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Excited-state lifetime of the NV\textsuperscript{−} infrared transition in diamond

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The negatively charged nitrogen vacancy (NV\textsuperscript{−}) defect in diamond serves as a popular platform for manipulating and exploiting long-lived coherent spin dynamics at room temperature combined with optical readout. The required spin polarization of the spin triplet \(1A_2\) electronic ground state occurs through a cycle of repetitious optical photoexcitation events to the \(2E\) electronic excited state that is accompanied by a series of electronic transitions to a \(1A_1\) and a \(1E\) electronic state, and back to the \(3A_2\) state. The timescales of these transitions are largely known, yet for the relaxation time of the \(1A_2 \rightarrow 2E\) infrared transition, which predominantly occurs via nonradiative recombination, only an upper limit of 1 ns could be determined so far. Here, we employ ultrafast transient absorption spectroscopy to probe the dynamics of the nonradiative relaxation from the \(1A_1\) to the \(1E\) state after photoexcitation of the \(2E\) state and find a relaxation time of 100 ps at a temperature of 78 K.

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I. INTRODUCTION

The last decade has seen an impressive rise in the interest of utilizing the negatively charged nitrogen-vacancy (NV\textsuperscript{−}) center in diamond \cite{1} for various applications in quantum information and metrology, such as quantum computing \cite{2–4}, photonics, electric and magnetic field sensing \cite{5–8}, thermometry \cite{9,10}, nanoscale NMR \cite{11,12}, and quantum optomechanics \cite{13,14}. As a result of this effort, the optoelectronic properties of the NV\textsuperscript{−} defect have been investigated to great detail, making it the one of the best-studied solid-state defects. Nevertheless, some crucial aspects in the understanding are still missing \cite{1}.

The predominantly utilized feature of the NV\textsuperscript{−} center is the spin-triplet \(1A_2\) electronic ground state whose spin projection states \(m\) can be manipulated with microwave radiation and read out through photoexcitation as optically detected magnetic resonance (ODMR). The utility of the NV\textsuperscript{−} defect for harnessing these coherent spin dynamics relies on the reproducible initialization of \(m\) through optical pumping. This spin polarization is the result of a series of radiative and nonradiative electronic transitions that set the \(1A_2\) state to \(m = 0\). Most parts of this spin polarization cycle have been thoroughly investigated and the timescales of their transitions been experimentally determined. The dynamics are summarized in Fig. 1(a), which shows the basic electronic structure of the NV\textsuperscript{−} center and illustrates its electronic relaxation dynamics after photoexcitation. For simplicity, we omit the electronic fine structure.

In a typical experiment, the defect is photoexcited by promoting an electron from the \(1A_2\) electronic state to the spin triplet \(2E\) excited state, most commonly using a 532-nm laser (green dashed arrow). In that case, the electron is promoted far above the zero-phonon line transition (1.95 eV, 637 nm) into the wide phonon sideband (grey-gradient shaded area). After nuclear reorganization of the excited NV\textsuperscript{−} center within less than 100 fs \cite{15}, the \(2E\) state has relaxed to its vibrational ground state (yellow arrow). From here, the electron can either relax back radiatively to the \(1A_2\) state by emitting photoluminescence (PL) within approximately 10 ns or transfer to the \(1A_1\) spin-singlet state via intersystem crossing (ISC) within about 10 ns \cite{16}. The radiative relaxation is equally probable for all three spin projection states, i.e., \(m = 0\) and \(m = \pm 1\), whereas ISC is more likely to occur from the \(m = \pm 1\) states, with the transition probability from \(m = 0\) being at least five times smaller \cite{16}. This spin-state-sensitive branching ratio constitutes the first spin-selective part of the spin polarization cycle. In the subsequent transition the electron relaxes to the spin singlet \(1E\) state (red arrow). Note that this state has double orbital degeneracy, with the transition dipole moments from the \(1A_1\) state to the \(E_x\) and \(E_y\) substates of \(1E\) being orthogonal.

The PL quantum yield (QY) of the \(1A_1 \rightarrow 1E\) transition has been measured to be more than three orders of magnitude lower than the QY of the \(1A_2 \rightarrow 3E\) transition, indicating a dominant nonradiative relaxation channel with a relaxation time orders of magnitude smaller than 10 ns \cite{17}. So far, however, only an upper limit of 1 ns could be determined for the lifetime of \(1A_1\) \cite{18}. As the main result of this publication, we report the nonradiative recombination time \(\tau_{rr}\) of the \(1A_1 \rightarrow 1E\) transition to be 100 ps. The last electronic transition eventually closes the spin polarization cycle by returning the electron back to the \(3A_2\) triplet ground state within 200–400 ns, depending on the temperature \cite{19,20}. At
temperatures above 50 K, this ISC is predominantly occurring to the $m = 0$ state, thus forming the second spin-selective step in the cycle [21]. Due to the long lifetime of the $^1E$ state, the absorption arising from the $^1E \rightarrow ^1A_1$ transition has been used as an ODMR probe [22,23].

**II. METHODS**

We employ femtosecond transient absorption spectroscopy [24,25] to measure the population dynamics of the $^1A_1$ and $^1E$ states with an infrared (IR) femtosecond probe pulse that is resonant with the singlet transition after photoexcitation of the $^3A_2 \rightarrow ^3E$ transition with a femtosecond pump pulse. The transient absorption setup is pumped by a Ti:Sapphire amplified laser (Coherent Legend Elite Duo-USX) that operates at a repetition rate of 1 kHz and delivers nominally 25-fs pulses with an average power of 4 W. Spectral broadening by self-phase modulation in a helium-filled hollow-core fiber followed by chirped mirror compression furnishes <5-fs pulses with wavelength spanning $\sim$500–950 nm. About 80% of this supercontinuum output is used as the pump pulse and sent to a 4-f-pulse shaper where the spectrum is cut to 500–740 nm and the spectral phase optimized to yield as short as 10-fs pulses with 40-μJ pulse energy. Further spectral shaping is accomplished by using appropriate dielectric bandpass filters. In the experiments featured here, a bandpass filter at a center wavelength of 620 and 40 nm bandwidth is used to shape the pump spectrum with a fluence of 5 mJ/cm$^2$ in the focal spot. About 12 μJ of the supercontinuum output is focused on a 2-mm BBO crystal ($\Theta = 36.7^\circ$; $\Phi = 30^\circ$) where intrapulse difference-frequency generation generates probe radiation from 1020–1600 nm. The probe is sent to another 4-f-pulse shaper, in which pulses are compressed to durations as short as 10 fs with an energy of 3 nJ. Both pump and probe beams are focused with a spherical mirror of 20-cm focal length on the sample at a small angle ($\sim 5^\circ$) between them. The time delay between pump and probe pulse is varied with a motorized translation stage in the pump path. The pump transmission is modulated with a mechanical chopper at half the laser repetition rate, i.e., 500 Hz. For each pump-probe time delay, the difference $\Delta T$ between probe transmission of photoexcited and non-photoexcited sample is recorded, normalized by the transmission through the non-photoexcited sample $T$, giving the differential transmission spectrum $\Delta T/T$. Positive values of $\Delta T/T$ indicate increased probe transmission through the photoexcited sample, for instance caused by stimulated emission, whereas negative values originate from less probe transmission, usually arising from absorption. All measurements were performed in a cryostat at a sample temperature of 78 K. Two permanent magnets were placed next to the sample to reduce the degree of spin polarization in $^3A_2$ and thus promote enhanced ISC to the singlet levels.

We investigated two samples of type 1b high-pressure-high-temperature-grown diamond (Element Six). NV$^-$ defects were introduced in the standard fashion by irradiation with 1-MeV electrons and subsequent annealing in vacuum to facilitate vacancy diffusion. Sample NV-A has dimensions $4 \times 4 \times 0.3$ mm$^3$ and contains single substitutional nitrogen defects (Ns) of about 100 ppm concentration and NV$^-$ of 1.5 ppm. Sample NV-B measures $2 \times 2 \times 2$ mm$^3$, with Ns concentration of around 200 ppm and an NV$^-$ density of 0.2 ppm.

The sketch in Fig. 1(b) illustrates the measurement principle. The pump pulse at a center wavelength of 620 nm with 40-nm bandwidth excites the $^3A_2 \rightarrow ^3E$ transition and the time-delayed IR probe pulse interrogates the pump-induced differential transmission $\Delta T/T$ of the $^3E \rightarrow ^1A_1$ singlet transition at 1042 nm. Immediately after photoexcitation, the $^3E$ state is populated but practically no population resides yet in either $^1A_1$ or $^3E$. $\Delta T/T$ at 1042 nm is thus close to zero. With progressing time delay after photoexcitation, population in $^1A_1$ starts to increase due to ISC from $^3E$. This process is rather slow, with an ISC time $\tau_{ISC}$ of about 10 ns. Nevertheless, a finite population will build up in $^1A_1$ even after a few ps, visible as a finite positive value of $\Delta T/T$ at 1042 nm due to stimulated emission (SE) to $^3E$. At the same time, nonradiative recombination to the $^3E$ state will drain population from $^1A_1$, contributing negative $\Delta T/T$ values at 1042 nm, since now $^3E \rightarrow ^1A_1$ will appear as an absorptive response. Eventually, since $\tau_{ISC} \gg \tau_{nr}$, the absorptive response will prevail and $\Delta T/T$ will become negative. Measuring the dynamics of this transition sequence will allow the determination of the nonradiative relaxation time $\tau_{rel}$ and thus the lifetime of $^1A_1$. To illustrate that, in Fig. 1(c) we plot the results of a simple model simulating the time dependence of $\Delta T/T$ after...
photoexcitation for three values for $\tau_{nr}$ of 100, 200, and 300 ps and $\tau_{ISC} = 10$ ns over time delays up to 15 ns, with the inset showing a magnified view of the first 1 ns. The rate equations we used are $N_{1E} = -\tau_{ISC}^{-1}N_{3E}$, $N_{1A} = \tau_{ISC}^{-1}N_{3E} - \tau_{nr}^{-1}N_{1A}$ and $N_{1E} = \tau_{nr}^{-1}N_{1A}$, where $N$ denotes the population of the electronic state specified in the subscript. All initial photoexcited population is in $N_{3E}$. Population in $^1A_1$ contributes positive values to the calculated $\Delta T/T$ signal (SE) whereas population in $^1E$ contributes negative values (absorption). In the absence of orbital degeneracy of $^1E$, we would thus get $\Delta T/T = N_{1A} - N_{1E}$. Since, however, $N_{1E} = N_{Ex} + N_{Ey}$, with $N_{Ex} = N_{E1}$, and the transition dipole moments from $^1A_1$ to $N_{Ex}$ and $N_{Ey}$ are orthogonal, we get $\Delta T/T = N_{1A} - 1/2 \times N_{1E}$, i.e., the absorptive contribution to $\Delta T/T$ is half the SE contribution. We note that excited-state absorption (ESA) to the conduction band (CB) potentially occurs within the probe spectral range as well, but its contribution to the signal is expected to be minor due to the low oscillator strengths associated with continuum transitions. Such ESA would be visible as a negative contribution to $\Delta T/T$ that is broad and featureless over the whole probe spectrum, which we do not observe at all timescales.

III. RESULTS AND DISCUSSION

The measured spectrally resolved $\Delta T/T$ of the IR probe as a function of time delay for sample NV-A is shown in Fig. 2(a), with spectral lineouts at time delays of 1, 100, and 350 ps plotted in Fig. 2(b). Despite the nanosecond-long ISC time, already after a few ps, population in the $^1A_1$ state becomes visible and starts to gradually build up. This is recognizable as positive differential transmission (red), i.e., $\Delta T/T > 0$ at 1042 nm, due to SE from $^1A_1 \rightarrow ^1E$. The SE signal is increasing up to a time delay of $\sim 100$ ps, after which it reverses its trend and starts to decrease, a clear sign of the $^1A_1 \rightarrow ^1E$ relaxation starting to dominate the dynamics through absorption from $^1E \rightarrow ^1A_1$, contributing a $\Delta T/T < 0$ signal (blue). One can even recognize a small peak shift: the peak of the absorptive part is blue-shifted by $\sim 2$–3 nm ($\sim 15$–25 cm$^{-1}$) with respect to the SE part. This shift is unexpected, given that previous reports of PL and absorption measurements have not observed any differences in the respective detected peak center wavelengths [26], and we are currently unable to explain the origin of the shift.

To quantify the dynamics, we spectrally integrate $\Delta T/T$ from 1032 to 1048 nm and plot the results in Fig. 2(c) for samples NV-A and NV-B and verified that the result does not change with the integration range. The rise and decay of the positive $\Delta T/T$ values is clearly visible, and after about 250 ps $\Delta T/T$ has become negative. We fit the integrated $\Delta T/T$ data to the same set of rate equations that produced the plot in Fig. 1(c) to model the transition dynamics and leave the $^1A_1 \rightarrow ^1E$ relaxation time $\tau_{nr}$ as a fitting parameter. The results of the fits for both samples are shown as red solid lines in Fig. 2(c). We obtain $\tau_{nr} = 102.3(3)$ ps for sample NV-A and $\tau_{nr} = 92.1(5)$ ps for sample NV-B. The two values are reasonably close to each other (within about 10%), the difference between them is, however, much larger than the fitting error. This suggests modest sample-dependent variations in the electron-phonon coupling of the defect ensembles that leads to the observed variation in $\tau_{nr}$. Stating a final value for $\tau_{nr}$ of about 100 ps thus appears justified.

In conclusion, we have measured the dynamics of the nonradiative relaxation of the IR $^1A_1 \rightarrow ^1E$ singlet transition of the NV$^-$ center using transient absorption spectroscopy. We monitored the time-dependent contributions of stimulated emission and absorption from the singlet transition to obtain the population dynamics of the involved electronic states. Using a rate model, we inferred a relaxation time of 100 ps.
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