Proposal for observing dynamic Jahn–Teller effect by single solid-state defects

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Keywords: nitrogen-vacancy, Jahn–Teller effect, spin echoes

Abstract

The Jahn–Teller effect (JTE) widely exists in polyatomic systems including organic molecules, nanomagnets, and solid-state defects. Detecting the JTE at single-molecule level can provide unique properties about the detected individual object. However, such measurements are challenging because of the weak signals associated with a single quantum object. Here, we propose that the dynamic JTE of single defects in solids can be observed with nearby quantum sensors. With numerical simulations, we demonstrate the real-time monitoring of JT axis jumps between different stable configurations of single substitutional nitrogen defect centers (P1 centers) in diamond. This is achieved by measuring the spin coherence of a single nitrogen-vacancy (NV) center near the P1 center with the double electron-electron resonance technique. Our work extends the ability of NV center as a quantum probe to sense the rich physics in various electron-vibrational coupled systems.

1. Introduction

The Jahn–Teller effect (JTE) is one of the most important phenomena caused by electron-vibrational interaction, which has broad impact on both physics and chemistry. In fundamental physics, JTE relates to the symmetry-breaking concept, where the system Hamiltonian has a certain symmetry, but the ground state does not. In chemistry and condensed matter physics, the JTE is essential in understanding the structure, the optical and magnetic properties of polyatomic systems like molecules and solid state point defects.

The dynamic JTE describes the transitions of the system from one stable configuration to another. This configuration transition can happen with the help of thermal excitation or quantum tunneling\cite{1}. The dynamic JTE is usually measured by the change of optical or magnetic resonance properties under different conditions (e.g., temperature and strain). The characteristic parameters of the JTE, including the potential barrier height and the tunneling rate, are usually inferred indirectly from the ensemble averaged quantities such as optical and magnetic transition frequencies and line widths\cite{2-5}, or from the optical transition linewidth and spin polarization of single nitrogen-vacancy (NV) center\cite{6,7}. Directly monitoring the JT axis jumps of individual systems in real-time by single solid-state defects is intriguing. However, to our knowledge, the directly real-time measurement of dynamic JTE of an individual system is not achieved because of the weak signal associated with a single molecule or a single defect. Here, we demonstrate that, with high spatial resolution and the fast readout techniques developed in recent years, it is now possible to use NV centers to directly monitor the dynamic JTE at the single molecule (or single defect) level. Thus, the NV-center-based method can be a powerful complementary technique to the widely used traditional Raman spectroscopy for observing vibrations. Particularly, measuring the JT axis jumps of a single P1 center has some potential applications: (i) the JT axis jump rate is sensitive to the temperature of the detected P1 center. By measuring the reorientation rate, one can extract the information about local temperature with high spatial resolution. This will have broad biological applications, for example, in measuring the temperature difference across a cell; and (ii) in principle, our
proposal can be generalized to detect the vibration of single external molecules outside the diamond (e.g., the lattice vibration of JTE of a single molecular magnet).

In this work, we propose to measure the dynamic JTE of a typical kind of single solid-state defects, namely, the substitutional nitrogen defect centers (P1 centers) in diamond [8]. Although the undistorted structure has a tetrahedral symmetry, the energetically stable configurations of P1 center have triangle symmetry due to the Jahn–Teller distortion. There are four equivalent orientations of P1 centers corresponding to the nitrogen atom shifting along the direction of four N–C bonds. The JTE of P1 centers was observed via electron spin resonance [2] and electron–nuclear double resonance [3, 5], and the orientation relaxation (reorientation) rate was measured and calculated in a wide range of temperature. At temperature \( T > 250 \text{ K} \), the reorientation rate \( \nu \) follows the Arrhenius law \([8, 9]\)

\[
\nu = \nu_0 \exp \left[ -\frac{V}{k_B T} \right],
\]

where \( k_B \) is the Boltzmann constant, \( \nu_0 \approx 4 \times 10^{12} \text{ s}^{-1} \) and \( V = 0.76 \text{ eV} \). At low temperature (\( T \lesssim 200 \text{ K} \)), the reorientation rate deviates from the Arrhenius law, ranging from \( 10^{-3} \text{ to } 10^{-5} \text{ s}^{-1} \) [9]. The low rate at low temperature allows us to observe the reorientation process of individual P1 centers in real-time.

We propose to monitor the reorientation process of single P1 centers using the NV centers in diamond as quantum probe. The NV centers have been demonstrated to be ultra-sensitive magnetometers ranging from nanoscale \([10, 11]\) to atomic-scale resolution \([12, 13]\). Particularly, single NV centers were used to detect the weak magnetic signals emitted from individual nuclear spins \([12–15]\), nuclear spin clusters \([16]\) and large nuclear spin ensembles \([17, 18]\). Also, non-magnetic signals can be detected by converting to magnetic ones \([19]\). Notice that the Jahn–Teller distortion modifies the magnetic resonance frequency of the P1 centers electron spins \([20, 21]\), and the spins couples to the NV center electron spin through the magnetic dipolar interaction. Thus, it is possible to readout the P1 center state via an adjacent NV center.

The readout of the individual P1 center orientation can be realized by using the double electron–electron resonance (DEER) technique \([22, 23]\). It is well-established that high concentration P1 centers in diamond (e.g., \( \sim 10^5 \text{ ppm} \)) serve as an electron spin bath, which causes the electron spin decoherence of the NV centers \([20, 21]\). The decoherence effect can be partially removed by resonantly driving the P1 center bath spins using microwave pulses \([24]\). Due to the hyperfine interaction to the nitrogen nuclear spins, the P1 centers with different orientations can have different magnetic resonance frequencies in strong magnetic fields \([3, 20, 24]\). This enables driving P1 centers with particular orientation using frequency-selective microwave pulses \([24]\). In the following we show that, among a large number of P1 center bath spins, the nearest P1 center to the NV center usually has much more significant impact on the NV center spin coherence, whose orientation can be readout in a single-shot manner \([25]\) by repetitive measurement on the NV center. The proposed method is not limited in specific detected systems and, in principle, can be generalized to measure the JTE of other single quantum systems. This work extends the physical processes that NV centers can detect, and makes the investigation of JTE at single-molecule level possible.

2. Observing dynamics JTE

2.1. Double electron-electron resonance

We consider a type Ib diamond sample, where single NV centers are embedded in the electron spin bath of P1 centers (see figure 1). In a strong magnetic field \( \mathbf{B} \) (e.g., \( B > 200 \text{ Gauss} \)) along the NV axis (assumed to be the z-axis), the NV center spin \( \mathbf{S}_0 \) couples to \( N \) P1 center bath spins \( \mathbf{S}_k \) (for \( k = 1 \ldots N \)) via dipolar interaction, and the Hamiltonian reads

\[
H = D (S_0^z)^2 - \gamma B \sum_{k=0}^{N} S_k^z + \sum_{k=1}^{N} \sum_{l=1}^{N} J_{kl} S_k^z S_l^z,
\]

where \( D = 2.87 \text{ GHz} \) is the zero field splitting of the NV center, \( \gamma \) is the gyromagnetic ratio of electron spins, and the last term describes the dipolar interaction in strong field with \( b_k = \frac{4\pi\mu_0}{3\gamma^2} [1 - 3(n_k^z)^2] (\mu_0 \text{ is the vacuum permeability, and } n_k^z \text{ is the directional cosine of the } k \text{th bath spin}) \) [20]. In equation (2), we have omitted the dipolar coupling between bath spins, since it has negligible effect in the short time scale (\( \sim \mu\text{s} \)) we are interested in.

For a typical concentration \( c = 20 \text{ ppm} \) of P1 centers, the NV center electron spin coherence decays in about \( T_2^* \lesssim 1 \mu\text{s} \) (i.e., the free-induction decay, or, FID) due to the noise field created by the bath spins (i.e. the inhomogeneous broadening). With the well-known spin–echo technique, where a \( \pi \)-pulse is applied on the NV center at time \( t = \tau \), the static fluctuations will be refocused and the coherence recovers at time \( t = 2\tau \). In this case, the coherence time is extended to \( T_2 \) which is much longer than \( T_2^* \) [20].
The DEER sequence uses an additional $\pi$-pulse to flip the P1 center spins at $t = \tau$. The resonant frequency of the P1 center depends on its orientations and nuclear spin states $[3, 20, 24]$. In strong magnetic fields, the electron spin of the P1 center couples to its nitrogen nuclear spin by the hyperfine interaction

$$H_{\text{hf}} = \sum_{k=1}^{N} A_k^{(v)} S_k \cdot I_k^z,$$

where the coupling strength $A_k^{(v)}$ depends on the P1 center orientation $v \in \{a, b, c, d\}$. For the P1 centers with $^{14}$N nuclear spin, when the Jahn-Teller distortion axis parallels with the magnetic field direction (the $v = a$ case), the coupling strength $A_k^{(a)} = 114$ MHz. Otherwise, if the distortion axis lies in the other three equivalent directions (i.e., $v = b, c$ or $d$), the coupling strength $A_k^{(v)} = 86$ MHz. For a given orientation $v$, the hyperfine coupling results in three resonant peaks corresponding to nuclear spin magnetic quantum number $I_z = 0$ and $\pm 1$. The resonant frequencies for $I_z = 0$ are degenerate for all four orientations, while the parallel orientation (the $v = a$ case) has larger splitting for the $I_z = \pm 1$ resonant frequencies (see figure 1(c)).

The effect of the two $\pi$-pulses cancels each other if both NV center and P1 centers are resonantly flipped. The resultant pulse sequence, in this case, is equivalent to the FID case (with two $\pi/2$-pulses only). Thus, the microwave $\pi$-pulse on P1 centers divides the bath spins into two groups (see figure 1): (i) the resonant group $G_{\text{res}}$, in which the spins are flipped by the pulse; and (ii) the off-resonant group $G_{\text{off}}$, in which the spins are unaffected. The P1 centers in the off-resonant group contribute little to the NV center spin decoherence due to the refocusing pulse on NV center, while the bath spins in the resonant group, as long as the spin number $|G_{\text{res}}|$ is not too small, dominate the decoherence. In this case, the coherence decays as (see appendix B)

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**Figure 1.** (a) Schematic illustration of NV center (the black spin) in an electron spin bath consisting of P1 centers (the red and blue spins). The structure of P1 centers is shown on the left, and the red arrow indicates the elongated N–C bond. In a strong magnetic field $\mathbf{B}$ along the [111] crystallographic direction (the z-axis), the bath spins are randomly aligned parallel or anti-parallel in the z direction. All the bath spins are classified as the resonant group (blue) and the off-resonant group (red) according to their magnetic transition frequencies (see text). (b) Optical and microwave pulse sequences used in this proposal. Laser pulses are used both to initialize and readout the NV center spin state. The $\pi/2$-pulses create coherent superposition between the states $m_s = 0$ and $m_s = 1$ and convert the coherence echo to population. In the DEER measurement, two $\pi$-pulses are designed to flip the NV center and P1 centers simultaneously, while the check measurement (a pure spin echo sequence on the NV center) is designed to confirm the JT axis jumps of P1 center (see text). $M = 10^5$ times are repeated to collect the photon counts. (c) Magnetic resonance spectroscopy of P1 centers. Five dips associate with different orientation $v$ and $^{14}$N nuclear spin state $I_z$. In this paper, we focus on driving the P1 centers with the 3 resonant frequencies indicated by the arrows.
where the product is performed over all the $P_1$ centers in the resonant group.

By setting excitation frequencies of the microwave pulses, we can choose the orientation and nuclear spin states, in which the $P_1$ centers contribute to the NV center decoherence. To be concrete, we consider the microwave pulses drive the three peaks separated by $114$ MHz (see figure 1(c)). In this case, the resonant group $G_{\text{res}}$ contains the $P_1$ centers with $14$N nuclear spin ($I = \frac{1}{2}$) in 6 states $\{\nu, I_z\} = \{a, \pm 1\}$ and $\{\nu, 0\}$, for $\nu = a, b, c$ and $d$. Assuming that the 12 states of $P_1$ centers $\{\nu, I_z\}$ are randomly populated with equal probability, we have about half $P_1$ centers belonging to the resonant group $G_{\text{res}}$. Notice that the presence of other $P_1$ orientations ($\nu = b, c, d$ with $I_z = 0$) in the resonant group will cause fake signals in the monitoring of JT axis jumps. This problem could be circumvented by choosing samples with $15$N bath spins ($I = \frac{1}{2}$), the details are presented in appendix F. Considering the low natural abundance of $15$N (about 0.37%), the artificial enrichment of $15$N can be achieved through implantation of $15$N ions into type IIa diamond [26].

2.2. Single-shot readout of $P_1$ center orientation

Because of the inverse-cubic dependence of the dipolar coupling strength on distance, the adjacent $P_1$ centers to the NV centers have much more significant contributions to the spin coherence. For the moment, we focus on the nearest $P_1$ center to the NV. In the case of $P_1$ center concentration $c = 20$ ppm, the typical distance between the NV center and the nearest $P_1$ center is several nanometers, and the coupling strength, denoted by $b_1$, is in the order of $\sim$MHz. To quantify the contribution of the nearest $P_1$ center, we define the ratio

$$
\eta_1 = \frac{b_1^2}{\sum_{k=1}^{N} b_k^2},
$$

where $b_k^2$ characterize the size of the fluctuation due to the $k$th $P_1$ center. Our simulation shows that the probability of strongly coupled $P_1$ center is not too small. About 13% randomly generated bath configurations have the ratio $\eta_1 > 0.5$ (see appendix A).

For a given configuration with large $\eta_1$ (see figure 2), the NV center decoherence behavior in time domain strongly depends on whether or not the the nearest $P_1$ center is in the resonant group $G_{\text{res}}$. Figure 2 shows the calculated NV center coherence under DEER sequence for a given bath configuration and with random states $\{\nu, I_z\}$ being assigned to each $P_1$ centers. The decoherence behavior dramatically changes if the state of the nearest $P_1$ center changes from the resonant group to the off-resonant group, while the state change of other $P_1$ centers only causes small modifications. By choosing appropriate working point (the vertical dashed line shown in figure 2(a)), we can choose the orientation and nuclear spin states, in which the nearest $P_1$ center contribute to the NV center decoherence.
according to the working point, see equation (1). The nitrogen nuclear spin life time $T_{1v}$ is much shorter, assumed to be 50 ms [25]. Note that the results obtained in this paper are not sensitive to the value of nuclear spin life time $T_{1v}$, as long as the condition $T_{1v} \ll M T_{DEER}$ is satisfied. On the other hand, if the nuclear spin life time is long enough (e.g., in very strong magnetic fields or at very low temperature), in the opposite limit $T_{1v} \gg M T_{DEER}$, it is possible to monitor JT axis jumps of both nuclear spin flipping and reorientation of the strongly coupled P1 center using the same technique. We analyze the nuclear spin flipping effect in detail in the appendix D.

The JT axis jump of P1 center can be monitored by measuring the NV center coherence with DEER sequence. A single DEER sequence is completed in about $T_{DEER} = 5 \mu s$, which consists of the time for laser initialization/readout of NV center spin state ($3 \mu s$), microwave pulse duration ($\sim 10^2$ ns), and the time for coherent evolution ($1 - 2 \mu s$ according to the working point, see figure 2(a)). During the time of a single DEER sequence $T_{DEER}$, the P1 center state is hardly changed (i.e., $T_{DEER} \ll T_{1v}$ and $t_{i}$). Figure 3(c) shows the evolution of the NV center spin coherence, which is calculated according to the P1 center states at each instant. The spin coherence switches between two values $L_{low}$ and $L_{high}$ whenever the nearest P1 center jumps into or out of the resonant group $G_{res}$. The state change of those P1 centers with much weaker coupling causes the small fluctuation of NV center coherence around $L_{low}$ or $L_{high}$.

In realistic measurements, one has to repeat the DEER sequence, e.g., $M = 10^5$ times, to build up statistics. The total measurement time $T_{M} = M T_{DEER} = 0.5 s$ is much longer than the nuclear spin relaxation time $T_{1v}$, but can be much shorter than the orientation relaxation time $t_{i}$ at low temperature. By recording the number of photons collected in every 0.5 s, one averages out the coherence change due to nuclear spin flipping events, leaving only the reorientation events being monitored.

Figure 3(e) shows a numerical simulation of the JT axis jump process. Each data point represents the photon number collected in 0.5 s. Higher counts correspond to the nearest P1 center in the $v = b, c, d$ orientations, while the lower counts indicate that its orientation is along the $a$ axis ($v = a$). With the strongly coupled nearest P1 center and an appropriately chosen working point, the photon counts of every 0.5 s follow a well-separated double-Gaussian distribution (see figure 3(f)). The peak separation (the contrast) is determined by the coherence

in figure 2(a)), one can realize the single-shot readout of the P1 center state by repetitive measurement on the NV centers.

2.3. Monitoring JT axis jump in real-time

At finite temperature, both the P1 center orientation and its nuclear spin state are changing in time. The change of P1 center state is simulated by a Markov stochastic process (see appendix C). Figure 3(a) shows a typical realization of the jump process of the nearest P1 center. The P1 centers located at different positions have similar random jump behavior (not shown). In figure 3, we use the orientation relaxation time $t_{i} = 100$ s corresponding to the temperature $T = 262$ K (see equation (1)). The nitrogen nuclear spin life time $T_{1v}$ is much shorter, assumed to be 50 ms [25]. Note that the results obtained in this paper are not sensitive to the value of nuclear spin life time $T_{1v}$, as long as the condition $T_{1v} \ll M T_{DEER}$ is satisfied. On the other hand, if the nuclear spin life time is long enough (e.g., in very strong magnetic fields or at very low temperature), in the opposite limit $T_{1v} \gg M T_{DEER}$, it is possible to monitor JT axis jumps of both nuclear spin flipping and reorientation of the strongly coupled P1 center using the same technique. We analyze the nuclear spin flipping effect in detail in the appendix D.

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difference $L_{\text{high}} - L_{\text{low}}$ at the working point. The peak widths (photon number fluctuations) come from the photon shot noise, the fluctuation of spin coherence around $L_{\text{low}}$ and $L_{\text{high}}$ due to the weakly coupled bath spins (see figure 2), and the fluctuation caused by nuclear spin flipping. Setting an appropriate threshold photon number (e.g., $n_{\text{th}} = 2.54 \times 10^4$ in the case of figure 3(f)), one can define the fidelity of the single-shot readout (see appendix D for more analysis of the photon count distribution and the fidelity). As shown in the case of figure 3, the fidelity of single-shot readout of P1 center orientation is 99.4%.

One aspect that must be considered is that some other processes, (e.g., the trapping-releasing of an electron at a nearby charge trap, the presence of other two-state defects, and so on), may also change the spin dynamics of the NV center in a similar way, and may lead to the appearance of a similar ‘darker’ peak in the photoluminescence (PL) statistics of the NV center. Therefore, how to distinguish the JT axis jumps of a P1 center from the effect of other two-state defects in diamond is of great importance for this proposal. This could be realized with an extra check measurement after the DEER measurement, as shown in figure 1(b). The check measurement is nothing but a spin echo on the NV center. It monitors the change of PL intensity caused by other reasons (e.g., other two-state defects or charge traps). Notice that the change of PL statistics caused by these reasons will occur no matter the bath spins are flipped or not, while the JT axis jumps can only be observed in the DEER measurement, i.e., driving the electron spin of the NV center and the electron spins of P1 centers (the bath spins) simultaneously. Without the microwave pulses resonantly flipping the bath spins, the NV center is blind to the JT axis jump. Thus, if we record the photon numbers $n_{\text{DEER}}$ and $n_{\text{check}}$ collected during the DEER sequence and the check sequence in each 0.5 s respectively, the JT axis change could be identified with the assistance of PL statistics of check measurements. As we simulated in figure 4(a), if we observe that $n_{\text{DEER}}$ and $n_{\text{check}}$ experience a sudden change at the same time, then we cannot deduce whether this change is induced by the JT axis jump or by other two-state defects since both JT axis jump and the presence of other defects may result in the similar ‘darker’ peak in the PL statistics of the NV center. However, figure 4(b) shows a ‘smoking gun’ experimental evidence of the JT axis jumps of a P1 center, where the JT axis jump only causes a change of $n_{\text{DEER}}$ but $n_{\text{check}}$ remains unchanged.

Furthermore, due to the presence of charge traps or other two-state defects, the coherence of NV spin may not be completely refocused by the $\pi$-pulse during the DEER measurement, and thus a noise (i.e., unexpected darker peak) is created. Considering that the charge traps or other two-state defects are not directly affected by the $\pi$-pulse applied to the P1 center, this noise also exists in the subsequent check measurement, which could be treated as a background noise in our proposal. The effective PL statistics of the JT axis jumps of a P1 center will be determined if and only if the subsequent $n_{\text{check}}$ has higher counts. By this we find that a well-separated double-Gaussian distribution of $n_{\text{DEER}}$ can be obtained, as shown in figure 5(b), where we have assumed that 30% of $n_{\text{check}}$ has the lower counts due to the presence of charge traps or other two-state defects. It is obvious that the presence of background noise does not show significant influence on the observation of dynamic JTE.
2.4. Temperature dependence of JT axis jumps process

The reorientation rate is very sensitive to temperature $T$ (see equation (1)). With a given nuclear spin relaxation, we investigate the reorientation process at different temperatures. Figure 6 shows the simulation results. The fidelity is decreasing when increasing the temperature, because of the more frequent orientation change during $t_{JTE} = 0.5$ s. If the temperature is high enough (e.g., $T = 319$ K), the signal of JTE will be completely averaged during the time of photon collection. Hence, we expect only one Gaussian peak of the photon counts. Numerical simulation confirms this behavior, as shown in figure 6(f).

Figure 5. Simulated histograms of the effective $n_{\text{DEER}}$. (a) The distribution of $n_{\text{DEER}}$ without considering the effects of charge traps or other two-state defects. The parameters are the same as figure 3. (b) Assuming that the presence of charge traps or other two-state defects will result in 90% lower counts of $n_{\text{DEER}}$, the number of effective $n_{\text{DEER}}$ is reduced but a well-separated double-Gaussian distribution of $n_{\text{DEER}}$ is still observable.

Figure 6. Simulated JT axis jumps and single-shot readout of P1 center orientation at different temperatures. (a) $\tau_0 = 1000$ s (with $T = 246$ K). (b) Histogram of the photons collected in 0.5 s of (a). The red curves are the Gaussian fitting of the two peaks and the fidelity of single-shot readout of P1 center orientation is 99.8%. (c) $\tau_0 = 10$ s (with $T = 282$ K). (d) Histogram of the photons collected in 0.5 s of (c). The red curves are the Gaussian fitting of the two peaks and the fidelity of single-shot readout of P1 center orientation is 94.8%. (e) $\tau_0 = 0.25$ s (with $T = 319$ K). (f) Histogram of the photons collected in 0.5 s of (e). Only one Gaussian peak is visible, and the single-shot readout of orientation fails at this temperature. In all simulations nuclear spin relaxation time $T_1 = 50$ ms is used.
3. Discussion and conclusion

We have considered the JT axis jumps of P1 center with $^{14}$N nuclear spin. The transition frequencies of four orientations are degenerate when the nuclear spin in the state with $I_z = 0$. This degeneracy prevents us from driving P1 centers with a specific orientation but regardless of their nuclear spin state. Indeed, the fast nuclear spin relaxation reduces the signal contrast by a factor of $2/3$, in the driving scheme discussed above (see figure 1(c)). This will be different if the bath consists of P1 centers with $^{15}$N nuclear spins. The degeneracy of transition frequency will be lifted, and readout signal can have a full contrast (see appendix F).

The above analysis demonstrates the real-time measurement of dynamic JTE of a single P1 center. In our simulation, we notice that, for randomly generated spin bath, it is possible to have several P1 centers that are strongly coupled to the NV center. In this case, the NV center spin coherence will be sensitive to the states of these P1 centers. Using the same DEER sequence demonstrated here, it is possible to observe JT axis jumps of more than one P1 centers.

Before conclusion, we point out that our proposal does not strongly depend on the details of detected quantum objects (e.g., their detailed electronic structures). The single-shot readout measurement will work if (i) the detected object carries either electron spin or nuclear spin, and it couples to the NV center spin; (ii) the reorientation process causes the change of magnetic resonant frequency; and (iii) the readout sequence is fast enough in comparison with the reorientation rate. It is possible to fulfill these conditions in various systems such as molecular nano-magnets at low temperature. Detailed analysis of other physical systems is beyond the scope of this paper. However, we believe that, using shallow NV centers close to diamond surface, people can observe of the dynamic JTE of external single molecules in the near future.

In this work, we propose to measure the dynamic JTE of single P1 defect centers in diamond. Thanks to the hyperfine interaction with the nitrogen nuclear spins, the defect center orientation is correlated with the magnetic resonant frequency. Thus, the orientation can be readout by applying a DEER sequence. Our work extends the ability of NV centers as an outstanding quantum sensor in atomic scale, particularly, when the proposed method is generalized to detect the vibrational dynamics of single molecules outside diamond.

Acknowledgments

We acknowledge R B Liu’s comment on the manuscript and the suggestion for the future work. We thank X Y Pan for the discussions of the DEER measurement. We thank L M Zhou for the assistance of the numerical simulation. This work is supported by NKBPRP (973 Program) 2014CB848700 and NSFC No. 11374032, No. 11665004, No. 61403014 and No. 11121403, and by Scientific Research Foundation of Jiangxi Provincial Education Department under Grants No. GJJ150996.

Appendix A. Statistics of random spin bath configurations

In order to observe the JTE, we need the nearest P1 center spin has much stronger interaction with the NV center in comparison with other P1 center spins in the given spin bath configuration. Since the dipolar coupling strength between P1 center and NV center inverse-cubically depends on their distance, it is not difficult to find a spin bath configuration in which the nearest P1 center has a significant contribution to the NV center decoherence, which is characterized by the parameter $\eta_{1}$ (see equation (5)). For a typical P1 center concentration $c = 20$ ppm, we randomly generate $10^{6}$ P1 center spin bath configurations and calculate the parameter $\eta_{1}$ of each configurations. Figure A1 shows that the probability of the ratio $\eta_{1} > 0.5$ is about 13.4%.

Appendix B. Calculations of NV center spin coherence under DEER sequence

This section presents the calculation of the NV center electron spin coherence under the DEER sequence. We will focus on the situation discussed in the main text, where about half of the P1 center bath spins are resonantly flipped by the microwave $\pi$-pulse. Since the P1 center orientation $\nu$ and its nuclear spin state $I_z$ are hardly changed in the time scale of NV center decoherence (i.e., $\sim \mu$s), the states $\{|\nu, I_z\}$ of each P1 centers are assumed to be static when calculating the coherence. The effect caused by the jumps of states $\{|\nu, I_z\}$ in a longer time scale is analyzed in the main text.

As discussed in the main text, with given states $\{|\nu, I_z\}$ of each P1 centers and given excitation frequencies of microwave pulse, the bath spins are classified into the resonant group and the off-resonant group (see figure 1 of the main text). Since the microwave pulse on the P1 centers has different effect on the resonant and off-resonant groups, the decoherence due to these two groups are treated differently.
For the resonant group, the physical effect of the $\pi$ pulses on the NV center and P1 centers cancels each other. In this case, the DEER sequence is indeed equivalent to the free-induction decay (FID, i.e., with only the two $\pi/2$ pulses on the NV center) case. During the period of several ms, the interaction between bath P1 centers (usually <$10$ kHz) in the resonant group can be neglected, and the decoherence $L_{\text{res}}$ caused by the P1 centers in the resonant group is

$$L_{\text{res}}(t = 2\tau) = \text{Tr}[e^{-iH_{\text{res}}^{\text{tot}}t}e^{iH_{\text{res}}^{\text{tot}}t}] = \prod_{k \in \text{Gres}} \cos\left(\frac{b_k t}{2}\right),$$

where

$$H_{\text{res}}^{\text{tot}} = -\gamma B \sum_{k \in \text{Gres}} S_k^z,$$

$$H_{\text{res}}^{\text{tot}} = -\gamma B \sum_{k \in \text{Gres}} S_k^z + \sum_{k \in \text{Gres}} b_k S_k^z,$$

are the conditional Hamiltonians of P1 center bath spins for the NV center electron spin in two eigen-states of $S_k^z$, $|m_z = 0\rangle$ and $|m_z = +1\rangle$, respectively.

For the off-resonant group, the pulses on the P1 centers do not take effect. Thus, the $\pi$ pulse on the NV center refocuses the static fluctuations due to the P1 center bath spins in the off-resonant group. In fact, the spin echo of NV center in P1 center electron spin bath has been well-studied. The noise due to the bath spins in the off-resonant group can be modeled by an Uhlenbeck stochastic process [21] with correlation function

$$C(t) = b^2 \exp(-|t|/\tau_c),$$

where $b$ is the characteristic noise strength, and $\tau_c$ is the noise correlation time. With this model, the NV center spin echo signal decays as [21]

$$L_{\text{off}}(t = 2\tau) = e^{-b^2t^2/12} \equiv e^{-(t/\tau_c)^2}.$$

The typical value of coherence time $T_2 = 3.5$ $\mu$s was observed in similar diamond sample (with P1 center concentration about $c \sim 20$ ppm) considered in our work. Notice that, the effective bath spin concentration of the off-resonant group is twice smaller than the full concentration. The coherence time due to the off-resonant group should be prolonged by a factor of 2, i.e. $T_2 \sim 7$ $\mu$s in this case, since the coherence time is inversely proportional to the bath spin concentration in the dipolar coupled systems [27]. With the single-shot readout with working point $t = 1.8$ $\mu$s used in the main text, the off-resonant group has negligible effect on the NV center spin coherence, i.e., $L_{\text{off}}(t = 1.8 \mu s) \approx 1$.

Indeed, the bath spins in the off-resonant group can be further decoupled by applying multi-$\pi$-pulse dynamical decoupling sequence, and the coherence time $T_2$ can be, at least, extended to $10^2$ $\mu$s [21]. If $\pi$ pulses are also applied on the P1 centers simultaneously (a generalized multi-pulse DEER sequence), the decoherence due to the bath spins in the resonant group is not changed, while the contribution of the off-resonant group can be completely neglected.

The inter-group spin interaction has little effect on the NV center spin coherence. Because of the large frequency mismatch between the resonant and the off-resonant groups, the inter-group spin pair flip-flop process is greatly suppressed. Thus, it is reasonable to assume that the parameters characterizing the noise from the off-resonant group (i.e. $b$ and $\tau_c$) are not affected by the spins in the resonant group. Accordingly, the NV coherence time should be prolonged by a factor of 2.
center decoherence is caused independently by the two groups

\[ L_{\text{DEER}}(t = 2\tau) = L_{\text{off}}(t) L_{\text{res}}(t) \approx L_{\text{res}}(t). \]  

(B.5)

Appendix C. Simulation of JT axis jump process

The real-time change of each P1 center state is simulated by a continuous-time Markov stochastic process \([28]\). For P1 centers with \(^{14}\text{N}\) nuclear spins, the Markov chain \(X(t), t \in [0, +\infty)\) has a twelve-state space \(E = \{ (\nu, L) \} \) with \(\nu \in \{ a, b, c, d \}\) and \(L \in \{-1, 0, +1\}\). The Q-matrix (or infinitesimal generator) of the process is given in table C1.

The JT axis jump of P1 centers is studied by a hold-and-jump process, which is particularly useful for computer simulation. For a given P1 center in the bath, at random times \(t = t_1, t_2, \ldots, t_n, \ldots\) it changes to a new state, and the sequence of states constitutes a discrete-time process \(S = \{ S_n | S_n \in E \}\). Usually, we call \(t_n\) the jump times and \(\tau_n = t_n - t_{n-1}\) the holding times (with \(t_0 \equiv 0\)). For example, \(\tau_n\) is the time that the P1 center stays in \(S_i\) before it jumps to \(S_j\). The holding times of the \(i\)th state are random variables following exponential distribution with mean value \(q_i = -q_{ij} = \sum_{j \neq i} q_{ij}\), where \(q_{ij}\) is the matrix element of the Q matrix.

The following algorithm is performed to implement the hold-and-jump process of each single P1 center in the bath:

1. Set a total evolution time \(T_{\text{tot}}\); start the process at \(t = 0\) with a randomly generated initial state \(i \in E\);
2. For the current state \(i\), generate a holding time \(\tau\), which follows an exponential distribution with parameter \(q_i\);
3. Replace the value of \(t \leftarrow t + \tau\); set the jump matrix \(\Pi = (\pi_{ij})\) with \(\pi_{ii} = 0\) and \(\pi_{ij} = q_{ij}/q_i\).
4. Randomly choose a new state \(j\) with the probability distribution given by the \(i\)th row of the jump matrix \(\Pi\);
5. If \(t < T_{\text{tot}}\), set \(i \leftarrow j\) and return to step (2); otherwise, the simulation is completed.

The simulated jump process of the nearest P1 center to the NV center is shown in figure 3(a) of the main text. Other P1 centers located at different positions have similar random jump behavior.

Appendix D. Single-shot readout fidelity

In this appendix, we analyze the fidelity of the single-shot readout process. To this end, we first study the photon count distribution.

**Photon count distribution.** The photon count distribution, in general, is of a double-Gaussian shape. The broadening of the Gaussian peaks comes from three sources: (i) the photon shot noise; (ii) the fluctuation of NV center coherence caused by the weakly coupled P1 centers; and (iii) the \(^{14}\text{N}\) nuclear spin flipping of the detected (nearest) P1 center. The influence of these mechanisms on the photon count distribution is discussed as follows.

**Photon shot noise.** The single-shot readout process is essentially a repetitive measurement on the NV centers. With \(M\) times independent measurements, one can collect \(n\) photons, which is a random variable and follows a normal distribution in the large \(M\) limit (i.e., \(M \gg 1\))
\[ Q(n; M, L) = \frac{1}{\sqrt{2\pi\delta_M^2(L)}} \exp\left\{ \frac{(n - \bar{n}_L M)^2}{2\delta_M^2(L)} \right\}, \]  
(\text{D.1})

where \( \bar{n}_L M \) and \( \delta_M^2(L) \) is the expectation value and the variance of the photon number for a fixed coherence \( L \) of the NV center.

If the NV center is prepared in \( |n_S = 0 \rangle \) state, \( M \) readout measurements result in \( \bar{n}_{|0\rangle} = M\xi \) photons on average, where a typical value \( \xi = 0.3 \) is used for the mean photon number of each measurement (determined by the count rate, photon collection efficiency, and the duration of the readout laser pulse). An NV center in \( |n_S = 1 \rangle \) state emits less photons than in the \( |n_S = 0 \rangle \) state. With a contrast factor \( C = 0.7 \), the mean photon number for the \( |n_S = 1 \rangle \) state is \( \bar{n}_{|1\rangle} = C \cdot \bar{n}_{|0\rangle} \). An arbitrary coherence value \( L \) is mapped to a mean photon number as

\[ \bar{n}_{L M} = \frac{1}{2} M\xi \left[ (1 - C)L + (1 + C) \right] \]  
(\text{D.2})

and the variance is

\[ \delta_L^2(L) = M \cdot \xi L \left( 1 - \xi L \right), \]  
(\text{D.3})

where \( \xi_L = [(1 - C)L + (1 + C)]\xi/2 \) is the mean photon number per measurement with the given coherence \( L \).

**Fluctuation due to weakly coupled P1 centers.** In fact, the coherence \( L \) is changing due to the weakly coupled P1 centers. As shown in figure 2(b) of the main text, the NV center spin coherence \( \log \) DEER under DEER sequence follows two normal distribution \( P_{low}(L) \) and \( P_{high}(L) \) centered at \( L_{low} \) and \( L_{high} \) and with variances \( \sigma_{low}^2 \) and \( \sigma_{high}^2 \), respectively, i.e.

\[ P_{low}(L) = \frac{1}{\sqrt{2\pi\sigma_{low}^2}} \exp\left\{ -\frac{(L - L_{low})^2}{2\sigma_{low}^2} \right\}, \]  
(\text{D.4})

\[ P_{high}(L) = \frac{1}{\sqrt{2\pi\sigma_{high}^2}} \exp\left\{ -\frac{(L - L_{high})^2}{2\sigma_{high}^2} \right\}. \]  
(\text{D.5})

As explained in the main text, with a strongly coupled P1 center close to the NV center, and with a properly chosen working point, the two Gaussian peaks are well-separated (i.e. \( L_{high} - L_{low} \gg \sigma_{low} + \sigma_{high} \)), and their overlap can be neglected. The fluctuation of the NV center coherence \( L \) causes the broadening of the photon count distribution as

\[ D_{low/high}(n; m; L) = \int Q(n; m, L) \cdot P_{low/high}(L) dL, \]  
(\text{D.6})

where the integral region can be safely extended to \((-\infty, +\infty)\) as long as the coherence distribution \( P_{low/high} \) is narrow enough (i.e. \( \sigma_{low/high} \ll 1 \)).

When the P1 center is in the \( v = a \) orientation (parallel to the magnetic field), with \( M \) measurements (e.g., \( M = 10^5 \)), the photon count distribution follows a normal distribution

\[ D_{a}(n; M) = D_{low}(n; M) \approx N\left( \bar{n}_L |a|, \Sigma^2 \right), \]  
(\text{D.7})

with mean value \( \bar{n}_L \) and variance \( \Sigma^2 \)

\[ \bar{n}_L = \frac{1}{2} M\xi \left[ (1 - C)L_{low} + (1 + C) \right], \]  
(\text{D.8})

\[ \Sigma^2 = \frac{M^2\xi^2(1 - C)^2}{4} \sigma_{low}^2 + \delta_M^2(L_{low}). \]  
(\text{D.9})

In equation (\text{D.7}), we have neglected the coherence \( L \) dependence of the variance \( \delta_M^2(L) \) (i.e., \( \delta_M^2(L) \approx \delta_M^2(L_{low}) \)). This is a good approximation as long as the fluctuation of coherence \( L \) is small (i.e., \( \sigma_{low/high} \ll 1 \)), which is the case in this work.

For the P1 center in \( v = b, c \) or \( d \) orientations (the non-parallel orientations), the \(^{14}\text{N} \) nuclear spin flipping will mix the two distributions \( D_{low} \) and \( D_{high} \). The coherence \( L \) follows the distribution \( P_{low}(L) \) when \( L_e = 0 \), while it follows \( P_{high}(L) \) when \( L_e = \pm 1 \). For a given measurement number \( M \), \( xM \) measurements are performed with \( L_e = 0 \) and \( (1 - x)M \) measurements are performed with \( L_e = \pm 1 \), where \( 0 < x < 1 \) is the probability of the nuclear spin in the \( L_e = 0 \) state (see figure 3(d)). With a given value of \( x \), the photon number distribution is the convolution of the two distributions \( D_{low} \) and \( D_{high} \)

\[ D_{f}(n; M, x) = \int D_{low}(k; xM) \cdot D_{high}(n - k; (1 - x)M) dk. \]  
(\text{D.10})
Essentially, the probability $x$ itself is a random variable. For the moment, we consider the fast relaxation limit of the $^{14}$N nuclear spin. When nuclear spin relaxation time $T_{1n}$ is much smaller than the measurement time $MT_{DEER}$ (i.e. $T_{1n} \ll MT_{DEER}$), the nuclear spin flips many times during the time of $M$ measurements. In this case, three nuclear spin states $L_z = 0, \pm 1$ are equally populated, and the fluctuation of $x$ is negligible. With the random variable $x$ replaced by its expectation value $\bar{x} = 1/3$, and with the similar approximation applied in equation (D.7), the distribution $D_{\parallel}(n; M)$ of the non-parallel case in the fast nuclear spin relaxation limit is also a normal distribution

$$D_{\parallel}(n; M) \approx D_{\parallel}(n; M, x) \approx \mathcal{N}(\bar{x}, \Sigma_{\parallel}^2),$$

where the mean value $\bar{x}$ and the variance $\Sigma_{\parallel}^2$ are calculated as

$$\bar{x} = M\left[\frac{1}{2} C \left(\frac{L_{\text{low}}}{3} + \frac{2L_{\text{high}}}{3}\right) + \frac{1}{2} \right],$$

$$\Sigma_{\parallel}^2 = M^2 \left[\frac{1}{2} \left(1 - C\right)^2 (\sigma_{\text{low}}^2 + 4\sigma_{\text{high}}^2) \right] \frac{9}{4} + \delta_{\text{low}}^2 (L_{\text{low}}) + \delta_{\text{high}}^2 (L_{\text{high}}).$$

**Broadening due to nuclear spin flipping.** Now, we analyze the effect of fluctuation of $x$ at finite nuclear spin flipping rate $\gamma_{1n} = 1/T_{1n}$. In this case, the photon count distribution of the non-parallel case must be averaged over the distribution $W(x)$ of $x$, i.e.

$$D_{\parallel}(n; M) = \int_0^1 D_{\parallel}(n; M, x) \cdot W(x) \, dx.$$  

The mean phonon number $\bar{\gamma}$ is insensitive to the fluctuation of $x$, while the width $\Sigma_{\parallel}$ is broadened when taking into account the finite variance $\sigma_x^2$ of the distribution $W(x)$. Our numerical result shows that the variance $\sigma_x^2$ decreases as $\sigma_x^2 \propto \gamma_{1n}^{-1}$, which is understandable in the spirit of the central-limit theorem. Figure D1 demonstrates the simulated photon count distribution variance $\Sigma_{\parallel}^2$ and $\Sigma_{\parallel}^2$ as functions of nuclear spin relaxation rate $\gamma_{1n}$ with a fixed $M = 10^5$. The variance $\Sigma_{\parallel}^2$ follows similar behavior as the variance of $\sigma_x^2$ when increasing the relaxation rate $\gamma_{1n}$, while the variance $\Sigma_{\parallel}^2$ keeps constant.

Figure D2 shows the width $\Sigma_{\parallel}$ (normalized by the peak separation of the two distributions $D_{\text{low}}$ and $D_{\text{high}}$) as a function of the nuclear relaxation rate $\gamma_{1n}$ and the measurement number $M$. With a given nuclear spin relaxation $\gamma_{1n}$, increasing measurement number $M$ reduces the relative width, which is the expected result of decreasing the photon shot-noise and the fluctuation of $x$.

**Fidelity of single-shot readout.** In this subsection, we analyze the fidelity of the single-shot readout. One obvious reason for the readout error is the overlap of the two Gaussian distributions $D_{\parallel}$ and $D_{\parallel}$. Increasing measurement number $M$ will decrease the overlap (see figure D2). However, another mechanism, namely, the
The state change of the nearest P1 center during the single-shot readout process (i.e., during the period $T_M = M T_{\text{DEER}}$), will cause the readout error when increasing the measurement time (i.e., increasing $M$).

To quantify the readout fidelity, we define a threshold $n_{\text{th}}$ value of photon number collected with $M$ times repetition measurements as the weighted average of $\bar{n}_||$ and $\bar{n}_\perp$:

$$n_{\text{th}} \equiv \frac{\sum \bar{n}_|| + \sum \bar{n}_\perp}{\sum \bar{n}_|| + \sum \bar{n}_\perp}.$$  

The readout fidelity because of the distribution overlap is quantified as

$$F_1 = \frac{1}{4} \text{erf} \left( \frac{n_{\text{th}} - \bar{n}_||}{\sqrt{2} \Sigma||} \right) + \frac{3}{4} \text{erf} \left( \frac{\bar{n}_\perp - n_{\text{th}}}{\sqrt{2} \Sigma||} \right).$$  

where $\text{erf}(x) \equiv \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2) \, dt$ is the error function. The pre-factors (i.e., $1/4$ and $3/4$) account for the equilibrium populations of the parallel and the non-parallel orientations.

The state change of the detected nearest P1 center during a single measurement period $T_M$ causes additional readout error, which is characterized by the ratio of measurement time $T_M = M T_{\text{DEER}}$ to the orientation relaxation time $\tau_v$. In this case, the fidelity due to the state change is characterized by

$$F_2 = 1 - \frac{MT_{\text{DEER}}}{\tau_v}.$$  

The total measurement fidelity is the combination of the two components above

$$F = F_1 + F_2 - 1.$$  

The two components $F_1$ and $F_2$ of the fidelity have different behavior when increasing the measurement time $T_M$. In the short-time case, the readout error is dominated by the overlap between two Gaussian peaks, while in the large $M$ case, the frequent change of orientation during the measurement time $T_M$ reduces the fidelity. The tradeoff of these two errors gives an optimal measurement period, as shown in figure D3. In the case discussed in the main text, numerical simulation suggests that the optimal measurement scheme is near $M = 10^5$ (corresponding to $T_M = M T_{\text{DEER}} = 0.5$ s).

**Appendix E. Different driving scheme: driving a single resonance ($v = a$, $I_z = -1$)**

The reorientation process can be monitored with different driving schemes. One can drive the bath spins with a single microwave frequency resonant to P1 centers in the state ($v = a$, $I_z = -1$). The spin coherence switches to $L_{\text{low}}$ when the nearest P1 center jumps to the ($a$, $-1$) state, otherwise it stays at $L_{\text{high}}$. However, due to the fast relaxation of nuclear spin, the nearest P1 center will quickly switch to different nuclear spin states and cannot keep in the state ($a$, $-1$) for a long time. Therefore, the photon number collected in 0.5 s has large fluctuation.
and the signal contrast is also reduced (see figure D4). Nevertheless, one can read out the orientation of the nearest P1 center with fidelity $F \sim 80\%$.

**Appendix F. P1 center with $^{15}$N nuclear spin**

Due to the degeneracy of four orientations in the state $I_z = 0$ of $^{14}$N P1 center, the signal contrast is reduced by a factor of $2/3$. If the spin bath consists of P1 centers with $^{15}$N nuclear spins, four dips will be observed corresponding to the electron spins in states $\{|a, \pm 1/2\}$ and $\{|\nu, \pm 1/2\}$ for $\nu = b, c$ and $d$. By driving the two outer peaks (i.e., $\{|a, \pm 1/2\}$), we can define the resonant group $G_{\text{res}}$ unambiguously with the P1 center in $a$ orientation and the off-resonant group $G_{\text{off}}$ with the P1 center in $b$, $c$ and $d$ orientations. In this situation, the relaxation of nuclear spin states no longer mixes the resonant and off-resonant groups. Figure D5 shows the...
jump process of the nearest $^{15}$N P1 center, evolution of the NV center spin coherence, the simulation of single-shot readout of P1 center orientation and the histogram of photons collected in 0.5 s. Being different with the results in the $^{14}$N P1 center case, the NV center spin coherence changes from $I_{\text{high}}$ to $I_{\text{low}}$ only when the nearest $^{15}$N P1 center jumps into the orientation (see the difference between figure 3(d) of the main text and figure D5(d)). On the other hand, the signal contrast is improved (to the full contrast of 30%) in the $^{15}$N P1 center case.

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