Optimization of the Double Electron–Electron Resonance for C-Centers in Diamond

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1. Introduction

Double electron–electron resonance (DEER)\(^1\) is often used in chemistry to determine the structure of radicals.\(^2\) This method, in its variation based on nitrogen-vacancy (NV) centers in diamond,\(^3\) has established itself as an excellent method for detecting various spin impurities both inside diamond\(^4–6\) and on its surface.\(^7\) The method uses the NV-center as a sensitive element for local magnetic fields.\(^8\) The spin echo\(^9\) signal responds to changes in the local field generated by the spin environment when a resonant radio frequency (RF) field is applied to this environment.\(^10\) Thus, by scanning the frequency of the RF field, it is possible to obtain the DEER spectrum containing information about the possible states of the spin environment of the NV-center.\(^10\)

The donor nitrogen or C-center is one of the most studied spin defects in diamond\(^11\) because, in addition to its natural high abundance, it also limits the performance of the NV-center as a sensor. Thus, NV-centers are naturally used to detect and study C-centers.\(^12\) To this end, DEER enables one to not only detect the spectrum for the defect\(^12\) but also determine its concentration,\(^13,14\) which, while not inferred from the spectrum itself, can be measured using a modified pulse sequence for DEER.

In this article, the influence of the free precession time of the NV-center on the observed contrast of the measured DEER spectrum for C-centers was investigated. The optimal precession time in terms of the contrast was found for each concentration of the C-center, showing a strong correlation with both the concentration of C-centers and the NV-center \(T_2\) time. The donor nitrogen or C-center is one of the most studied spin defects in diamond\(^11\) because, in addition to its natural high abundance, it also limits the performance of the NV-center as a sensor. Thus, NV-centers are naturally used to detect and study C-centers.\(^12\) To this end, DEER enables one to not only detect the spectrum for the defect\(^12\) but also determine its concentration,\(^13,14\) which, while not inferred from the spectrum itself, can be measured using a modified pulse sequence for DEER.

In this article, the influence of the free precession time of the NV-center on the observed contrast of the measured DEER spectrum for C-centers was investigated. The optimal precession time in terms of the contrast was found for each concentration of the C-center, showing a strong correlation with both the concentration of C-centers and the NV-center \(T_2\) time. The concentration of C-centers (from 1 to 60 ppm) in eight diamond plates was measured using both modified DEER spectroscopy\(^13,14\) and infrared (IR) spectroscopy.\(^15\) The dependence of the resonance amplitudes and width on the concentration of C-centers as well as the length of the combined C-center driving and NV-center \(\pi\)-pulse is also discussed.

2. Experimental Section

All investigated diamond plates were grown by the high-pressure high-temperature method,\(^16\) irradiated with electrons\(^17\) at a...
dose of $15 \times 10^{17} \text{cm}^{-2}$, and then annealed at a temperature of 1400 °C over 2 h. The nitrogen concentration was varied at the growing stage. The experimental setup used for the detection of the DEER spectrum is described in detail in the study by Rubinas et al.$^{13}$ Experiments were conducted in an 85G magnetic field created by permanent magnets, which allows us to split the degenerate levels of NV-centers and C-centers due to the Zeeman effect (Figure 1A). With this magnitude of magnetic field, the DEER spectrum of the C-center should be in the range of 100–500 MHz. The magnetic field was set so that its direction coincided with the (111) axis of the diamond plate.

NV-centers were driven at the frequency determined from the optically detectable magnetic resonance.$^{13}$ The chosen microwave transition $|m_s = 0 \rangle \rightarrow |m_s = -1 \rangle$ is indicated at Figure 1A. The chosen microwave transition $|m_S = 0 \rangle \rightarrow |m_S = -1 \rangle$ is indicated at Figure 1A. The experiment was conducted in the presence of magnetic field, such that the transition frequency was 2.64 GHz. Then, using the Rabi oscillations$^{18}$ at the resonant frequency of the NV-center, the duration of the $\pi$-pulse was determined, which can be controlled by the power of the microwave field applied to the ensemble of NV-centers. The DEER sequence is composed of a spin echo$^{9}$ sequence on an ensemble of NV-centers accompanied by a RF pulse (Figure 1B). The length of the RF pulse is chosen to match the NV $\pi$-pulse.$^{13}$ To obtain the DEER spectrum, the frequency of the RF pulse is varied, while all other parameters are kept the same (Figure 1C). In order to take into account laser fluctuations, the data acquiring had two measurement of the NV fluorescence in each measurement cycle, one after the MW and RF pulse and one after long laser polarization cycle (see Rubinas et al.$^{13}$ for pulse sequence details). The ratio of two is the normalized fluorescent signal in the definition of the contrast (1) below. Each data point was averaged over 100 cycles, and each curve was averaged over 150 measurements of a curve.

The free precession time $\tau$ was kept fixed for each specific measurement, but it is a parameter that requires optimization depending on the nitrogen concentration. As the NV-center serves as a sensor for the spectral measurements, it is expected that the properties of the NV-centers can have an effect on the measured spectrum. In particular, the free precession time is limited by the coherence time $T_2$ of the NV-center. The coherence time is known to correlate with the nitrogen concentration.$^{19}$ For diamond plates under study, the coherence time varied between a few microseconds for highly concentrated diamond (approximately 50 ppm of nitrogen) and 130 µs for low concentrated diamond plates (approximately 1 ppm of nitrogen). Longer $T_2$ times of up to 300 µs are possible for even lower nitrogen concentrations.$^{20}$ To measure the C-center concentration in diamonds, we used the method based on the modified DEER pulse sequence, as described in previous work.$^{13}$ The method is based on same sequence as depicted in Figure 1A, but with different time of the application of RF pulse. The RF pulse aligned with $\pi$-pulse inverts the external magnetic field, caused by the environment at the same time, when NV center inverts its state. Inversion of the NV center state has goal of compensating effect of the external field, but if the field is inverted at the same time, the echo sequence would not work and the echo signal would be low. As inversion time of the external filed becomes not synchronized with the echo sequence $\pi$-pulse, the echo sequence recovers its ability to subtract the effect of external field and therefore dip at the echo sequence signal, caused by presence of the RF pulse, starts to disappear. If one varies position of the RF pulse from the position of the $\pi/2$-pulse of the echo sequence to the position of the $\pi$-pulse, one could follow the speed of the echo signal decay. The speed of this decay depends on the concentration of C-centers and thus the concentration could be recovered from the slope of the dependence of the magnitude of the echo signal with respect to displacement of two pulses. To confirm the results,

Figure 1. A) The NV-center and C-center energy levels in a constant magnetic field. The arrows show the allowed transitions used in the experiment. B) $\omega_{NV}$—the frequency of the NV-center transition used; $\omega_{RF}$—the scanned RF frequency for C-center detection. C) DEER spectrum. The frequencies $\omega_{1,3}$ denote the resonances corresponding to the transitions at these frequencies in (A). The signs || and # denote the resonances of the C-centers that are aligned and not aligned with the external magnetic field, respectively.
the C-center concentration in these samples was also determined by IR spectroscopy.\textsuperscript{[23]} The idea of the method is based on measurement of the resonant to the C-center transition absorption coefficient, which is naturally proportional to the concentration (see more details in Rubinas et al.\textsuperscript{[13]}).

The measurement results obtained using these methods are in good agreement (see Figure 2A). The measurement results obtained using the two methods do not coincide completely due to the inhomogeneity of the defect concentration in the diamond plates and the different investigation volumes used for the two methods. The IR spectroscopy method averages the concentration over the whole plate, whereas the DEER method obtains the concentration from the focal spot volume. The focal spot in our setup is around 10 \textmu m. The collection of NV center emission is done through the whole width of diamond plate. Overall sample size is 1 \times 1 \times 0.6 mm for samples S1 & S5, 1.2 \times 1.2 \times 0.3 mm for sample S7 and 0.7 \times 0.7 \times 0.5 mm for samples S2, S3, S8. To minimize concentration fluctuations, several spots were measured by DEER methods, and all other measurement for the measured concentration were done at the same laser spot location. For each diamond plate, several focal positions were randomly selected to have some representation of the concentration fluctuations.

The coherence time \( T_2 \) was measured for all samples (S1 – S8) studied using the spin-echo method.\textsuperscript{[22]} Figure 3A demonstrates the measurement of \( T_2 \) for the plate with a nitrogen concentration of 50 \pm 1.5 ppm. Plates with low nitrogen concentrations experience modulation of the echo sequence by \(^{13}\text{C}\) nuclear spin,\textsuperscript{[15]} as shown in Figure 3B. The measured coherence times in our experiment also correlate with the measured values for the C-center concentrations, as shown in Figure 2B, and indeed follows the dependence \( T_2 [\mu s] = 165 [\mu s \cdot ppm]/n[ppm] \) from Barry et al.\textsuperscript{[19]} Additionally, \( T_2 \) sets the upper limit on the possible free precession time \( \tau \), thus affecting the parameters for the observed DEER spectra (Figure 3C,D).

### 3. Results

To better understand the spectrum parameters, the measured spectra were fitted by the Lorentz fitting function

\[
L(\omega) = 1 - \sum_{i=1}^{6} C_i \frac{\Delta \omega_i^2}{(\omega - \omega_i)^2 + \Delta \omega_i^2}
\]

where \( C_i \) is the contrast, which is defined here as amplitude of the dip in echo signal caused by the presence of RF field normalized to echo signal without RF, \( \Delta \omega_i \) is the half width at half maximum (HWHM) of the resonance peak, and \( \omega_i \) is the resonance frequency. First, it is useful to compare the DEER resonance width at different concentrations of the C-centers. With fit (1), for an optical DEER spectrum measured at \( \approx 50 \text{ ppm} \) (Figure 3C) C-centers ensemble, the HWHM on average is 3.7 MHz and that for a 1 ppm ensemble (Figure 3D) on average is approximated as 2.3 MHz, which, thus, shows a change in the HWHM. Here, to take into account the efficiency of the antenna and differences in oscillation strengths, RF power was adjusted so that the RF pulse area is equal to \( \pi \) for different resonances. Therefore, the spectrum was taken piecewise.\textsuperscript{[13]} The relative change in linewidth is much smaller than both the change in concentration and the change in free precision time. Thus, in the range of the investigated concentrations, the linewidth is not defined by concentration and is not Fourier limited by the free precession time. A similar conclusion was previously reported,\textsuperscript{[23]} where inhomogeneous broadening of C-centers is believed to be the main contribution to the resonance widths.

Next, the effect of free precession time \( \tau \) on the DEER spectrum was investigated. This time was varied in the range from 200 ns to a value not exceeding twice the coherence time in each sample studied. It was observed that the contrast \( C_1 \) in (1) of the DEER spectrum varies in magnitude at different values of \( \tau \), as shown in the attached Figure 4A. It is easy to see that all six presented resonances (marked with different colors) have the maximum contrast at the same optimal free precession time. To find the value for this optimal free precession time, the dependence of the DEER contrast on \( \tau \) was approximated by the following function

\[
F(x) = A x e^{-(x/\sigma)^\beta}
\]

where \( A \), \( \beta \), and \( \sigma \) are fitting parameters. The choice of the approximation function is based on the following assumptions:

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{A) Correlation between IR spectroscopy and DEER method measurements of C-center concentrations. \( n_{IR} \) stands for the concentration measured by the IR method, and \( n_{DEER} \) stands for the concentration measured by the DEER method. The dashed line demonstrates a linear fit \( n_{IR}[\text{ppm}] = 0.8 n_{DEER}[\text{ppm}] + 0.3 [\text{ppm}] \). Stars on sample names stand for different spots on the sample. B) \( T_2 \) coherence time of the NV-center ensemble depending on the C-center concentration. The dashed line shows the empirical estimation \( T_2 [\mu s] = 165 [\mu s \cdot ppm]/n[ppm] \) from Barry et al.\textsuperscript{[19]}}
\end{figure}
at the high values of $\tau$ one would expect overall decay of the echo signal, which is usually exponent like at (2) with some power depending on the type of dominant dephasing interaction.\cite{24} Power 2 is chosen for simplicity rather than in anticipation of some specific mechanism. At low time one can expect linear rise of the effect of the environment would be proportional to the accumulated phase, or to the length of the sequence. This function was differentiated to find the point of maximum optimal $\tau$. As shown in Figure 4A, the optimal $\tau$ depends on the concentration of C-centers in the sample. A comparison of the measured $T_2$ time and optimal $\tau$ is provided in Figure 4B. The optimal free precession time is consistent

![Figure 3.](image)

**Figure 3.** A) NV-center spin-echo signal for diamond with a C-centers concentration of approximately 50 ppm. B) Same for a C-centers concentration of approximately 1 ppm. C) Partial optical DEER spectra obtained for diamond with the diamond plate from (A) and free precession time $\tau = 1 \mu s$ (red dot at (A)). D) Same with the diamond plate from (B) and free precession time $\tau = 22 \mu s$ (red dot at (B)). For (C) and (D), red dots and lines correspond to the part of the C-center ensemble aligned along the magnetic field, and the green dots and lines correspond to the part that is not aligned with the magnetic field. RF power was adjusted for each resonance so that the RF pulse was a $\pi$-pulse.

![Figure 4.](image)

**Figure 4.** A) Concentration dependence of optimal free precession time $\tau_{\text{opt}}$ obtained from DEER. Boxes are used to show the variation in the optimal free precession time between resonances of one sample (S5*). The inset shows the dependence of the DEER contrast on the free precession time for each resonance of a single sample. B) Correlation between optimal free precession time $\tau_{\text{opt}}$ and NV-center coherence time $T_2$. Boxes denote experimental data. The dashed line denotes the fit to the linear function $\tau_{\text{opt}} = 0.35T_2$. 

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with the linear dependence on the NV-center coherence time $T_2$.

In the next part of the experiment, RF and NV $\pi$-pulse durations in the DEER pulse scheme (Figure 1B) were varied. As displacement in time domain of the RF pulse causes significant decay in the echo sequence, one could expect from longer RF pulse as well. For each duration, the microwave power for the NV-centers and the RF power for the C-centers were tuned by observing Rabi oscillations to maintain pulse widths equal to $\pi$. As shown in Figure 5A, the contrast in the DEER spectrum depends on the $\pi$-pulse duration. The best contrast is achieved at the minimum $\pi$-pulse duration in the scheme. However, the linewidth of the spectrum also increases with decreasing $\pi$-pulse (Figure 5B).

The dependence of this linewidth behavior on the $\pi$-pulse duration correlates with the results obtained in the study by Fortman et al. The width also slightly changes with C-center concentration, as shown in Figure 5C; this change is also rather small.

Thus, the contrast in the DEER spectrum depends on two main parameters in the experiment: the free precession time and $\pi$-pulse duration. However, the DEER linewidth weakly depends on the $\pi$-pulse duration and does not change with changes in the free precession time (Figure 5B, inset).

4. Discussion

The fact that the linewidth of the DEER resonance barely deepens for all experimental parameters can be explained by the assumption that the linewidth for the C-center is limited by the inhomogeneous linewidth broadening of the C-center ensemble itself. This assumption agrees with previous study. The fact that the width does not change much with the concentration of C-centers suggests that the dynamics of the C-centers are weakly affected by their concentration in the studied range of concentrations. At the same time, the strong correlation of the DEER contrast with the optimal free precession time and the correlation of the latter with the NV-center $T_2$ time suggest that the contrast in the DEER spectrum is limited only by NV-center performance, and not by the dynamics of the C-center other than the effect of these dynamics on the NV-centers themselves.

5. Conclusion

We considered in detail the method of optical DEER in diamond using the example of detecting ensembles of C-centers through the fluorescence emitted from an ensemble of NV-centers. The influence of the duration of free precession in the optical DEER scheme on spectral contrast was investigated using samples of both highly concentrated and low-concentrated diamond plates. Using these dependencies, the optimal values for the duration of the free precession time in the optical DEER experiment were determined. We also demonstrated how the concentration of C-centers in a diamond plate affects the linewidth of the optical DEER spectrum.
The concentrations of C-centers in a number of diamond plates were measured using a modified DEER sequence and compared with concentrations measured by IR spectroscopy. The dependence of the DEER spectra on the parameters of the DEER sequence was investigated. It was shown that the most sensitive parameter for the DEER spectrum is its contrast, and that this strongly depends on both the free precession time and length of the $\pi$-pulse of the sequence. The free precession time has an optimal value in terms of the DEER spectrum contrast and is linearly dependent on the NV-center $T_2$ time. The width of the resonance has a weak dependence on the parameters of the sequence. The main influence of the resonance width arises from the length of the $\pi$-pulse of the sequence, but, overall, the width has other nonsequence-related sources, presumably the dynamics of the C-center themselves.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
C-centers, diamond, double electron–electron resonance, NV-centers

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