

Photophysics of Nitrogen Vacancy centres in Nanodiamonds

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Abstract

Blah

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^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 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^- 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 addi-

tional 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.

★ 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.

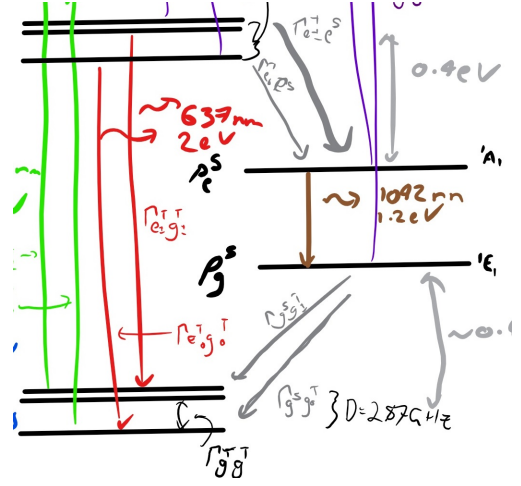


FIG. 1: Energy levels of the NV^- centre.

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 $m_s = 0$ 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 ≈ 6 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 nm and can be efficiently excited with spin conservation at most wavelengths below 640 nm (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 800 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 $2\pi \times 9.4 \times 10^6$ GHz = 16.9 ns, whereas the rate from the $m_s = 0$ excited triplet state is almost an order of magnitude smaller at $2\pi \times 1.8 \times 10^6$ GHz = 88.4 ns (ref18???). Whilst it not completely

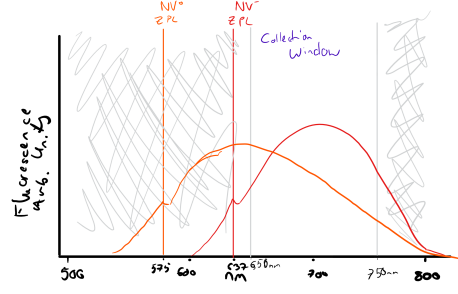


FIG. 2: Fluorescence profiles of NV charge states

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 ≈ 1 ns (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???

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. ??.

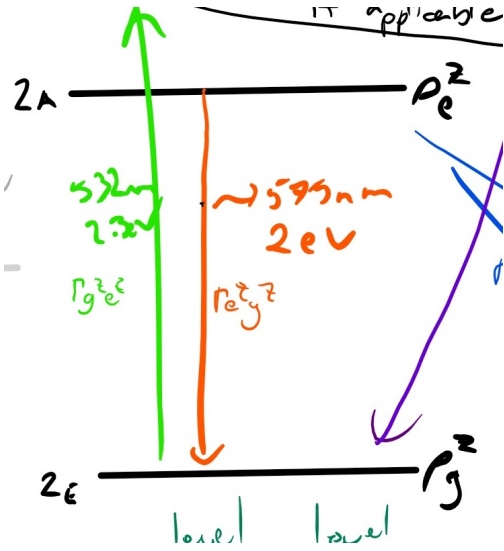


FIG. 3: Energy levels of the NV^- centre.

The NV^0 charge state consists of of a ground doublet 2E and an excited doublet 2A with a ZPL at $575\text{ nm} = 2.156\text{ eV}$ and can be efficiently excited at most wavelengths below 675 nm ref23???. 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 nm . However, no ODMR or optical read-out 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.

★ PUT THIS STUFF IN SOMEWHERE LATER, ALTHOUGH THE EXACT EXCITATION CROSS SECTION IS UNKNOWN THE RATIO OF EXCITATION CROSS SECTIONS BETWEEN NV^0 AND NV^- CAN BE MEASURED BY LOOKING AT THEIR RELATIVE EMISSION INTENSITIES. THE RATIO OF EXCITATION CROSS SECTIONS IS $\Gamma_{g^z e^z} = \frac{1}{3}\Gamma_{g^T e^T}$ REF25???. THE RADIATIVE LIFETIME OF THE EXCITED STATE IS $\Gamma_{e^z g^z} = 19 \times 2\text{ ns}$ REF26???. ★ 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^- .

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

Underlying assumptions and unknowns

Blah

Ionisation Process

Describe NV^- to NV^0 Process

'STED' model

Blah

Recombination Process

Describe NV^0 to NV^- Process

Simple Ionisation and Recombination Model

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

EXPERIMENTAL DETAILS

Describe the Quenching Experiment.

Wavelength Dependant I&R

QUENCHING MODELS

In order to determine the intrinsic photo-physics 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

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 $m_s = \pm 1$ and $m_s = 0$ 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.

Spin State

Blah

AKAIKE INFORMATION CRITERIA

COMPARISON WITH OTHER WORK

Blah Blah

Blah

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

DISCUSSION

CONCLUSION

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.

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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Charge state

Blah
