# ELECTRIC-FIELD-INDUCED MODULATION OF SPIN ECHOES OF N–V CENTERS IN DIAMOND

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We have studied the Stark effect involving the spin transition in the $^3$A ground state of the N–V defect center in type Ib diamond, using techniques for optical detection of spin echoes. Electric-field-induced modulations of the Hahn-echo decays are reported. The results are characteristic of a linear Stark effect, which proves that the defect lacks inversion symmetry. The spin-Hamiltonian parameters characterizing the linear Stark effect of the N–V center triplet state are $R_{3D}=0.35\pm0.02$ Hz cm/V and $R_{2E}=17\pm2.5$ Hz cm/V.

## 1. Introduction

The N–V center in type Ib diamond is believed to consist of a nitrogen atom substitutional for carbon and a nearest-neighbour carbon-atom vacancy filled with one electron [1]. Obviously, the idea that the defect lacks inversion symmetry, will be confirmed if linear Stark shifts of electronic transitions can be measured in the presence of an externally applied electric field [2,3].

Recently, two-laser hole-burning experiments involving the zero-phonon line absorption at 638 nm suggested that the N–V center has an electronic triplet-spin ground state [4]. Subsequent optically detected magnetic resonance (ODMR) and spin-locking experiments gave unambiguous evidence for the triplet-spin nature of the N–V center ground state [5]. In the latter experiments, optical excitation of the N–V center at pumped liquid helium temperatures gives rise to an appreciable spin alignment in the $^3$A ground state. Microwave pumping of the zero-field spin transition (at 2880 MHz) within the $^3$A state alleviates the spin alignment and this, in turn, affects the population of the optically pumped $^3$E state. The $^3$E state gives rise to an emission at 638 nm and thus the $^3$A spin resonance can be probed optically.

In this Letter, we focus on Stark shift measurements involving the spin transition within the $^3$A ground state. It will be shown that Stark shifts as small as a few kilohertz can be resolved despite the fact that the ODMR transition near 2880 MHz has an inhomogeneous line width of about 15 MHz. As suggested by Mims [3], the problem of inhomogeneous broadening was overcome by performing a Hahn-echo decay experiment, which in the present case was extended with a third pulse to allow optical detection.

The applied pulse sequence is shown in fig. 1a. The first two microwave pulses serve to generate a Hahn echo at time $t=2\tau$. In the rephasing period between $\tau$ and $2\tau$, a static electric field of strength $|E|$ is introduced. The magnetic-dipole moments may undergo a shift of $\Delta\omega$ in their spin-resonance frequency due to the electric field. The accumulated phase shift at $t=2\tau$ equals $+\Delta\omega\tau$ or $-\Delta\omega\tau$, depending on which of the "inversion image" sites is considered (see also figs. 1b and 1c). Application of a final microwave $\pi/2$ probe pulse converts the macroscopic magnetic transition dipole moment, representative of the spin echo, into an optically detectable population difference [6]. Note that the probe-pulse method is sensitive to the phase of the spin echo in the $e_1e_2$ plane. It follows that the probed echo amplitude will display oscillatory behaviour given by [3,7]

$$R(E,\tau)\propto\cos\Delta\omega\tau\,. \qquad (1)$$

In figs. 1d and 1e we give a schematic picture of

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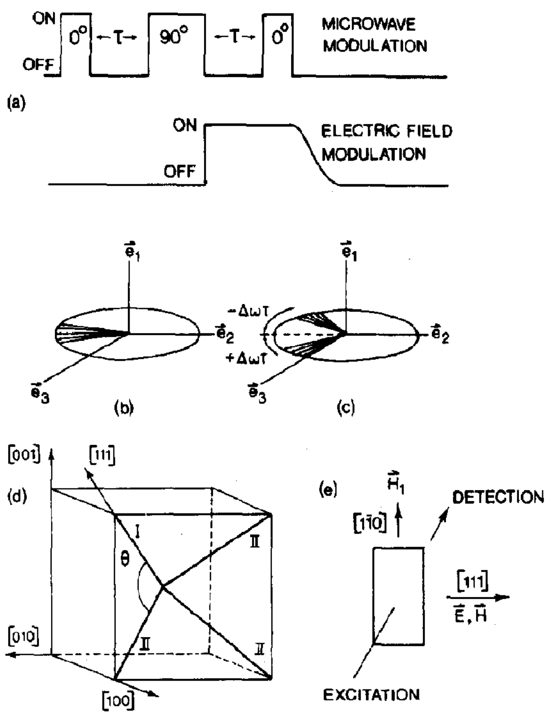


Fig. 1. (a) Microwave and electric-field pulse sequences used to measure optically the Stark effect on the spin-echo amplitude decay of the N–V centers in the $^3A$ ground state. (b) Generation of a Hahn echo at time $t=2\tau$ for $E=0$, as visualized in the rotating frame. (c) As in (b), but now an electric field in the time-interval between $\tau$ and $2\tau$ has been applied. For the "inversion image" triplet spins the Stark phase-shift is either $+\Delta\omega\tau$ or $-\Delta\omega\tau$, as indicated. The echo generated at $t=2\tau$ is phase-shifted by $\Delta\omega\tau$. (d) Orientation of the N–V center main axes with respect to crystallographic axes. For magnetic and electric fields along the [111] axis, two inequivalent subensembles of N–V spins (main axes labeled I and II) are distinguished. $\theta=109.28°$. (e) Directions of magnetic ($\boldsymbol{H}$) and electric ($\boldsymbol{E}$) fields, microwave polarization ($\boldsymbol{H}_1$), and optical excitation and detection direction with respect to the [111] and [1$\bar{1}$0] axes of the diamond crystal, as used in the Hahn-echo experiment.

the orientation of the molecular main axes of the N–V triplet sites, and the directions of the electric and magnetic fields applied to the crystal.

## 2. Experimental

The diamond sample containing N–V centers was the same as in previous work [8,9]. The crystal was mounted inside a slow-wave helix and immersed in a liquid helium bath. By controlled pumping of the helium the temperature was maintained at 1.4 K during the experiments. Optical excitation was by means of a cw $Ar^+$ ion laser at a wavelength of 514 nm. The $^3E \rightarrow {}^3A$ zero-phonon line (ZPL) fluorescence at 638 nm was detected in a direction parallel to the excitation pathway (see fig. 1e). The microwave $H_1$ field component was perpendicular to the detection pathway and the [111] crystallographic direction.

The spin-echo spectrometer for the optical detection of spin echoes has been described elsewhere [10]. The $\pi/2-\tau-\pi-\tau-\pi/2$ pulse sequences were applied at a repetition rate of 30 Hz. The microwave-induced changes in the fluorescence intensity were monitored using lock-in detection techniques.

Parallel {111} faces of the diamond crystal were coated with silver. The coated surfaces were used as electrodes. The spacing between the electrodes was 1.1 mm. In general, the Stark shift for N–V defects having their main axis along the electric field will be different from that observed for the defects having their molecular axes at an angle of 109.28° with the electric field vector. In order to study distinctly the Stark effect for the two N–V center subensembles (labeled I and II in fig. 1d), their respective spin-resonance frequencies were made to differ by the application of an additional static magnetic field along the [111] direction.

## 3. Results and discussion

Fig. 2a shows the optically detected Hahn-echo decay as observed for the $m_s=0 \rightarrow m_s=1$ spin transition of those N–V centers having their main axis along the magnetic field (parallel to the [111] direction). The magnetic-field strength in this instance is 60 G. Recently, it has been shown that the observed electron-spin echo-envelope modulation (ESEEM) effect is due to the magnetic dipole–dipole interactions between the N–V centers in the triplet state and the $I=1/2$ spins of the $^{13}C$ atoms in the lattice [9]. The ESEEM frequency appeared to increase linearly with the applied magnetic field and was shown to be representative of the $^{13}C$ nuclear spin resonance frequency $(\gamma_N/2\pi) \equiv g_N\mu_N = 1.071$ kHz/G s for $^{13}C$ ($I=1/2$) [11]. Figs. 2b and 2c show the observed

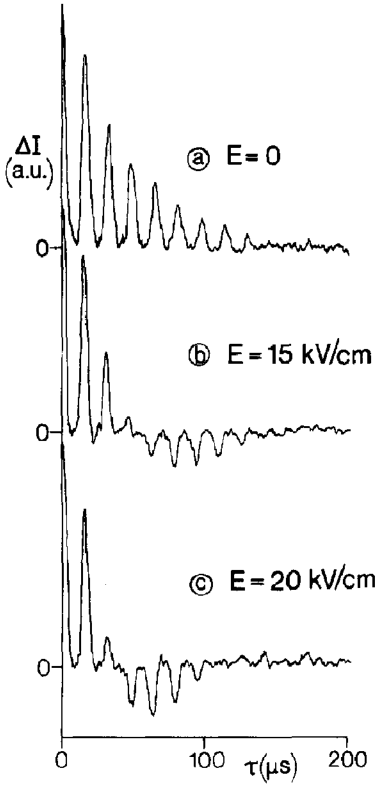


Fig. 2. Optically detected Hahn-echo decays as observed for the N–V center, when an electric field (strength as indicated) is applied in the time interval between $\tau$ and $2\tau$. $H=60$ G, $T=1.4$ K. Decay curves were monitored for the $m_s=0 \leftrightarrow m_s=1$ triplet-spin transition of the N–V centers that have their main axis parallel to the magnetic-field direction (cf. fig. 1d).

Hahn-echo decays when an electric field of 15 or 20 kV/cm, respectively, is applied. The displayed decay results show that for $\tau$ values of 50 and 35 μs the ESEEM patterns change sign, or equivalently, by means of an electric field it is possible to induce a phase reversal of the echo amplitude. When, however, electric fields were applied continuously during the whole microwave pulse sequence the echo envelope remained as shown in fig. 2a.

The electric-field-induced sign reversal of the echo-amplitude decay is understood on the basis of eq. (1). The echo decay changes sign when $\tau_i = \pi/2\Delta\omega$. As a result the Stark shifts, $\Delta\omega$, could be accurately determined experimentally for a series of electric-field values. As shown in fig. 3, a linear dependence of the Stark shift of the spin transition of the N–V center

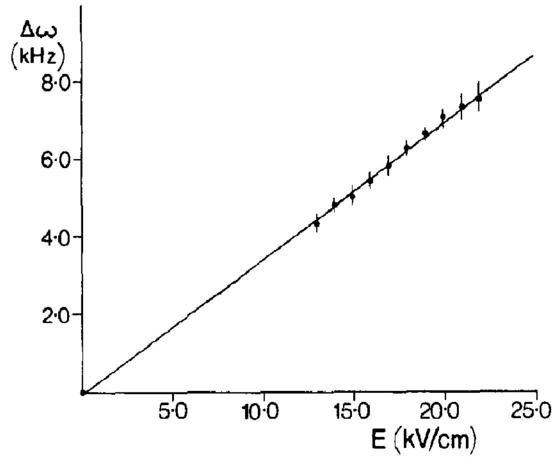


Fig. 3. Plot of the Stark shifts as measured for the N–V triplet spins of subensemble I; the experiment was performed in the presence of a magnetic field of 60 G along the [111] direction. The drawn line represents the best linear fit.

in its triplet ground state on the applied electric field is found. Furthermore, since the ESEEM frequency is not influenced by the electric field, the latter does not affect the hyperfine coupling to the $^{13}C$ nuclear spins. It follows that $\Delta\omega$ is limited to a linear shift in the triplet-state fine-structure splitting constants.

For $C_{3v}$ local symmetry, electric-field-induced linear shifts of the triplet-spin resonance are calculated from the following spin Hamiltonian [3,12]:

$$\begin{aligned} H_S = {} & R_{3D} E_z [S_z^2 - \tfrac{1}{3} S(S+1)] \\ & - R_{2E} [E_x (S_x S_y + S_y S_x) + E_y (S_x^2 - S_y^2)] \\ & + R_{15} [E_x (S_x S_z + S_z S_x) + E_y (S_y S_z + S_z S_y)] , \end{aligned} \quad (2)$$

where $S=1$, $E_x$, $E_y$, and $E_z$ denote the components of the electric field along the molecular axes of the N–V center, and $R_{3D}$, $R_{2E}$, and $R_{15}$ are the Stark-shift constants to be determined. Henceforth, we will consider the Stark shifts due to the $R_{3D}$ and $R_{2E}$ terms in eq. (2) only. The $R_{15}$ terms cause a mixing of $|0\rangle$ and $|\pm 1\rangle$ spin states, for which the energy splitting in zero field is $|D| = 2880$ MHz. The Stark energies being a few kilohertz only, the influence of the $R_{15}$ terms (which will be of second or higher order) can be ignored.

A linear shift of the $^3A$ spin transition of those defects having their main axes along the electric field is found on the basis of the spin Hamiltonian (cf. eq.

(2)) in first order as $\Delta\omega = R_{3D}E$. A best-fit analysis of the experimental shifts yields the straight line drawn in fig. 3; from the slope of this line we find $R_{3D} = 0.35 \pm 0.02$ Hz cm/V.

As illustrated by fig. 4, the Stark shift does not change when the strength of the externally applied magnetic field is increased. Hence, the electric field does not affect the N–V center $g$-factor. Thus, it is found that the $g$-factor as well as the hyperfine interaction with the $^{13}C$ nuclear spins remain unaffected by $E$; only the fine-structure splitting (as expressed by eq. (2)) is involved in the Stark effect.

Finally, Stark-modulation echo-decay experiments were performed in the absence of a magnetic field to determine the value of the $R_{2E}$ parameter in eq. (2). Echo-decay transients were measured while applying electric fields in the rephasing time interval. For field values larger than 2 kV/cm a weak oscillatory behaviour was found. The experimental echo-decay curves could be computer-fitted on the basis of eq. (2) taking into account the presence of two electrically inequivalent subensembles of N–V centers. The fits yielded $R_{2E} = 17 \pm 2.5$ Hz cm/V.

In conclusion, linear Stark shifts could be resolved showing that the N–V center indeed lacks inversion symmetry. The relevant spin-Hamiltonian parameters were determined from the measurement of the field dependence of the shift of the spin-resonance frequency.

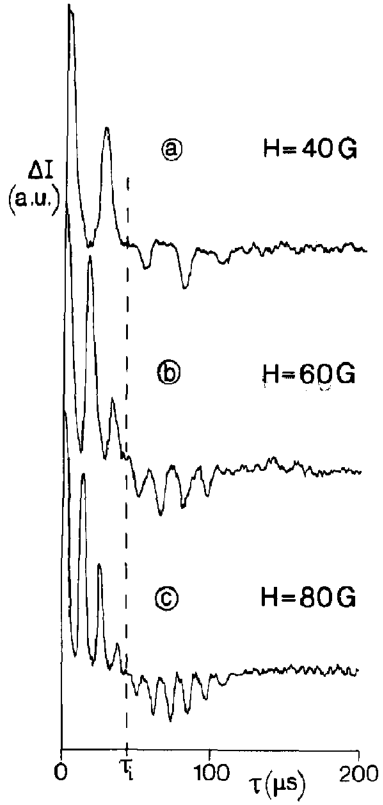


Fig. 4. Influence of the magnetic field on the Stark-induced modulation of the Hahn-echo decay observed for the N–V center. The electric field ($|E| = 18$ kV/cm) is applied between $\tau$ and $2\tau$ ($T = 1.4$ K). The decay curves were recorded for the $m_s = 0 \leftrightarrow m_s = 1$ triplet-spin transition of N–V centers belonging to subensemble I (cf. fig. 1d). The phase of the echo changes when $\tau = \tau_i$.

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