

# Photophysics of Nitrogen Vacancy centres in Nanodiamonds

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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 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<sup>0</sup>) and the negatively charged state (NV<sup>-</sup>), with photo-induced interconversion between these two states (ref2). The NV<sup>-</sup> charge state is an intensively studied material that has shown a wide range of applications in both Physics and Biology due to its high stability and interesting optical properties. Biologists have used them extensively for biolabelling and imaging of internal biological structures (ref3 and 4). Meanwhile, Physicists 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<sup>-</sup> 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<sup>-</sup> 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<sup>0</sup> 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 ref1). 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<sup>-</sup> centre can be observed in Fig. 3.

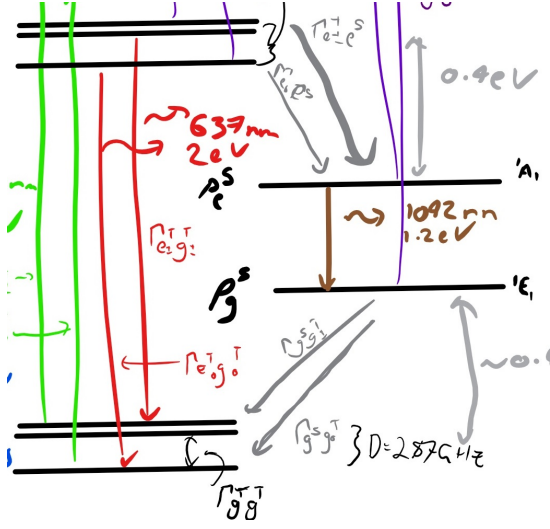


FIG. 1: Energy levels of the  $\text{NV}^-$  centre.

The  $\text{NV}^-$  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  $m_s = 0$  and  $m_s = \pm 1$  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 ground  $m_s = 0$  and  $m_s = \pm 1$  spin states is given by the spin-lattice relaxation time  $T_1$  and has been measured to be  $\approx 6 \text{ ms}$  at room temperature and zero magnetic field (ref13??). This spin mixing rate can be dramatically increased by applying 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  $637 \text{ nm}$  and can be efficiently excited with spin conservation at most wavelengths below  $640 \text{ nm}$  (ref15??). The radiative lifetime of the excited state is  $13 \text{ ns}$  for NV centres in bulk diamond (ref16??) and approximately  $25 \text{ ns}$  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  $800 \text{ nm}$  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  $2\pi \times 9.4 \times 10^6 \text{ GHz} = 16.9 \text{ ns}$ , 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 is not completely understood why there is a large discrepancy between these decay channels it is noteworthy that this discrepancy is what leads

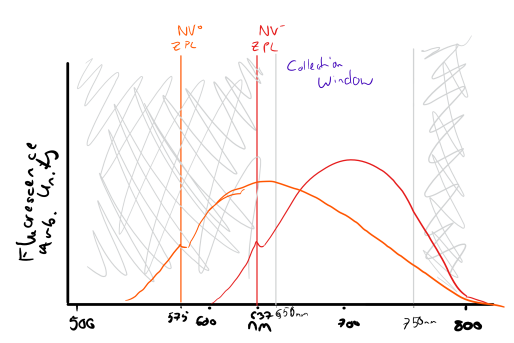


FIG. 2: Fluorescence profiles of NV charge states .

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  $\approx 1 \text{ ns}$  (ref19??) and populates the longer lived ground singlet state and it has been shown to emit fluorescence at a ZPL of  $1042 \text{ nm}$  ref20??. The longer lived ground metastable state has a lifetime of  $150 \text{ ns}$  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??.

### Neutral Charged State

As opposed to the rigorous study the  $\text{NV}^-$  charge state has received the  $\text{NV}^0$  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  $\text{NV}^0$  centre can be observed in Fig. ??.



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

The  $NV^0$  charge state consists of a ground doublet  $^2E$  and an excited doublet  $^2A$  with a ZPL at  $575\text{ nm} = 2.156\text{ eV}$ . It can be efficiently excited at most wavelengths below  $675\text{ nm}$  ref23??? and has a radiative lifetime of  $\Gamma_{e^z g^z} = 19 \times 2\text{ ns}$  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  $\approx 1$  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  $750\text{ nm}$ . 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  $\approx 532\text{ nm}$  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  $NV^0$  occurs in a two step process as shown in Fig. 4.

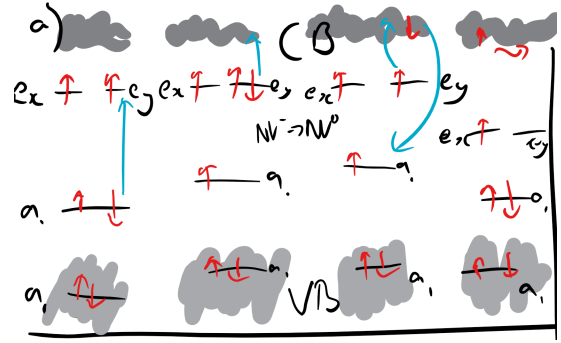


FIG. 4: **Ionisation Processes.** a, Ionisation from  $NV^-$  to  $NV^0$  electron view b, Ionisation pathways traditional view.

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.

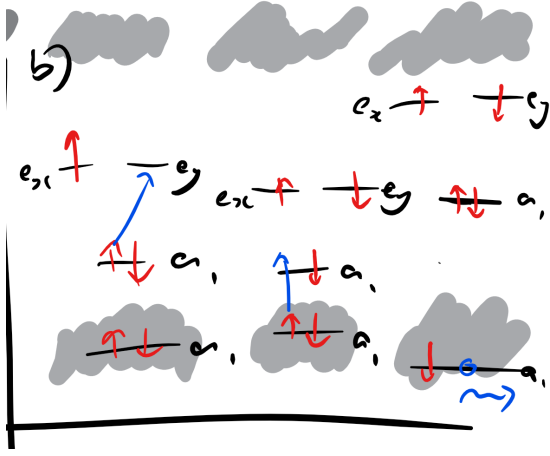


FIG. 5: **Recombination Processes.** a, Recombination from  $NV^-$  to  $NV^0$  electron view b, Recombination pathways traditional view.

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 valence 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.

## EXPERIMENTAL DETAILS

In our experiment, (???2) type and size nanodiamonds are dispersed on a glass coverslip placed on the sample

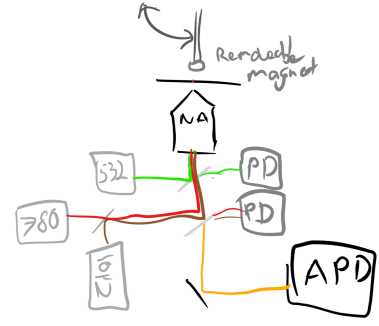


FIG. 6: **Experimental approach.** This is the setup ???

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 (APD) that collects all wavelengths between 550 – 700 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. 6.

For each nanodiamond the saturation curve of the fluorescence of the NV centre is measured. The power dependance of the fluorescence for the 780nm illumination wavelength is then measured for five powers of the 532nm excitation laser. The neodymium magnet is placed  $\approx 0.5$  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 get a series of plots that can be observed in figure 7.

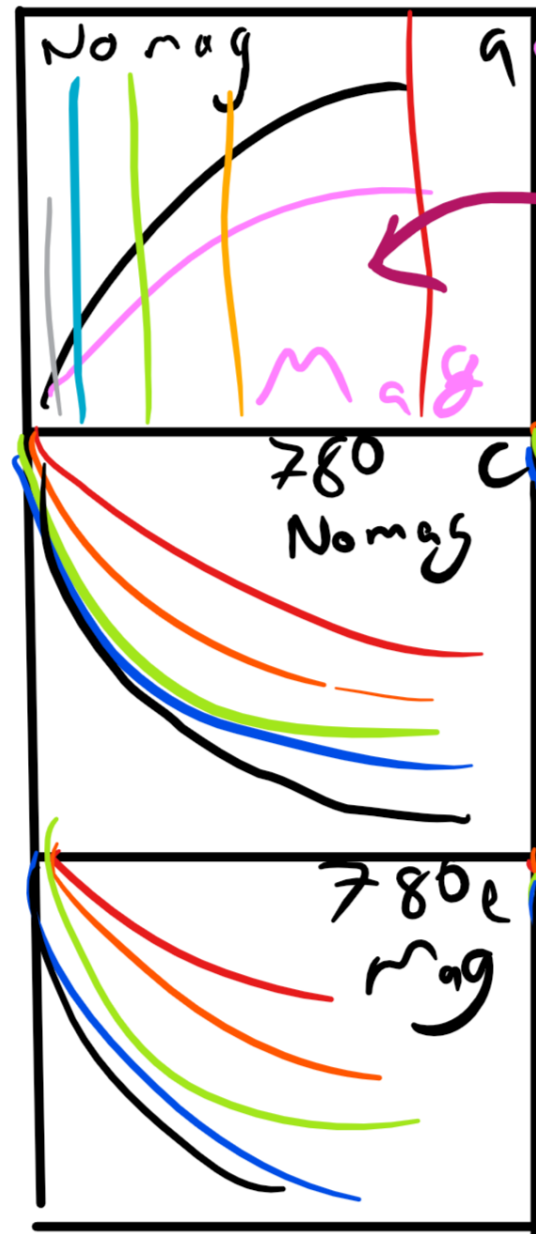


FIG. 7: **Experimental data.** a. This is the data swap a and b???

★ DESCRIBE WHAT THE DATA IS AND WHAT IT INDICATES. ★ I MANY ALSO WANT TO USE A MAGNET AND NO MAGNET TRACE IN ONE WINDOW AND SHOW THAT FOR HIGH QUENCHING THEY ARE SPIN DEPOLARISED.

## 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 parameters of the model were varied in order to

determine the most likely dynamics of the system. Six submodels were investigated and the most likely model was identified by the Akaike information criteria. The six models can be seen in figure 8.

	Spin Independent Quenching	Spin Dependant Quenching
STED Only		
I&R		
Both		

FIG. 8: **Experimental models.** a. This are the six models we looked at

The models can separated by their underlying quenching mechanism whether it be a STED like process, an Ionisation and Recombination process or a combination of the two. These three groups can then be split in two depending on if the model is a spin dependent quenching model or a spin independent quenching model. Below is a short description of each of the separate model types, for a comprehensive description of the rate equations and models refer to the supplementary material.

### STED like models

The STED like models are models that describe the quenching of the fluorescence through a true stimulated emission process or even by a processes that are mediated though an extra metastable fast decay state of the NV<sup>-</sup> centre ref???

### Ionisation and Recombination models

The ionisation and recombination models relies on the two step processes that convert the charge state of the NV centre. Each time the NV centre is excited the fluorescence of the NV centre is reduced due to the increased non radiative decay channels enabled by the conversion of charge state of the NV centre.



### Spin Dependency

In each of the above mechanisms the quenching of the fluorescence from the  $NV^-$  charge state can occur from either the  $m_s = 0$  or  $m_s = \pm 1$  excited state. One would initially assume that the ionisation and STED like mechanisms would be spin independent, however these energy levels already show a spin dependant nature towards the singlet states that leads to the spin polarisation properties of the  $NV^-$ . As a result we investigated the possibility that the interactional cross sections of the excited  $NV^-$  centre can be spin dependant.

★ MAYBE ADD: IN ADDITION THE DIPOLE STRENGTH OF THE EXCITED  $m_s = \pm 1$  STATE IN NANODIAMONDS CONTAINING A COLLECTIONS OF NV CENTRES IS  $\approx 10\times$  THAT OF THE DIPOLE STRENGTH OF THE EXCITED  $m_s = 0$  STATE. FIND REFERENCE

### AKAIKE INFORMATION CRITERIA

What is the Aikike infromation criteria. Which model is the best model?

### DISCUSSION

The most likely model identified by the Akaike Information criteria is model 3, the spin dependant ionisation and recombination model. This model indicates that the main quenching dynamic is dominated by the NV centre constantly transitioning from the excited energy level of one charge state to the ground state the other charge state. The final fitting parameters of each model are consistent between each of the nanodiamonds and a summary of the fitting parameters can be observed in figure ??? which also shows the diagram of the model that best describes the photophysics of the system. The final fitting parameters of all the models can be observed in the appendix. Whilst the model was kept general and the parameters unconstrained the model parameters are consistent with observations in previous experiments. The parameter for the recombination rate from the  $NV^0$  charge state to the ground state of the  $NV^-$  indicates that it is a spin depolarising process such that there is an  $\approx 50\%$  probability of occupying either the  $m_s = 0$  or  $m_s = \pm 1$  ground state which is consistent with observations made by ???. The recombination rate from the singlet states

to the ground state of the  $NV^-$  indicates that the spin state whilst varying between centres decays preferentially towards the  $m_s = 0$  ground state with a spin state ratio closer to  $\frac{m_s=0}{m_s=\pm 1} \approx 2$ , which is consistent with ref22???

In order to investigate the ionisation and recombination parameters we investigated the rate at which we would convert the charge state at small excitation powers as well as the final charge state polarisation. The Ionisation and recombination rates as well as the charge state can be observed in figure ???. Whilst these rates have not been measured with a magnet present, the non magnet Ionisation and recombination rates follow the expected quadratic dependence and have similar amplitudes to what has been measured for similar wavelengths and excitation energies ref???

The model also indicates that the ionisation mechanism is spin dependent such that the rate from the  $m_s = 0$  excited state is  $\approx 5\times$  stronger than from the  $m_s = \pm 1$  excited state. Further investigation using pulsed sequencing is needed to provide additional confirmation of the exact spin dependency of the ionisation mechanism.

In addition to investigating solely the model parameters, the model as a whole provides the complete internal steady state populations of each energy level. As a result we can investigate the spin state and charge state polarisation of the NV centre under normal 532nm excitation which can be observed in figure ???. The charge state and spin state polarisations are also consistent with the what is observed in the literature.

### CONCLUSION

Say that this indicates that this is the channels that are likely 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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