantum Systems, Macquarie University, NSW 2109, Australia*

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%. **Summary: Introduce NV, Show that NV- is the important charge state, lead that we neglect NV0 by exciting with 532nm**

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 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 addition, we are collecting the fluorescence of both charge states and do not believe that the NV^0 charge state can be neglected in a steady state regime. **Summary: NV is good when used alone, a second laser field leads to quenching of fluorescence, has been explained by many mechanisms but mostly look at only NV^-, NV^0 must be playing a role.**

In this paper we investigate the quenching effects of the NV centre fluorescence under near infra-red (NIR) exposure in order to provide insight into the charge and spin state photo-dynamics. By understanding the underlying 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. **Summary: Summary of what we aim to do ★** Should I add examples of further applications and systems that require additional laser wavelengths

In our experiment, 100nm 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 either a fibre spectrometer or a fibre coupled APD that collects all wavelengths between $550 - 700\,\mathrm{nm}$. 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. 1.

We first examined the spectral response of excited NV centres under NIR illumination. The NV was excited with ???mW of 532nm and the NIR power dependence of the florescence spectrum was acquired and can be observed in Figure ???.
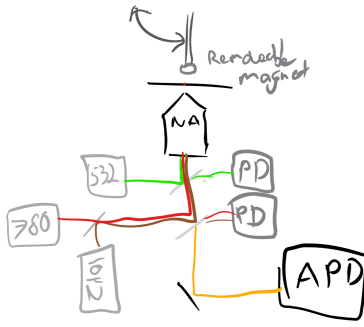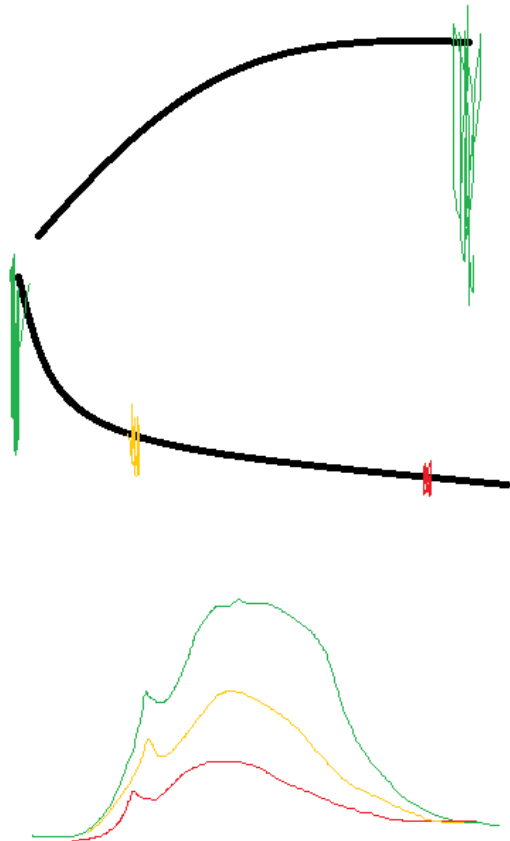
FIG. 1: **Experimental approach.** This is the setup ???

In order to investigate the entire photo-dynamics of the NV centres we used the APD to observe the flourescence over a much larger parameter space. For each nanodiamond the saturation curve of the NV centre is measured. The power dependence of the fluorescence for the 785 nm illumination wavelength is then measured for five powers of the 532 nm excitation laser. The neodymium magnet is placed ≈ 0.5 mm above the sample plane of the confocal microscope in order to mix the spin state of the NV-charge state. The above set of measurements are then repeated to provide more information on the internal spin state of the system. For each nanodiamond we obtain a series of plots that can be observed in figure 3.

FIG. 2: **Experimental data. a.** This is the data swap a and b???

Both the fluorescence of NV^0 and NV^- can be observed to be decreasing with increased NIR power. Additionally, there does not appear to be a significant charge transfer between the two charge states. Exact charge polarisation cannot be identified from the spectra due to the inability to spectrally separate the two charge states. It is clear however from the spectra that the quenching of fluorescence cannot be explained by simply investigating the negative charge state and neglecting the neutral charge state.
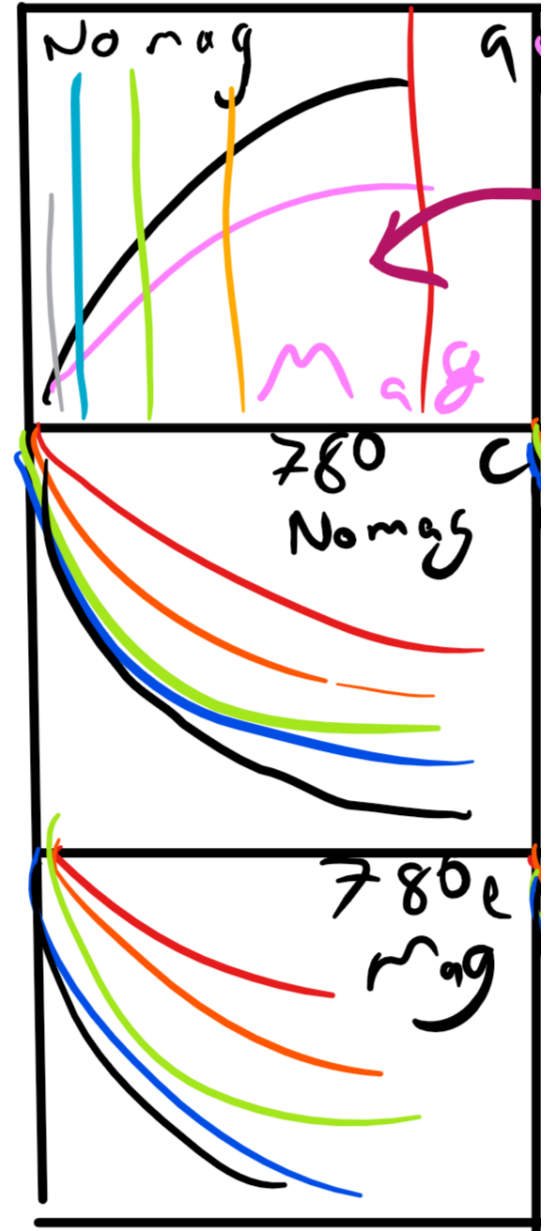

FIG. 3: **Experimental data. a.** This is the data swap a and b???

In order to determine the intrinsic photophysics of our nanodiamonds we developed an 8 level rate equation model using established physics of the NV centre that incorporates both the ionisation and recombination mechanisms as well as the STED like mechanisms. The free parameters of the model were varied in order to determine the most likely dynamics of the system. ??? submodels were investigated and the most likely model was identified by the Akaike information criteria. In the body of this paper only the most likely model selected by the Aikike information criteria is discussed, however, the full analyses of all the potential photo-dynamic models, are discussed in the Appendix.

From our analysis we found that the quenching mechanism is driven by the continuous charge state transfer between NV^0 and NV^- providing increased channels for non radiative decay from the corresponding excited states. In order to appreciate how the charge state transfer leads to a decrease in florescence as well as determining other implications of this result we must look into the energy level structure of the NV centre and the charge transfer mechaisms. **Summary: Summary of what we found lead into theory on NV centres**

Negatively Charge State

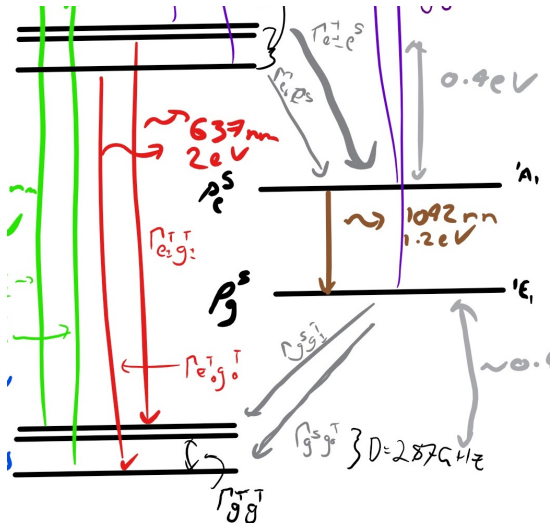The energy level diagram of the negatively charged NV^- centre can be observed in Fig. 6.

FIG. 4: Energy levels of the NV^- centre.

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 $m_s = \pm1$ spin states are split in energy at zero magnetic field by $D = 2.87\,\text{GHz}$ for the ground triplet and $D = 1.42\,\text{GHz}$ for the excited triplet (Ref12???). The spin transition rate between the
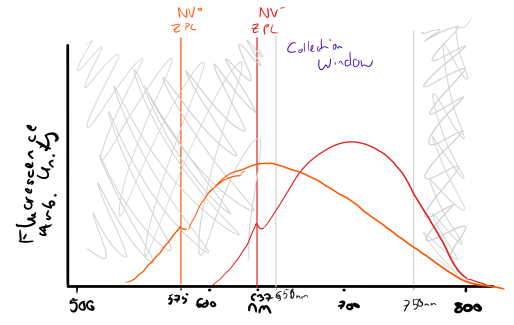

FIG. 5: Fluoresence profiles of NV charge states .

ground $m_s = 0$ ans $m_s = \pm1$ spin states is given by the spin-lattice relaxation time T_1 and has been measure to be $\approx 6\,\text{ms}$ 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. 5.

The excited triplet states can also decay to the excited singlet state, the rate from the $m_s = \pm1$ excited triplet state is $2\pi \times 9.4 \times 10^6\,\text{GHz} = 16.9\,\text{ns}$, whereas the rate from the $m_s = 0$ excited triplet state is almost an order of magnitude smaller at $2\pi \times 1.8 \times 10^6\,\text{GHz} = 88.4\,\text{ns}$ (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 be-

ing challenged and it has been claimed that the decay into the ground triplet has a spin state ratio closer to $\frac{m_s=0}{m_s=\pm1} = 1.1 - 2$ ref22???.

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. **??**.

FIG. 6: Energy levels of the NV$^-$ centre.

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 $\Gamma_{e^Zg^Z} = 19 \times 2$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 $\Gamma_{g^Ze^Z} = \frac{1}{3}\Gamma_{g^Te^T}$ 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.

★ 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 ≈ 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. 7.

FIG. 7: **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

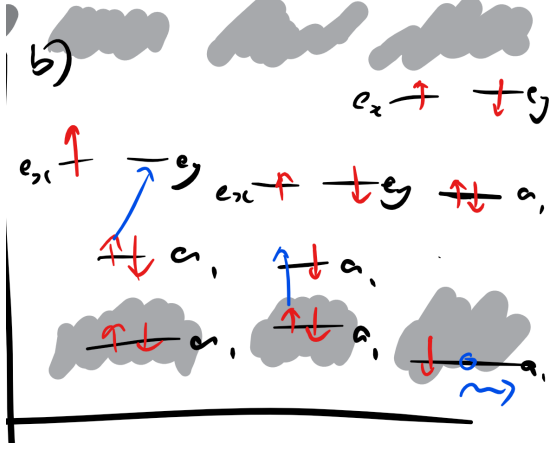The recombination process from NV^0 to NV^- also occurs in a two step process which is shown in Fig. 8.

FIG. 8: **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 $< 575\,\text{nm}$ satisfying the first stage of the recombination process and then promote electrons from the valence band with a wavelength longer than $575\,\text{nm}$. 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 $> 1.7\,\text{eV}$ for bulk diamond and slightly lower energy $> 1.6\,\text{eV}$ 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.