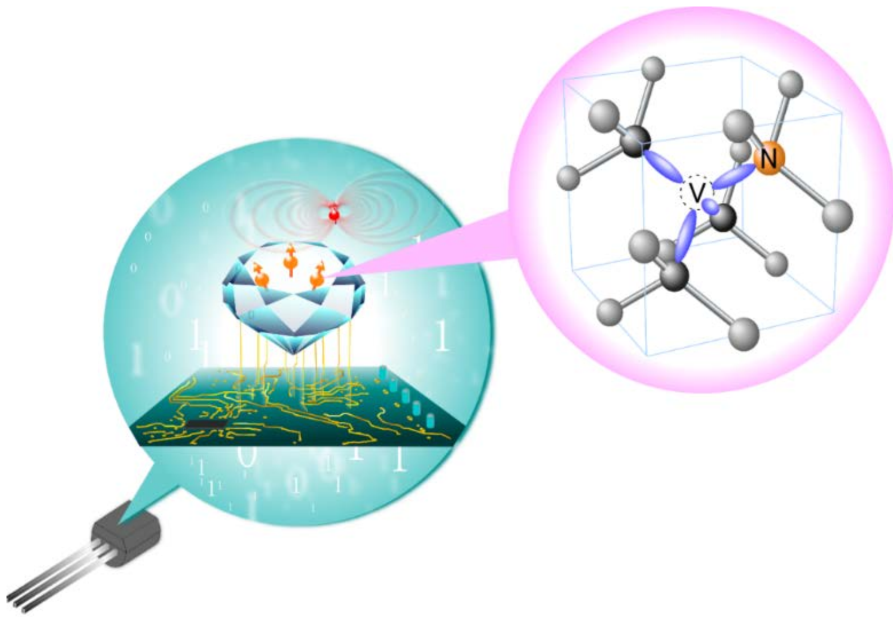
KEK IPNS-IMSS-QUP Joint workshop, 10th Feb 2022

Nitrogen-Vacancy centers in diamond for quantum sensing

Norikazu MIZUOCHI

Institute for Chemical Research, Kyoto University



Content

1. Overview: Quantum sensor, NV center in diamond
2. Characteristics of NV centers for sensor
   ～ Why can we improve sensitivity and spatial resolution? ～
3. How to measure? (Magnetic field, electric field, temperature)
4. Expected applications
5. Our recent studies

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Quantum science and technology

Quantum computers, Quantum cryptography

Quantum sensors

capitalize on the central weakness of quantum systems, their strong sensitivity to external disturbances.

Quantum sensor : Definition

C. L. Degen, F. Reinhard, P. Cappellaro, Rev. Mod. Phys., 89, 035002 (2017).

1. Use of a quantum object to measure a physical quantity. The quantum object is characterized by **quantized energy levels**. (ex. electronic, magnetic or vibrational states of superconducting or spins, neutral atoms, or trapped ions)

   Close to applications.

2. Use of **quantum coherence** to measure a physical quantity. (ex. Spin coherence of NV centers, …)

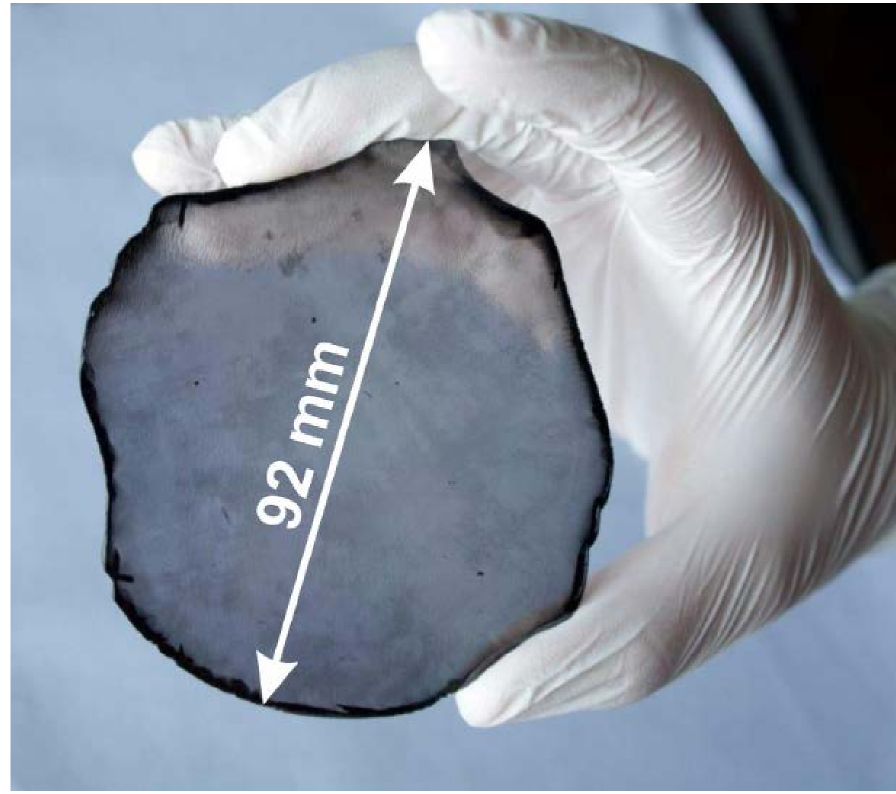
   Close to applications. Higher sensitivity and dynamic range than 1.

3. Use of **quantum entanglement** to improve the sensitivity or precision of a measurement, beyond what is possible classically.

   More stringent and a truly quantum definition. Use of it is the ultimate goal but so far, it is difficult to generate, …

Experimental implementations of high sensitive quantum sensors.

- Superconducting quantum interference devices (SQUID)
- Atomic vapors or atomic clocks
- Solid-state spins
- …



Synthetic Diamond
(CVD, HPHT)
Commercially available
(4-10 mm□, http://www.e6.com/)

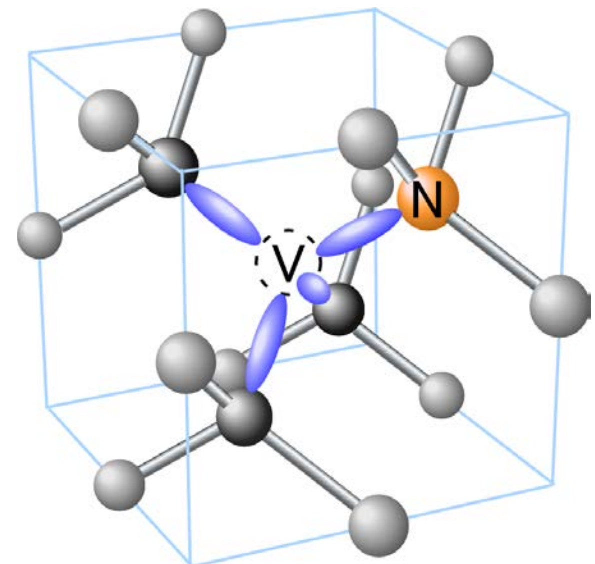
Hetero-epi, CVD,
single crystal

Scientific reports 7:44462 (2017)
doi:10.1038/srep44462

The diamond will lose its value as gem stones, but its excellent characters is interested by scientists.

NV center in diamond

Impurities/defects
cause Colors!



NV center

The atomic structure was identified by ESR in 1977.

J. H. N. Loubser & J. A. van Wyk, Diamond Res., p. 11, 1977

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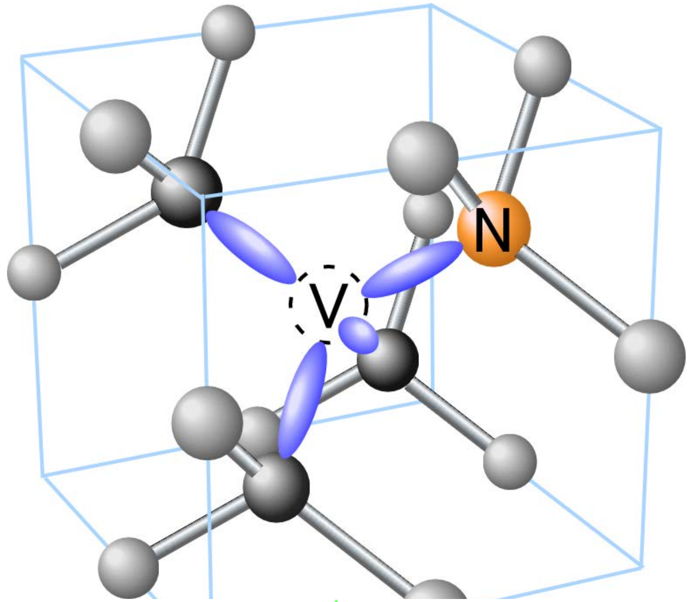
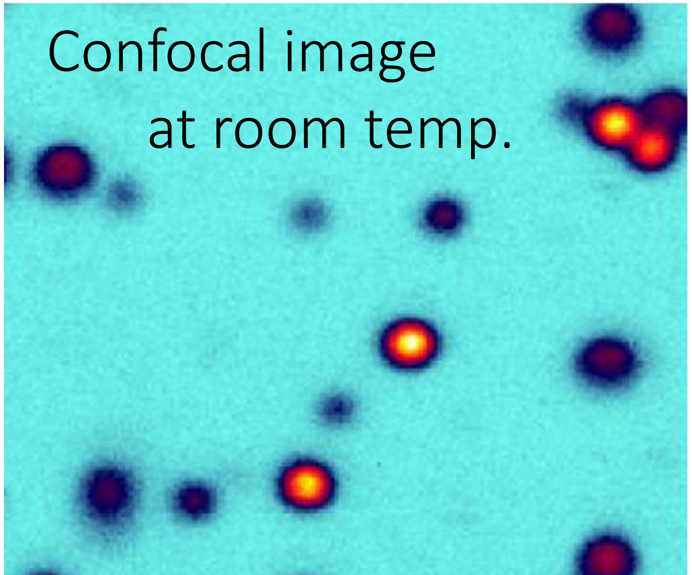
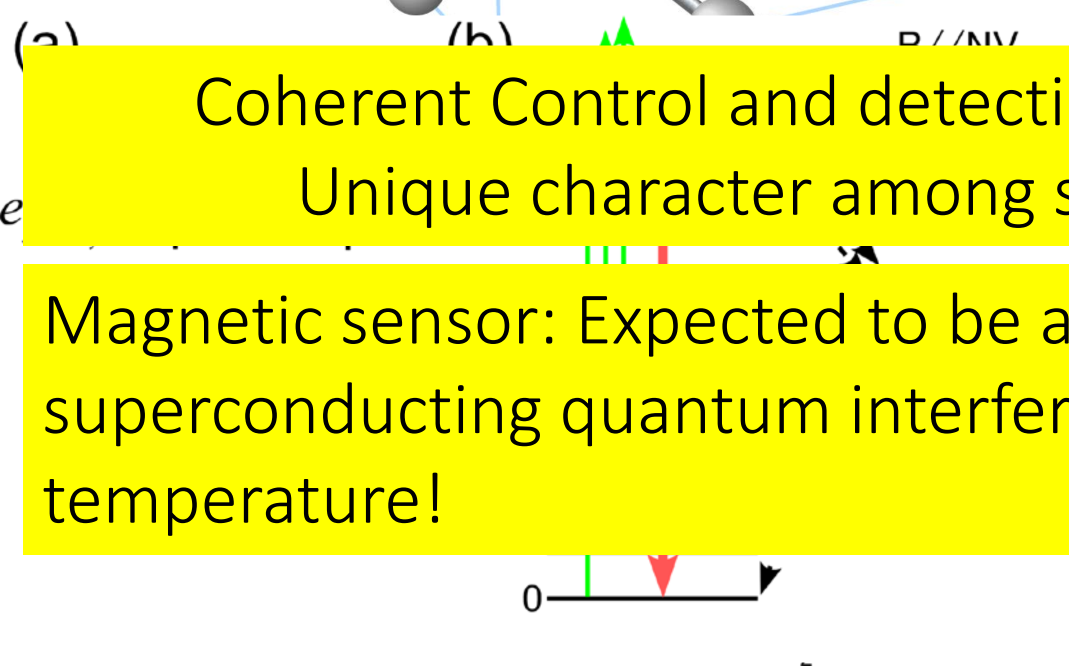
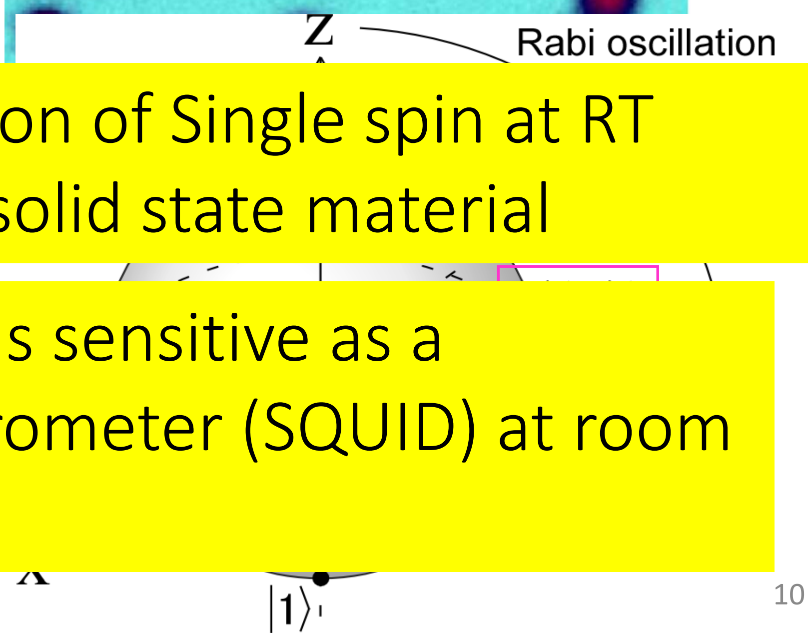
NV center in diamond









Coherent Control and detection of Single spin at RT
Unique character among solid state material

Magnetic sensor: Expected to be as sensitive as a superconducting quantum interferometer (SQUID) at room temperature!

Characteristics of NV center for sensing

Magnetic field sensitivity : η

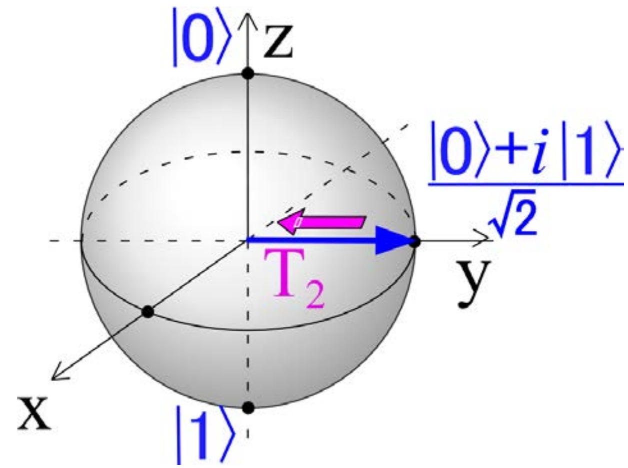
$$\eta \propto \frac{1}{\sqrt{n_{NV} T_2}}$$

n_{NV} : The number of NV

Superposition state

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)$$

Coherence time (T_2) :



Long T_2 : Longest T_2 among solid state electron spins at RT.

Sensing of magnetic field, electric field, temperature, pressure, pH

Why can we enhance sensitivity and spatial resolution?

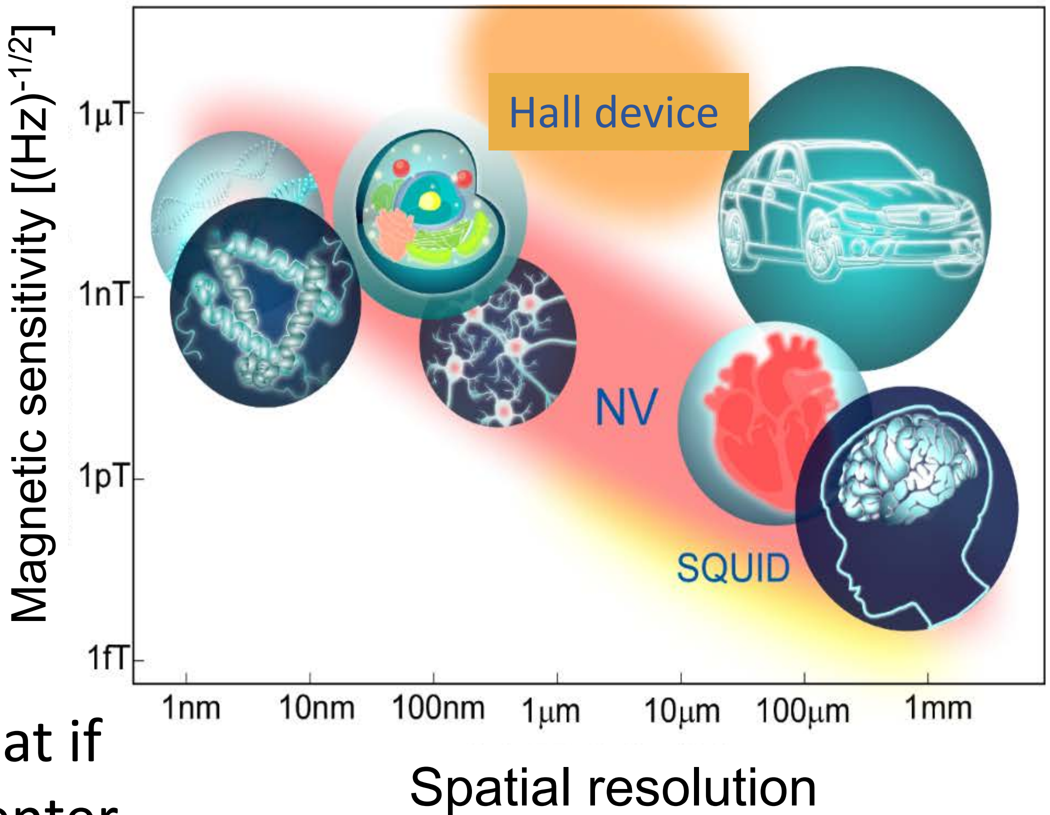
Sensitivity (η)

$$\eta \propto \frac{1}{\sqrt{n_{NV} T_2}}$$

n_{NV} : Number of NV

Not only T_2 but also the number of NV also contributes to the sensitivity.

The trade-off relationship is that if the concentration of the NV center increases, T_2 becomes shorter. If the concentration keeps constant and n_{NV} increases, the spatial resolution decreases.



Mizuochi, OYO BUTSURI, 87, 251-261(2018).

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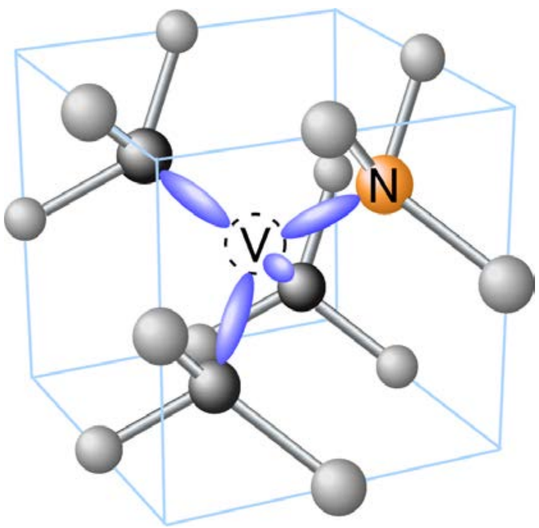
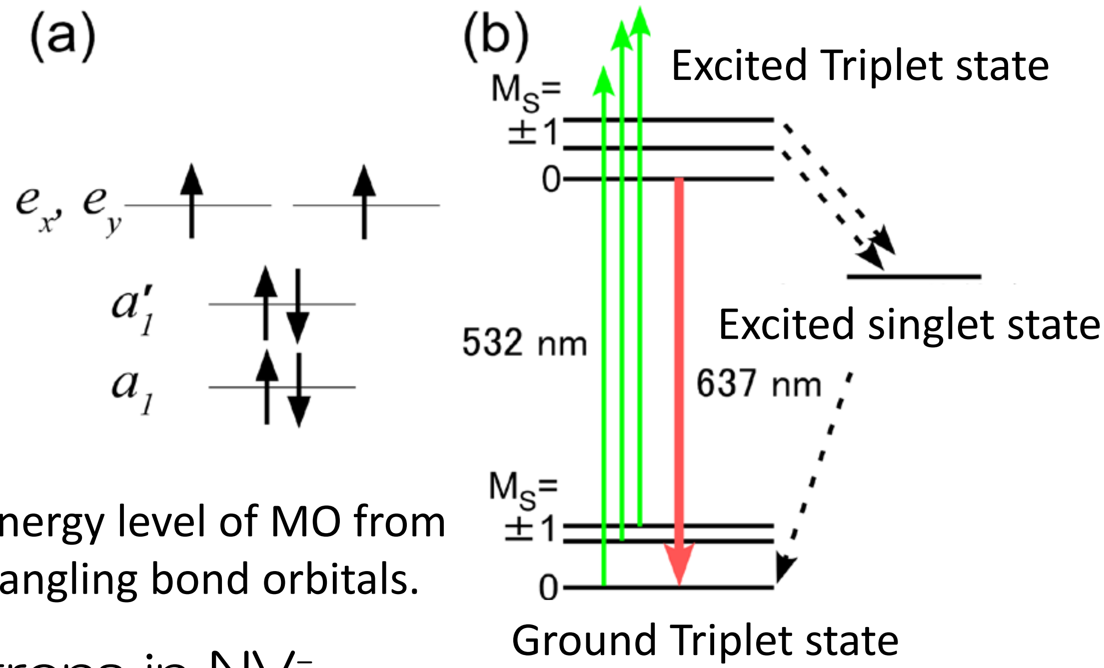
Why does NV center has ground triplet state (S=1)?



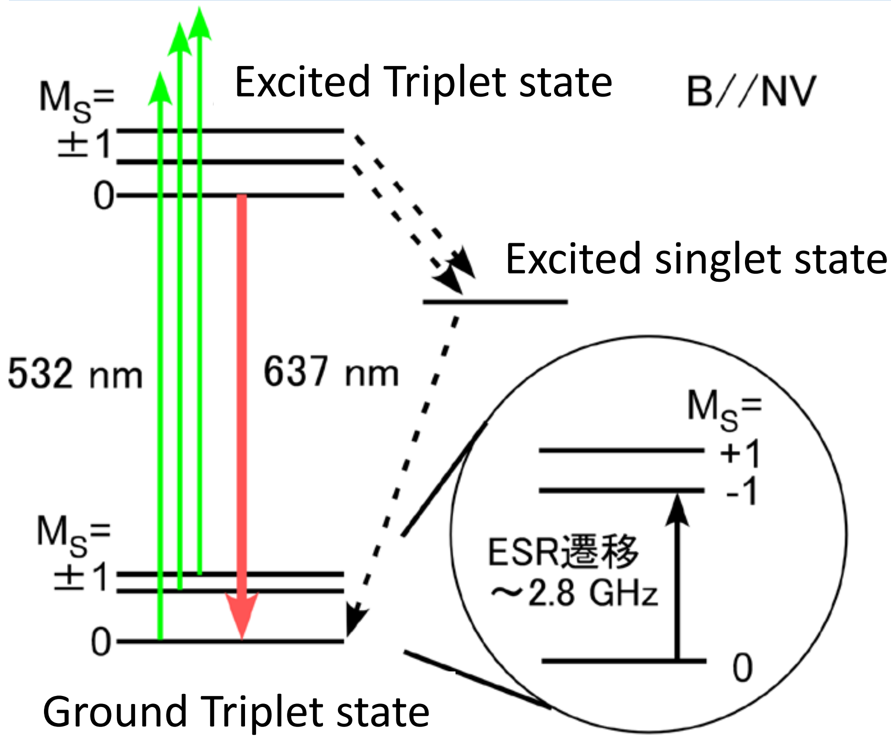


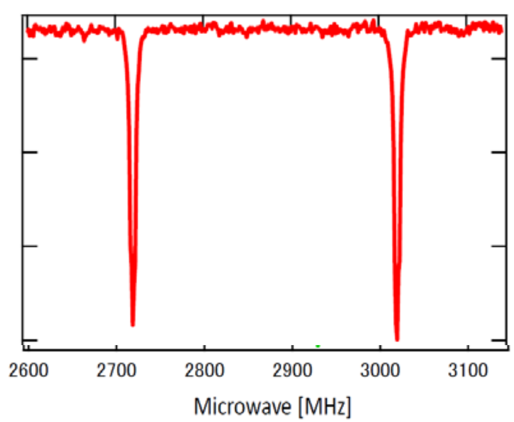
Energy level of MO from dangling bond orbitals.

6 electrons in NV^-

- In diamonds, it is often energetically advantageous to maintain high symmetry.
- According to Pauli exclusion principle, upspins are added to each of the two degenerate levels, and S = 1!

Measurement method : Optically detected magnetic resonance (ODMR)





1: Initialization（To M_S = 0）: Laser excitation (532 nm) and spin selective deactivation due to SOC.

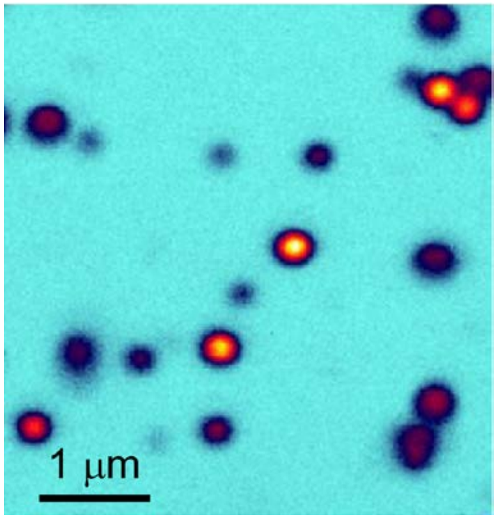
2: Magnetic resonance (To M_S=-1)

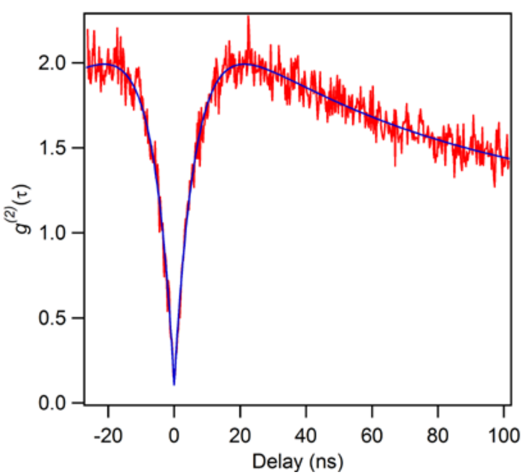
Microwave irradiation to Zero-field splitting (dipolar-dipolar interaction) = 2.87 GHz

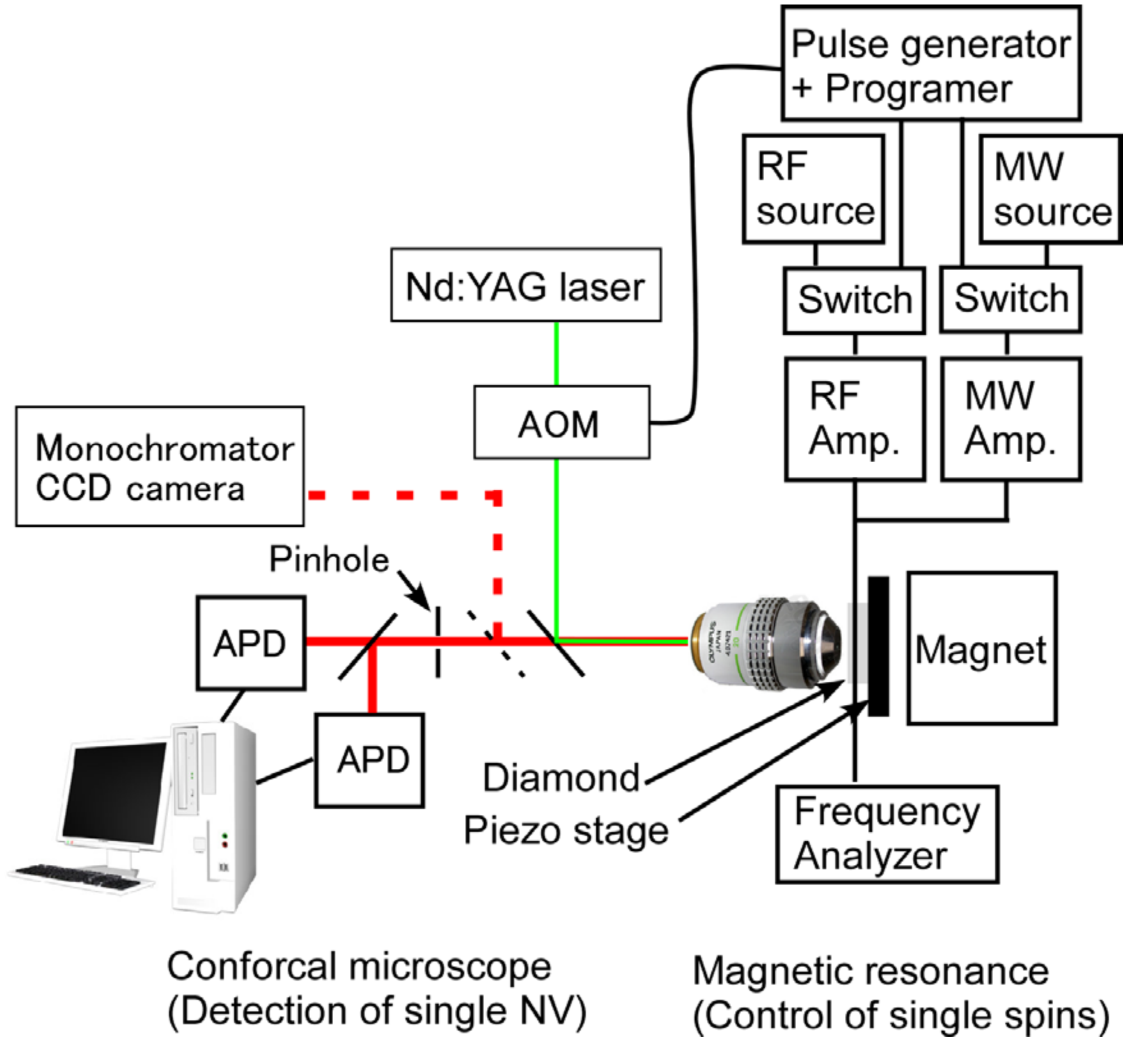
3: Optical detection:

Laser excitation (532 nm) and <u>detection of change of fluorescence</u>.

Measurement setup of individual centers
Confocal microscope with magnetic resonance system

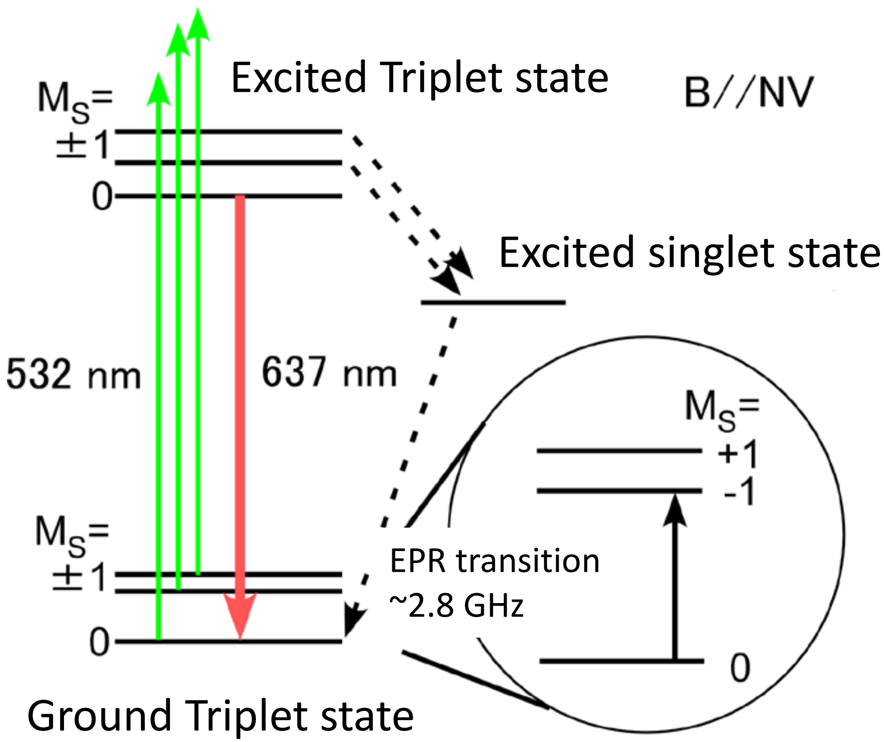


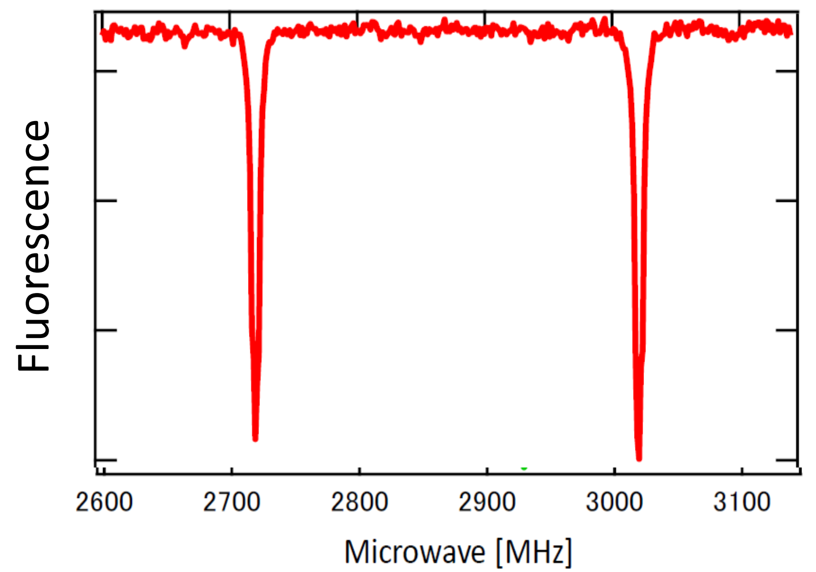




Measurement using a piezostage and observe each single emission center

How to sense the magnetic field?





ODMR spectrum of NV center

The resonance freq. of the ODMR signal shifts according to the magnitude of the magnetic field. Measurement of the magnetic field from the shift!

The narrower the line width, the smaller the shift can be detected. Namely, the sensitivity improves! (The longer T_2, the narrower the line width!)

Magnetic field, temperature, electric field, and pressure can be measured!

Spin Hamiltonian

$$H_{gs} \cong \underbrace{\mu_B g_e \mathbf{S}\cdot\mathbf{B}}_{\text{Zeeman}} + hD_{gs}\left[S_z^2 - \frac{1}{3}S(S+1)\right] - d_{gs}^{\perp}\left[E_x\left(S_xS_y + S_yS_x\right) + E_y\left(S_x^2 - S_y^2\right)\right]$$

Zeeman: Magnetic field

Spin-spin interaction (dipolar int.)

$hD_{gs}\left[S_z^2 - \frac{1}{3}S(S+1)\right]$: Temperature, Stress

$- d_{gs}^{\perp}\left[E_x\left(S_xS_y + S_yS_x\right) + E_y\left(S_x^2 - S_y^2\right)\right]$: Electric field

Demonstrated high sensitivity (room temperature)

Temperature (single)

5 mK/$\sqrt{Hz}$

Neumann, et al,. Nano Lett. 2013

Stress

0.6 MPa/$\sqrt{Hz}$

Doherty, et al., PRL 2014.

Electric field (single)

202 V/cm$\sqrt{Hz}$

Dolde, et al., Nat. Phys. 2011.

Magnetic sensor sensitivity using the NV center

Ensemble (RT)
B_{AC}=~ 0.9 pT Hz$^{-1/2}$

PRX 2015

Ensemble (RT)
B_{DC}=~ 15 pT Hz$^{-1/2}$

PNAS 2017

Spatial resolution : 50 μm × 50 μm × 0.5 mm

Single (RT)
B_{AC}=9.1 nT Hz$^{-1/2}$

Nature Commun. 2019

Single (RT)
B_{DC} = 10 nT Hz$^{-1/2}$

Nature Commun. 2019

Magnetic field sensitivity (Minimum detactable B) : η

$$\eta \propto \frac{1}{C\sqrt{n_{NV}\,\tau\,T_2}}$$

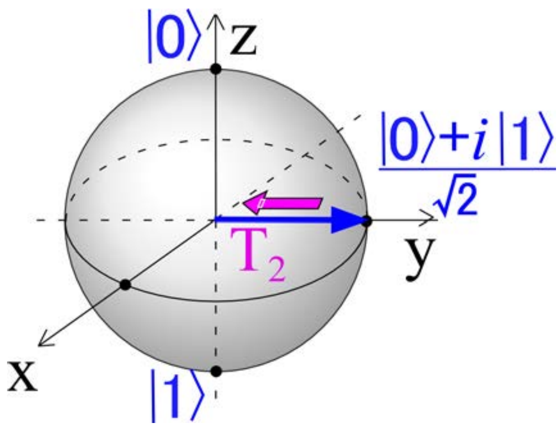
C : readout contrast

n_N : The number of NV

τ : Measurement time

Phase measurement

We can obtain information such as magnetic field from the phase of coherence!



Coherence is generated by 90 degree pulse. After that, when the magnetic field from the outside changes, the coherence begins to rotate in the xy plane when viewed in the rotating coordinate system. Information on the magnetic field from the outside can be obtained from the phase.

Magnetic field sensitivity (Minimum detactable B)：　η

$$\eta \propto \frac{1}{C\sqrt{n_{NV}\,\tau\,T_2}}$$

C : readout contrast

n_{NV}: The number of NV

τ : Measurement time

L. M. Pham, et. al., Phys. Rev. B **86**, 121202 (2012)

Accuracy of phase measurement

$$\phi = \phi_0 \pm \Delta\phi$$

The smaller $\Delta\phi$, the better the accuracy.

Classical measurement (when measuring with n spins)

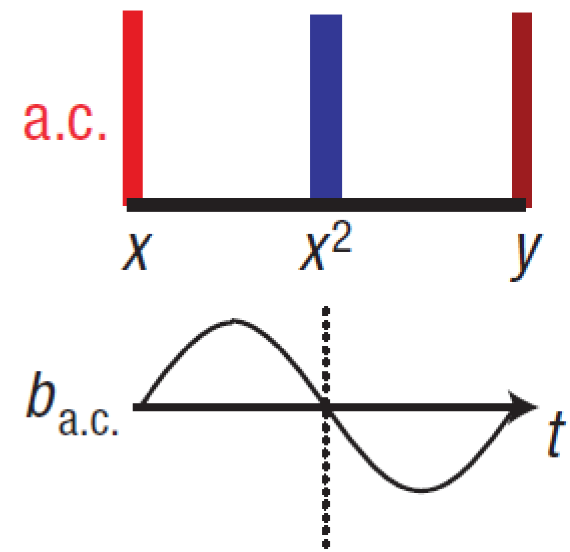
Limitation of accuracy : $\Delta\phi \approx \frac{1}{\sqrt{n}}$

Quantum measurement (when measuring using the quantum entangled state with n spins）

Limitation of accuracy : $\Delta\phi \approx \frac{1}{n}$

AC magnetic field detection

Echo - type sequence (π/2 – π – π/2)



$$\delta\phi = \left(\frac{g\mu_B}{\hbar}\right)\left[\int_0^{\tau/2} b(t)dt - \int_{\tau/2}^{0} b(t)dt\right]$$

$$b(t) = b\sin(\nu t + \phi_0)$$

ν:signal field frequency

ϕ_0: initial phase

$$\delta\phi = \left(\frac{g\mu_B}{\hbar}\right) b\tau f(\nu\tau, \phi_0)$$

$$f(\nu\tau, \phi_0) = \left(\sin^2(x/4)\cos\frac{\left(\frac{x}{2} + \phi_0\right)}{x}/4\right)$$

Optimum condition

$$\tau = 2\pi/\nu \text{ and } \phi_0 = 0$$

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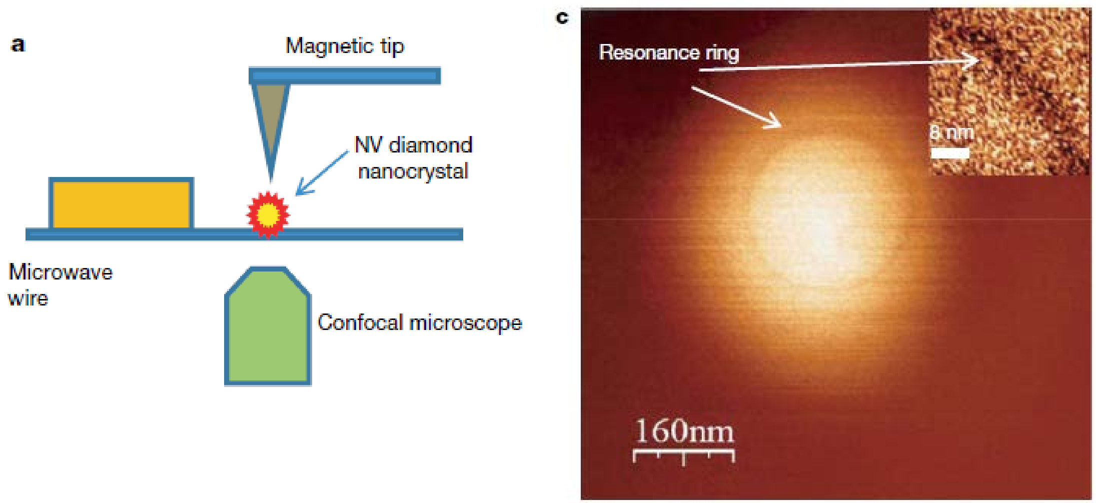
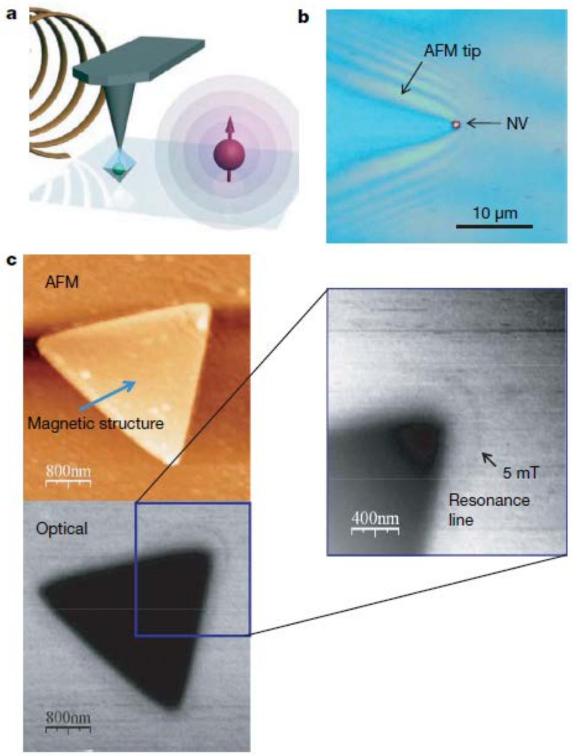
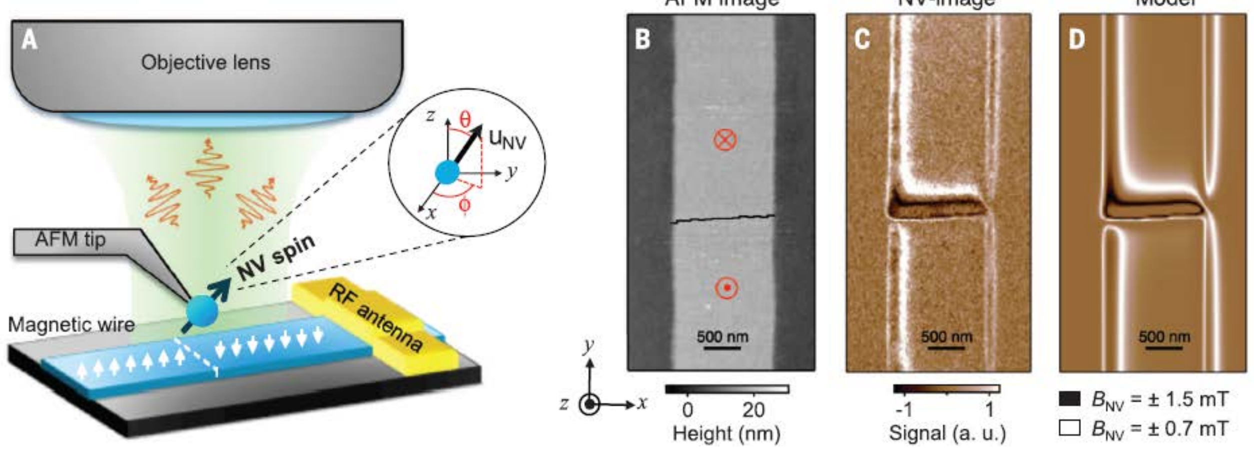
High magnetic field sensitivity and high spatial resolution

Nature, 455, 648, 2008





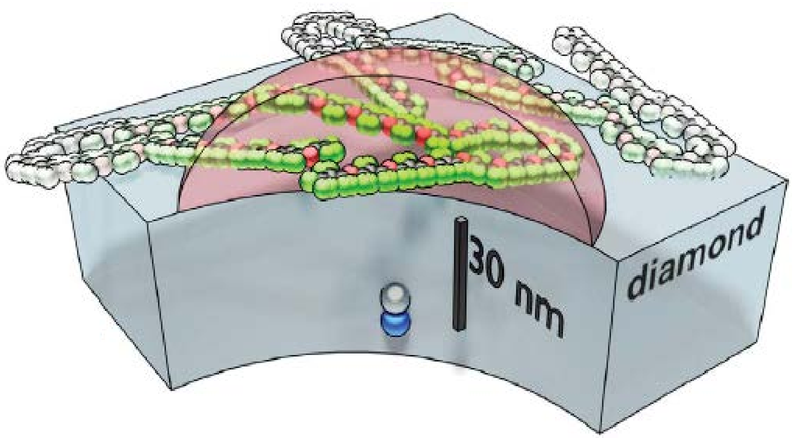
Science 2014



AC magnetic field sensing

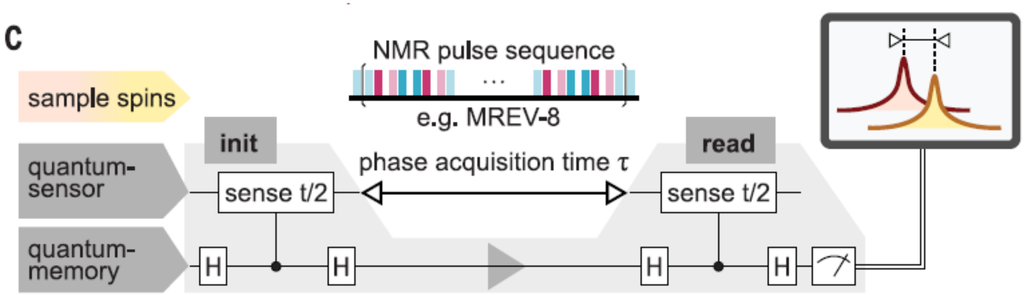
nanometer scale NMR

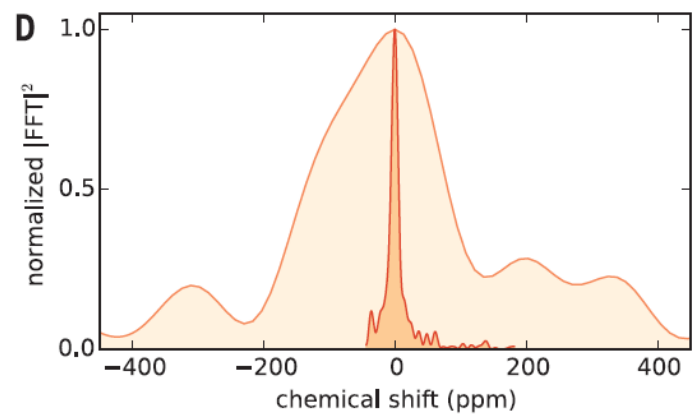
N. Aslam, et al., Science, 357, 65 (2017)



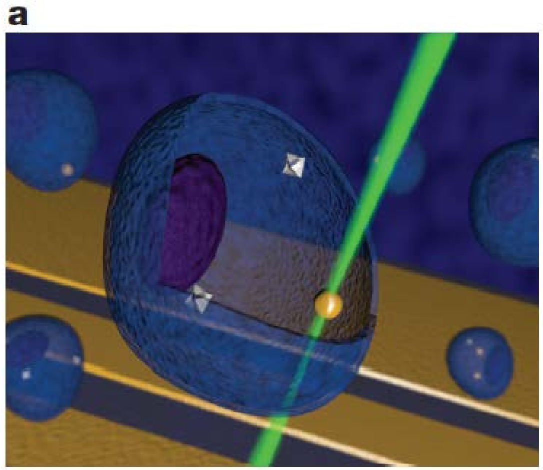
The nuclear spin of a molecule placed on the diamond surface is measured by the NV center.

To structural analysis of small amounts of molecules



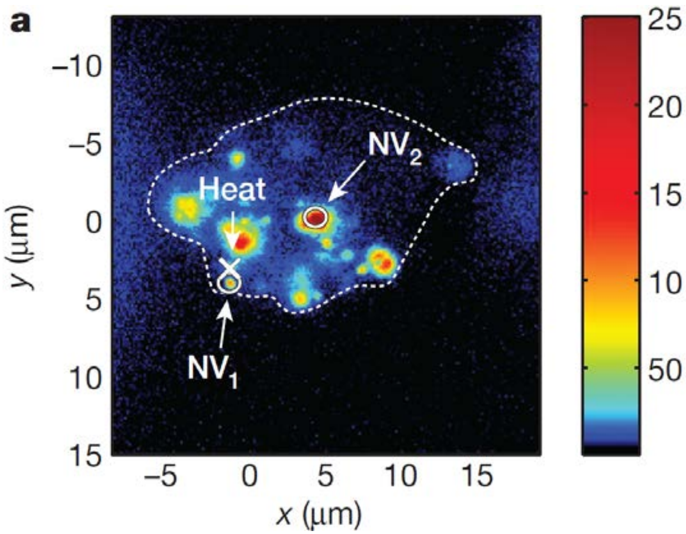


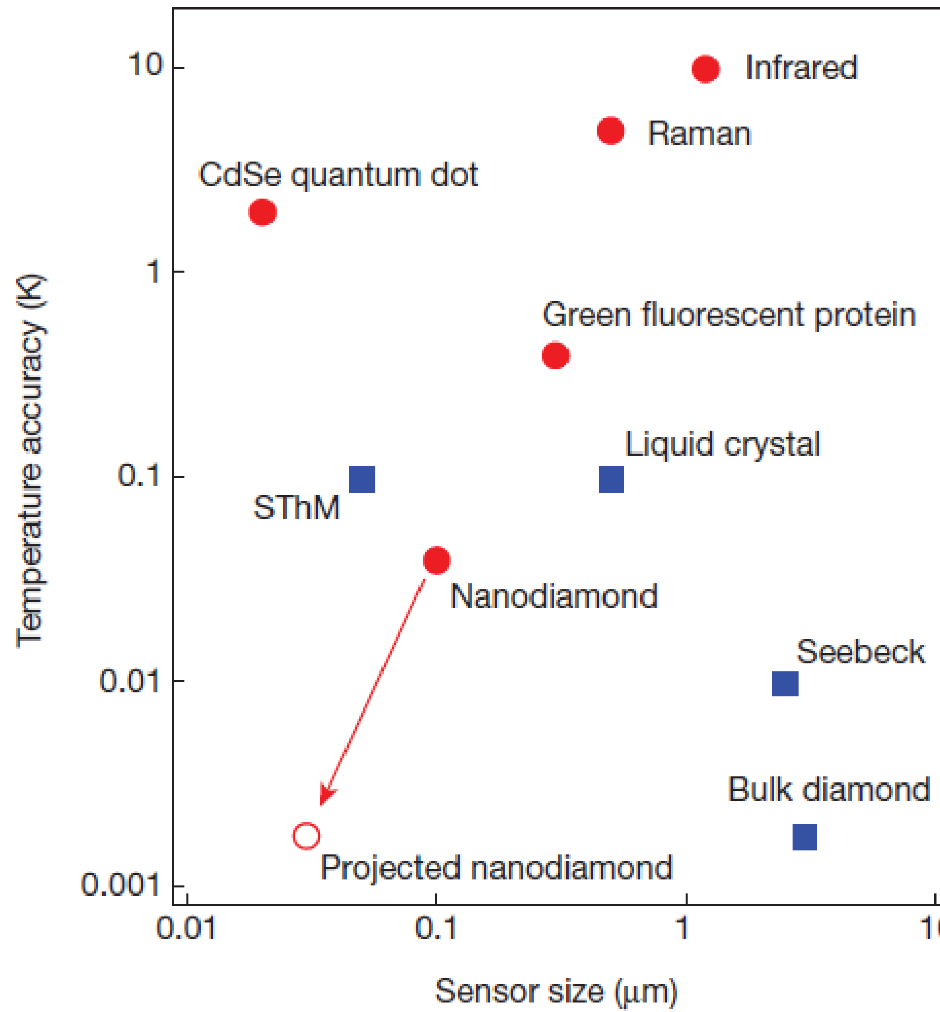
Intracellular nanometer scale thermometer



Kucsko et al., Nature 2013

Sensitivity：9 mK/Hz$^{1/2}$ (Bulk)
Nano diamond：200 nm





Testing Fundamental Physics by using NV centers

"Searching for an exotic spin-dependent interaction with a single electron-spin quantum sensor",
X. Rong, J. Du et al., *Nature Communications*, (2018) 9, 739.

"Testing quantum gravity by nanodiamond interferometry with nitrogen-vacancy centers"
A. Albrecht, A. Retzker, M. B. Plenio, *Physical Review A* 90, 033834 (2014).

Related study : "Constraints on bosonic dark matter from ultralow-field nuclear magnetic resonance",
A. Garcon, D. Budker et al., *Science Advances* 2019; 5 : eaax4539.

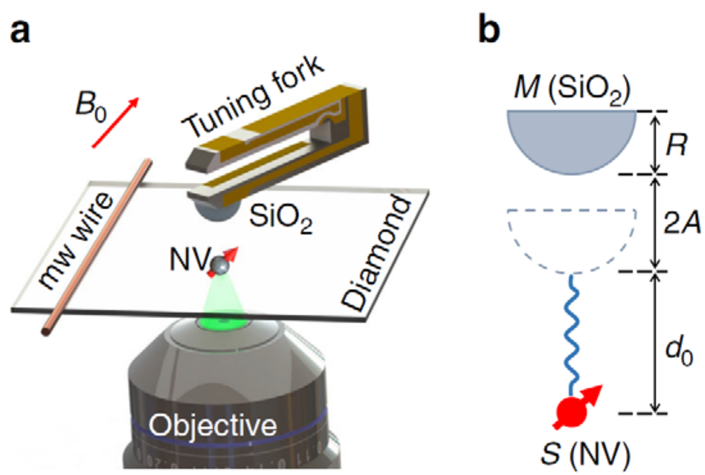
“Searching for an exotic spin-dependent interaction with a single electron-spin quantum sensor”,
X. Rong, J. Du et al., *Nature Communications*, (2018) 9, 739.

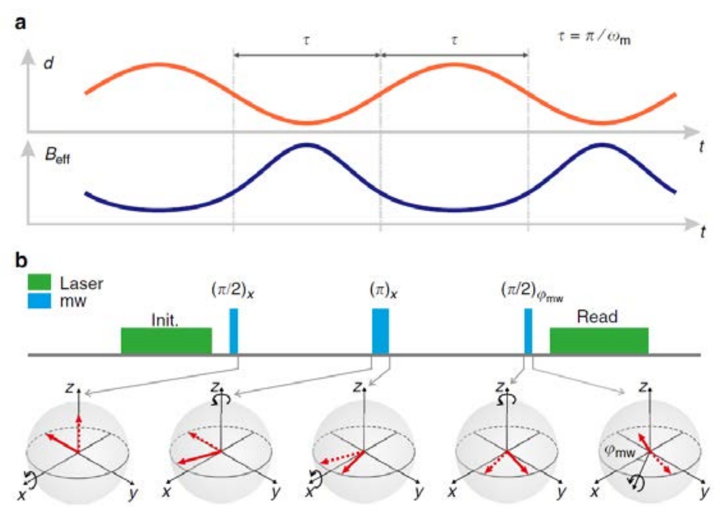
The axion-mediated monopole–dipole interaction can be described as

$$V_{\rm sp}(\mathbf{r}) = \frac{\hbar^2 g_s^N g_p^e}{8\pi m}\left(\frac{1}{\lambda r}+\frac{1}{r^2}\right)e^{-\frac{r}{\lambda}}\boldsymbol{\sigma}\cdot\mathbf{e}_r,$$

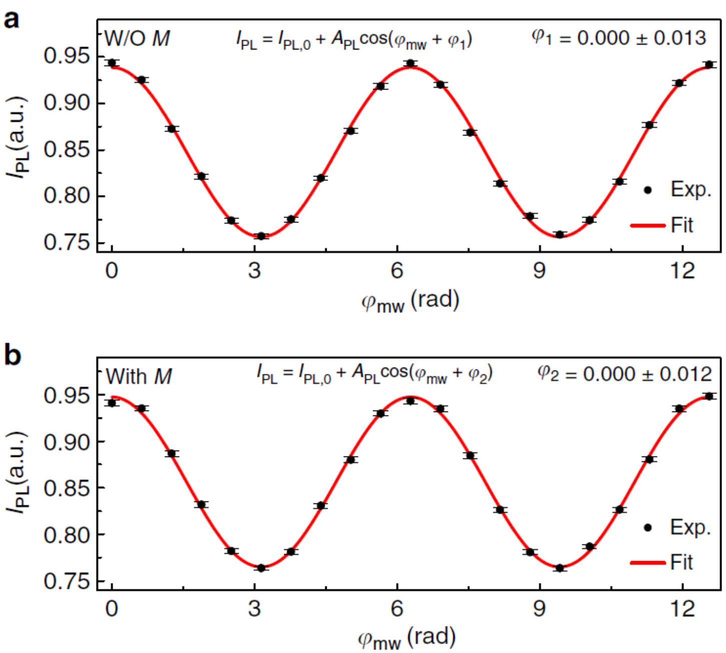
Such interaction is equivalent to the Hamiltonian of the electron spin in an effective magnetic field $B_{sp}(r)$ arising from the nucleon,

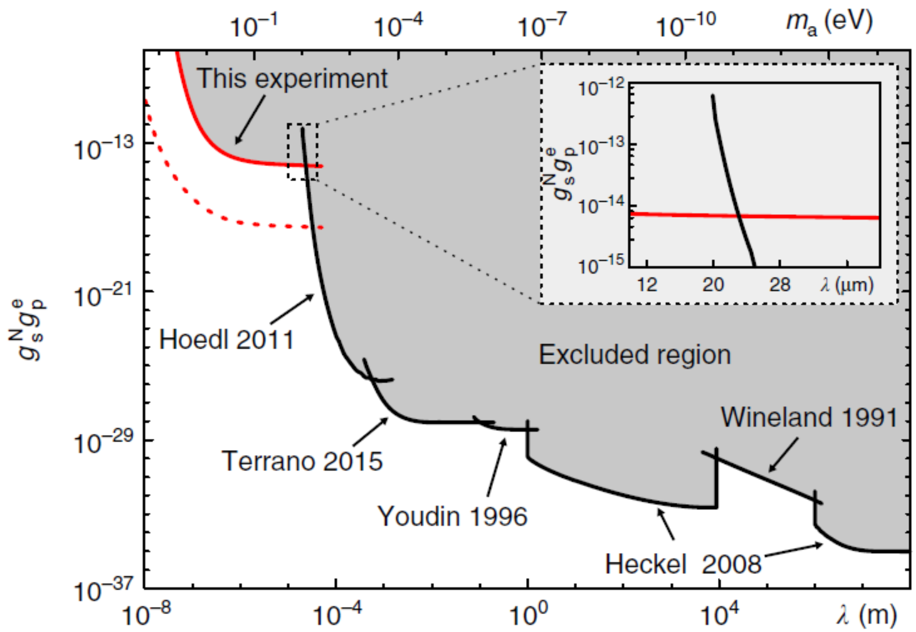
$$\mathbf{B}_{\rm sp}(\mathbf{r}) = \frac{\hbar g_s^N g_p^e}{4\pi m\gamma}\left(\frac{1}{\lambda r}+\frac{1}{r^2}\right)e^{-\frac{r}{\lambda}}\mathbf{e}_r,$$





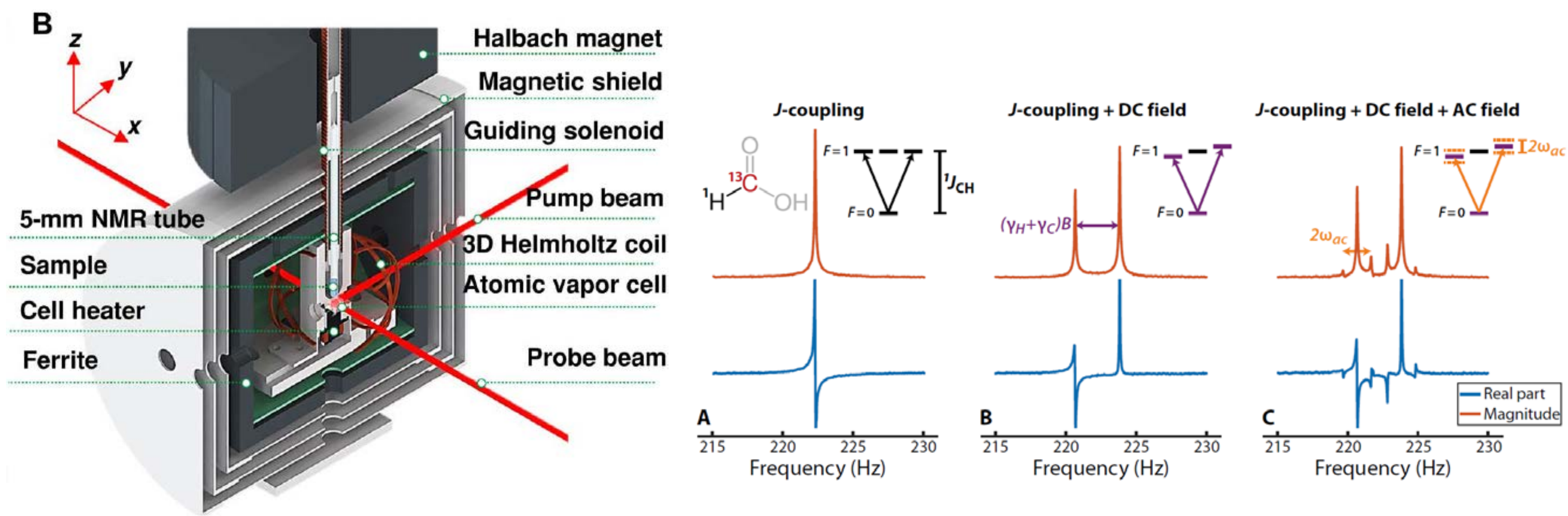
“Searching for an exotic spin-dependent interaction with a single electron-spin quantum sensor”,
X. Rong, J. Du et al., *Nature Communications*, (2018) 9, 739.





"Constraints on bosonic dark matter from ultralow-field nuclear magnetic resonance",
A. Garcon, D. Budker et al., *Science Advances* 2019; 5 : eaax4539.

Detected from NMR through coupling of dark matter and nuclear spin



Sensitivity of the sensor: 10 fT/(Hz)$^{1/2}$. 50 microL.

No dark matter signal was detected above background, establishing new experimental bounds for dark matter bosons with masses ranging from 1.8×10^{-16} to 7.8×10^{-14} eV.

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   Ultra-long coherence times among room-temperature solid-state spins

   Ultra-high dynamic range quantum measurements retaining its sensitivity

T_2 of electron spin of NV centers at RT

T_2 (electron spin in natural abundance of ^{13}C (I=1/2))

2003	50 μs	T. A. Kennedy, et al., APL, 2003
2006	200 μs	L. Childress, et al., Science, 2006
	350 μs	T. Gaebel, et al., Nature physics, 2006
2009	650 μs	N. Mizuochi, et al., PRB, 2009
2010	630 μs	R. L. Walsworth et al., PRB 2010

Longest T_2 in natural abundance of ^{13}C.

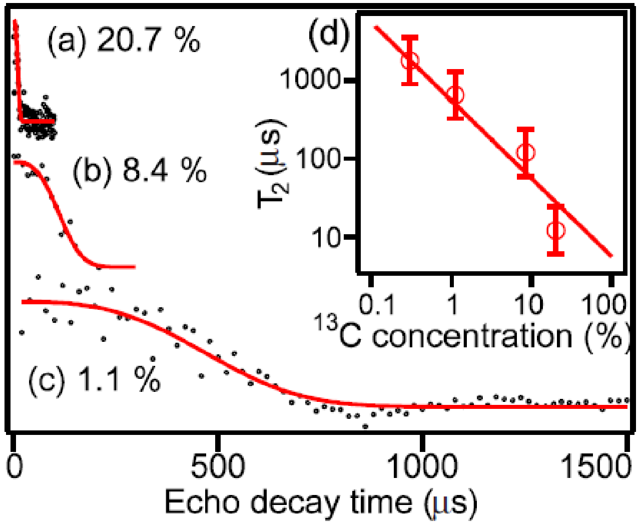
Due to suppression of paramagnetic impurities

T_2 (electron spin in ^{12}C (I=0) enriched diamond: 99.7%)

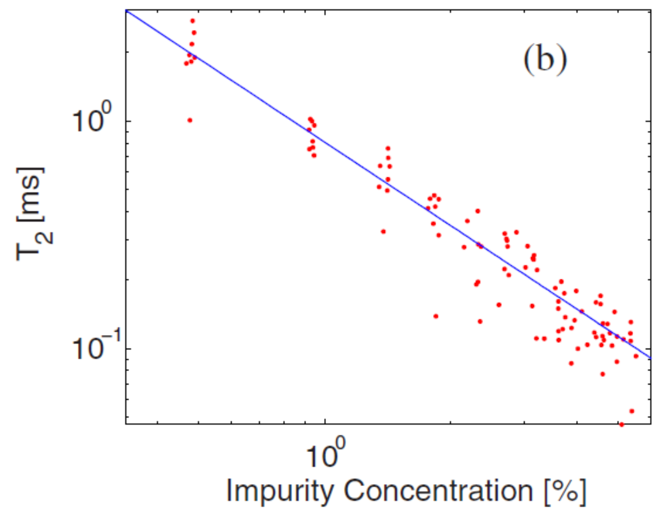
2009	1.8 ms	G. Balasubramanian, et al., Nat. Mater. 2009.

Due to reduction of nuclear spins

How to extend T_2?



N. Mizuochi, et al., PRB, 80, 041201(R) (2009).



J. R. Maze, et al., PRB **78**, 094303 (2008).

^{13}C (0.001 %, ^{12}C = 99. 999 %) methane is available:

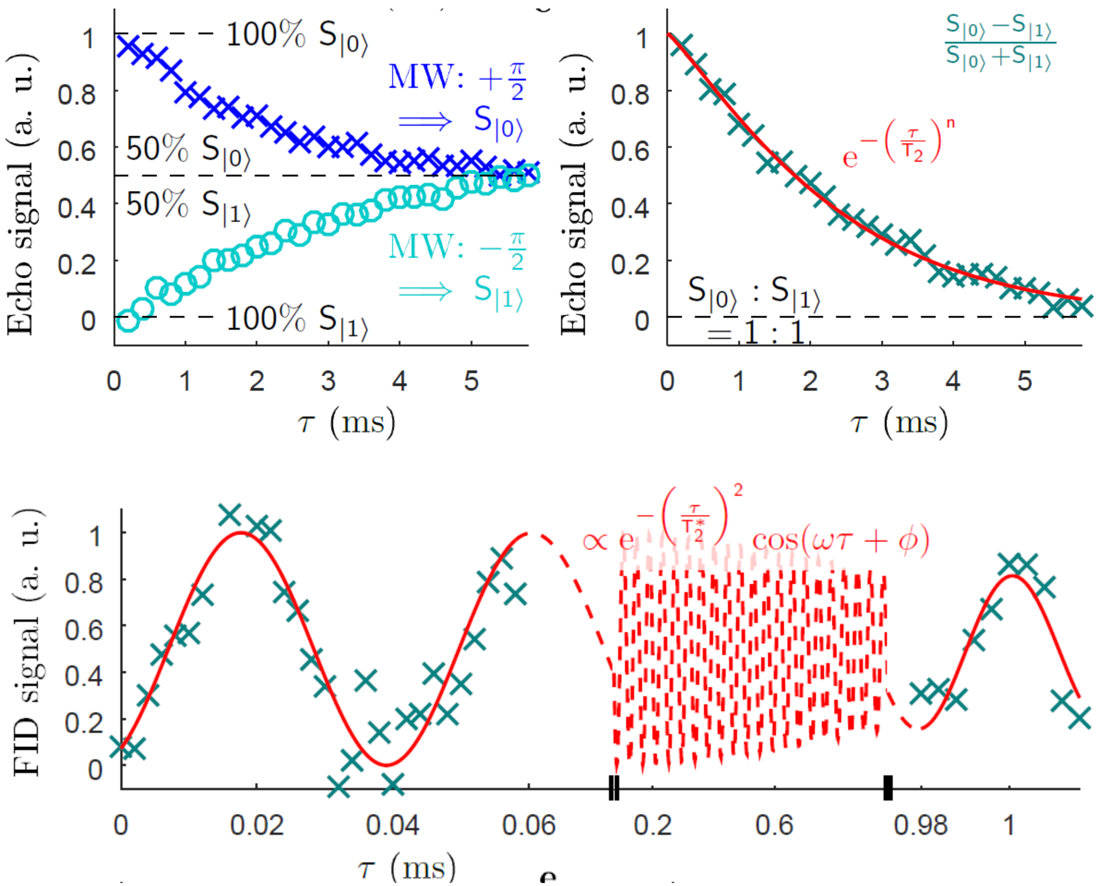
If T_2 is only limited by ^{13}C nuclear spin (0.001%), T_2 should be longer than 600 ms.

In diamond with extremely low ^{13}C (0.001%), T_2 is not limited by noises from nuclear spins.

Suggest: The remaining noise source may be paramagnetic impurities or defects. How to remove them?

Ultra-long coherence times among room-temperature solid-state spins

(synthesized at AIST) (Nature Communications, 10, 3766 (2019).)



$T_2 \approx 2.4$ ms

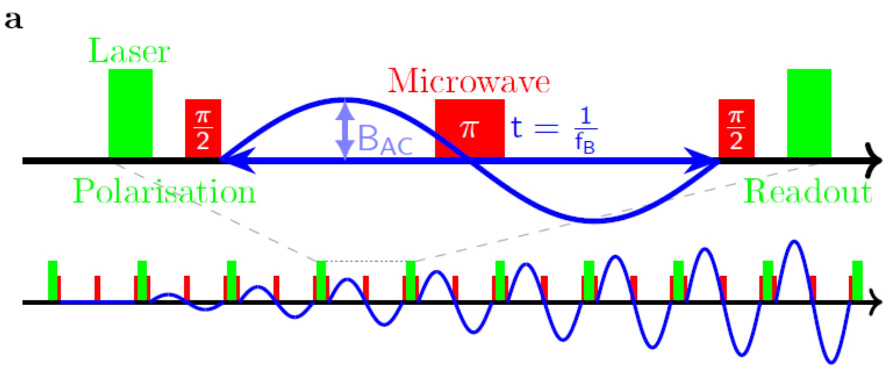
Previous report: T_2=1.8ms:
Nature Material 2009

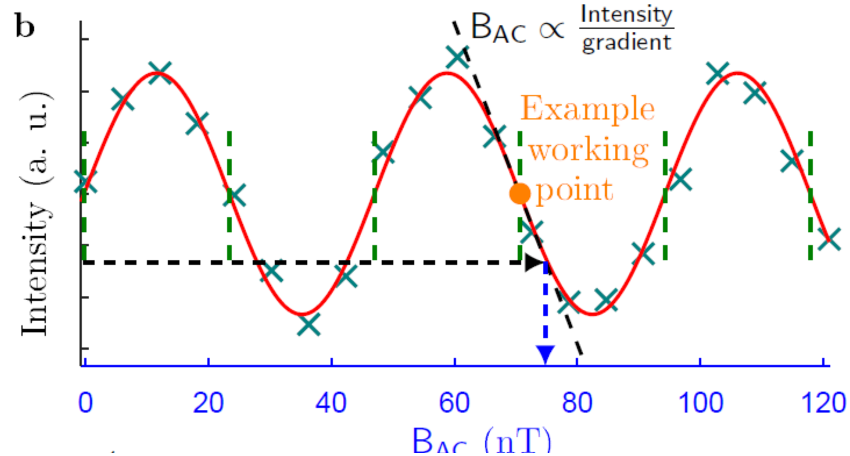
In case without the common mode noise subtraction, T_2 of our NV is estimated to 3.0 ms.

$T_2^* \approx 1.5$ ms

Previous report: T_2^*=0.47 ms
Science 2012

Longest coherence times among solid-state electron spins at room temperature.

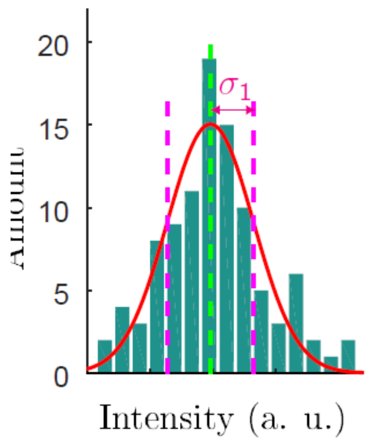




Sensitivity:

$$\eta = \delta B_{min}\sqrt{T_{meas}}$$

$$\delta B_{min} = \sigma_B = \frac{\sigma_1}{grad}$$



AC magnetic field sensitivity：
9.1 nT/(Hz)$^{1/2}$

DC magnetic field sensitivity：
<10 nT/(Hz)$^{1/2}$

Different estimation method : 4.3 nT /(Hz)$^{1/2}$
by Nature Mat. 2009

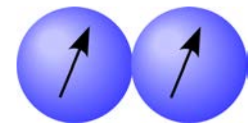
Highest magnetic field sensitivity of single NV at room temperature.

Effect of P-doped n-type diamond on T_2

Phosphorus is one of sources of magnetic noises due to its electron spin.
However, the P-doped n-type diamond realizes remarkably long T_2.

Non-doped diamond

Multiple vacancies/impurities complexes:
One of the sources of magnetic noise

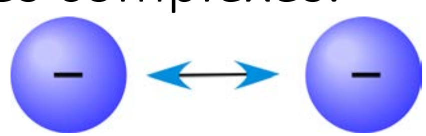


Vacancies/impurities

Vacancy: removable at 600℃. Multiple vacancies/impurities: Stable even at 1,500℃.
CVD growth temperature is about 900℃.

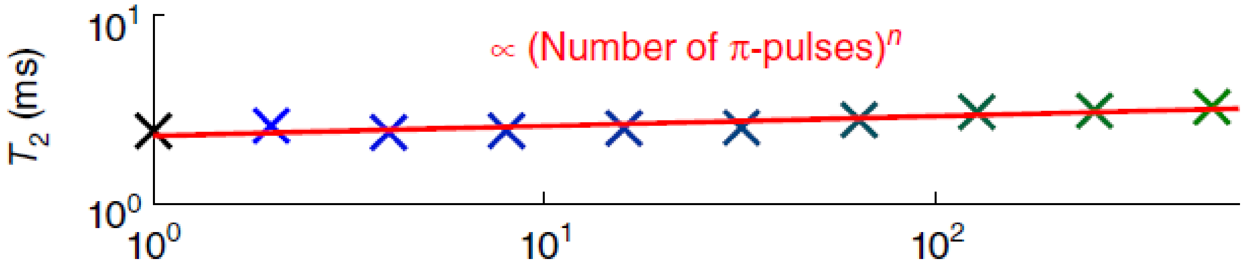
P-doped n-type diamond

Coulomb repulsion between vacancies/impurities prevents formation of Multiple vacancies/impurities complexes.



Related research: Model of suppression of multiple vacancies in p-type diamond. F. F. Oliveira, J Wrachtrup, et al., Nature Commun., 8, 15409 (2017).

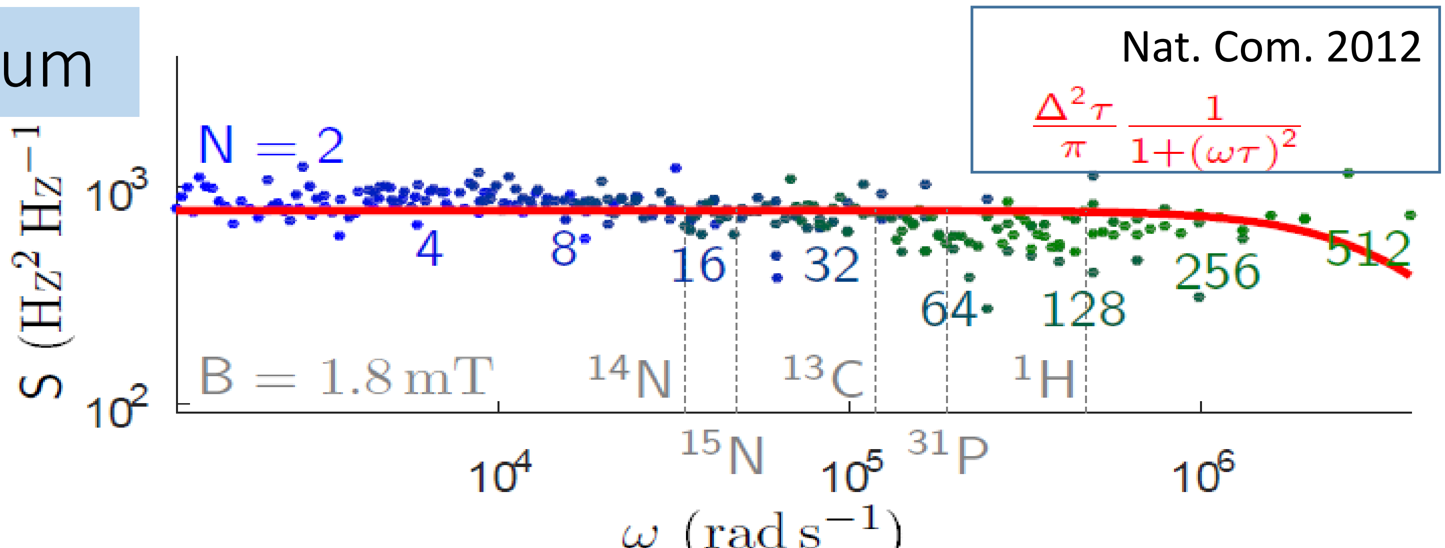
About origin of remaining noise source: CPMG dynamical-decoupling sequences



T_{2dd} = 3.3 ms

Still shorter than T_1 (~6ms-7.5 ms)

Noise spectrum



Nuclear spins of ^{14}N, ^{15}N, ^{13}C, ^{31}P were not detected.

The minimum density of the paramagnetic defects was derived from Δ (under the assumption of dipolar interaction) : 3×10^{17} cm^{-3}.

Suggestion: The main noise source is magnetic noises of electron spin.

Short Summary of first part

- The longest T_2^* (= 1.5 ms) and T_2 (= 2.4 ms) ever observed in room-temperature solid-state systems.
- The highest magnetic field sensitivities of single NV centers at room temperature.
- The elongation of coherence times in n-type semiconductor diamond paves the way to the development and application of diamond-based quantum-information and sensing devices.

E. D. Herbschleb, H. Kato, Y. Maruyama, T. Danjo, T. Makino, S. Yamasaki, I. Ohki, K. Hayashi, H. Morishita, M. Fujiwara, N. Mizuochi, Ultra-long coherence times amongst room-temperature solid-state spins, *Nature Communications*, **10**, 3766 (2019)

Ultra-high dynamic range quantum measurements retaining its sensitivity

- Important compared with high sensitive sensors such as SQUID, OPM, MR sensors.
- Interaction between the spins strongly depends on the distance (r^{-3}).

Basic quantum sensing protocols cannot simultaneously achieve both a high sensitivity and a large range.

AC field：$\underline{4 \times 10^3 \text{ times}}$ (=DR/sensitivity)（RT, Non-adaptive）

A. Lazariev, et al., *Scientific Reports*, 7, 6586 (2017)

DC field： $\underline{< 3 \times 10^5 \text{ times}}$ (=DR/sensitivity) （8K, Adaptive, B_{max} = 1.78 mT ）

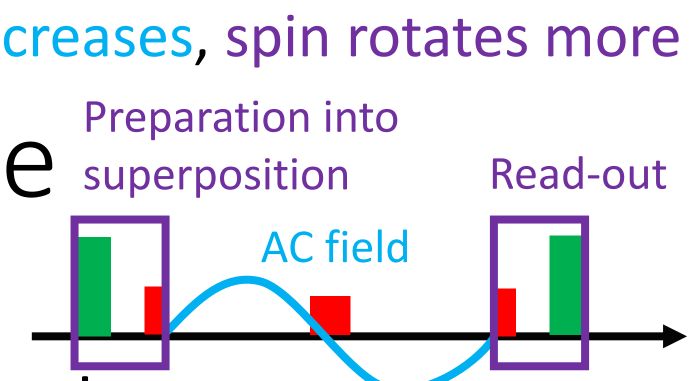
C. Bonato, et al., *Nature Nanotechnology* 11, 247 (2015)

DC field：$\underline{130 \text{ times}}$ (=DR/sensitivity) （Low temp. Non-adaptive）

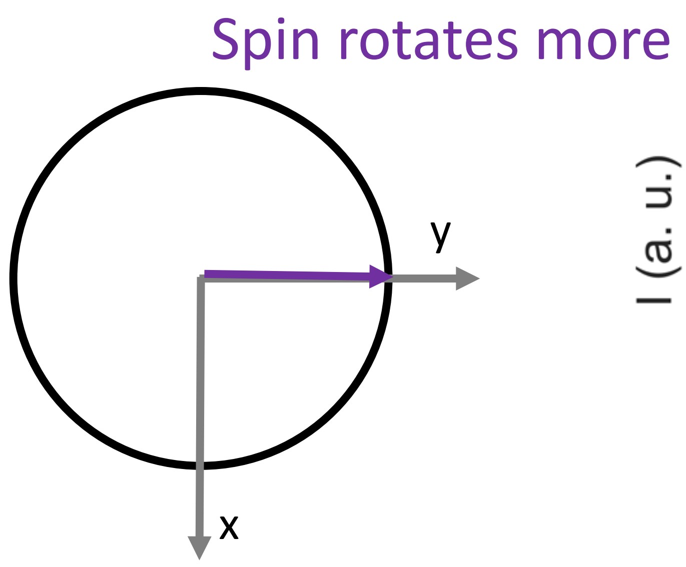
G. Waldherr, et al., *Nature Nanotechnology* 7, 105 (2011)

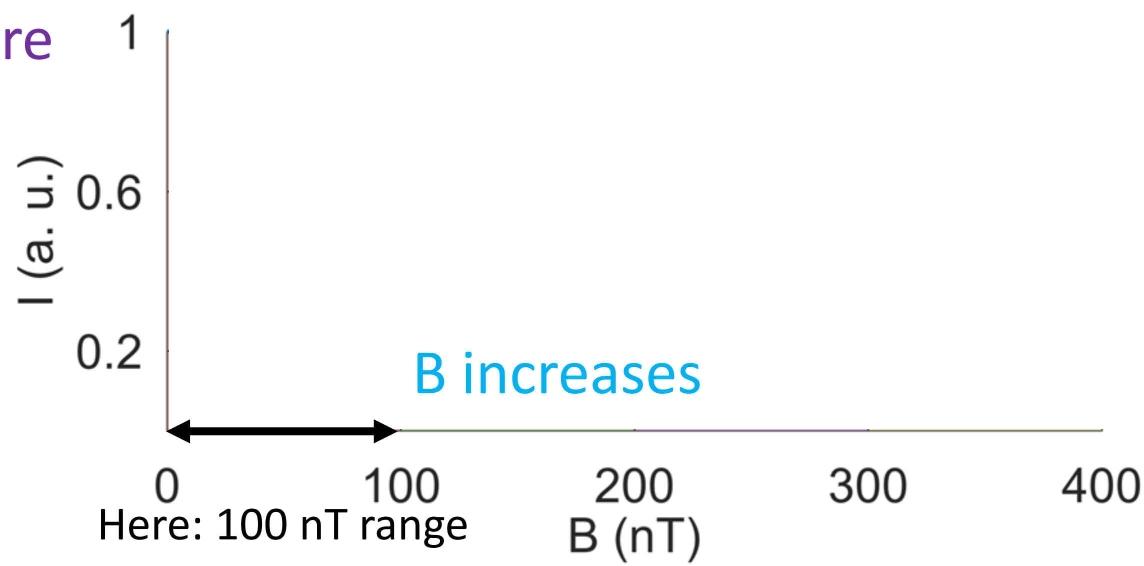
Sensitivity scales as sub-$1/T^{0.5}$ by applying different amounts of iterations, as opposed to the $T^{-1/2}$ of the standard measurement

Problem – limited range



- Standard AC measurement: Hahn-echo sequence with spin
- Limited range due to rotational symmetry





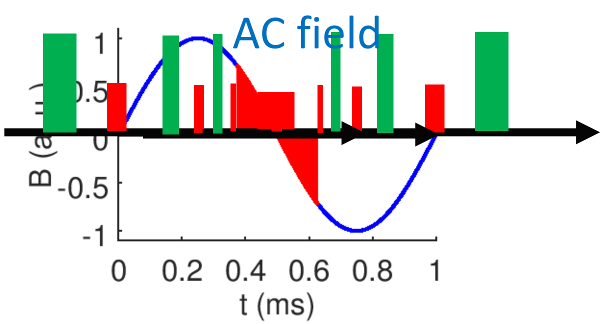
$$sensitivity \propto uncertainty \propto \frac{1}{maximum\ gradient}$$

Standard measurement DR

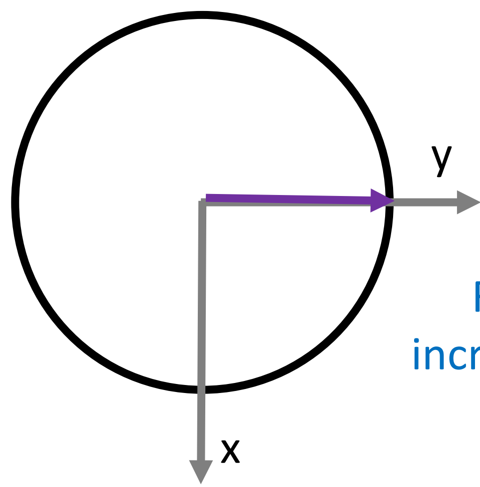
$$DR = \frac{Range \uparrow}{Sensitivity \uparrow}$$

Dynamic range remains the same: Trade-off

$B \propto spin\ phase \propto area$

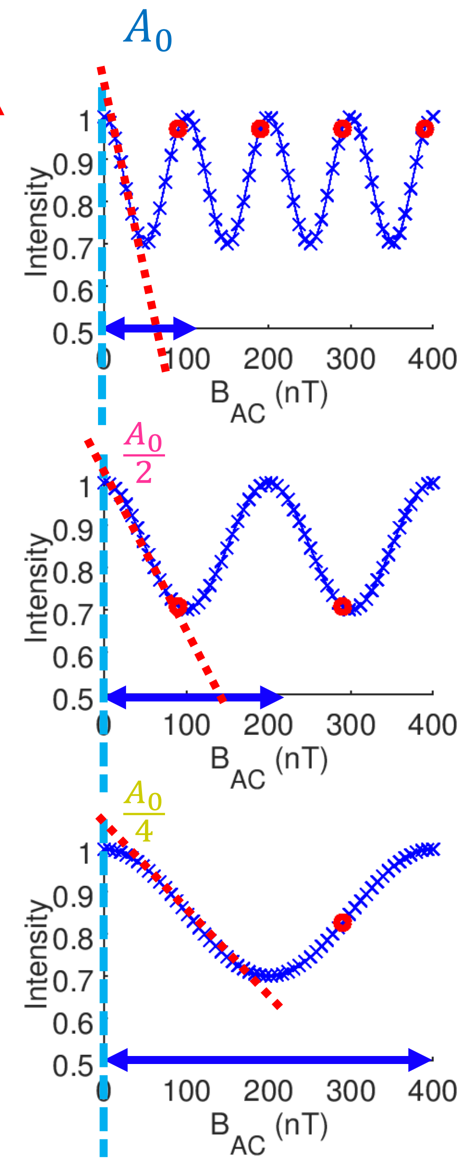


- Essentially, Hahn-echo measures the area
- Decrease the measured area
  - Period of the magnetic field increases



Sensitivity improves

Range increases

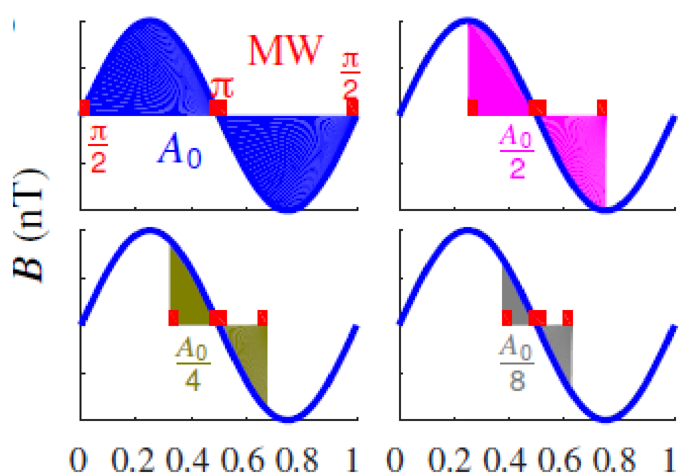


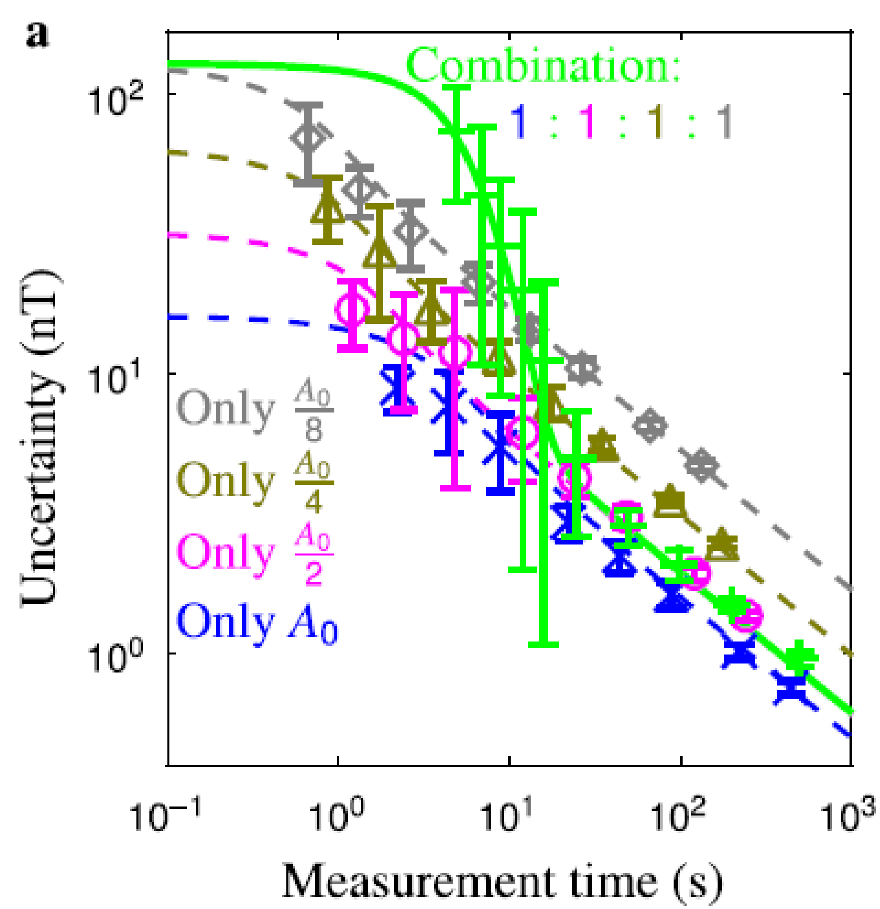
High dynamic range retaining its sensitivity

Our idea

- Change of the pulse interval and combine different sequences of area (A_n).
- Calculation of the optimal with an algorithm based o
- Calculation of the optimum measurement time.

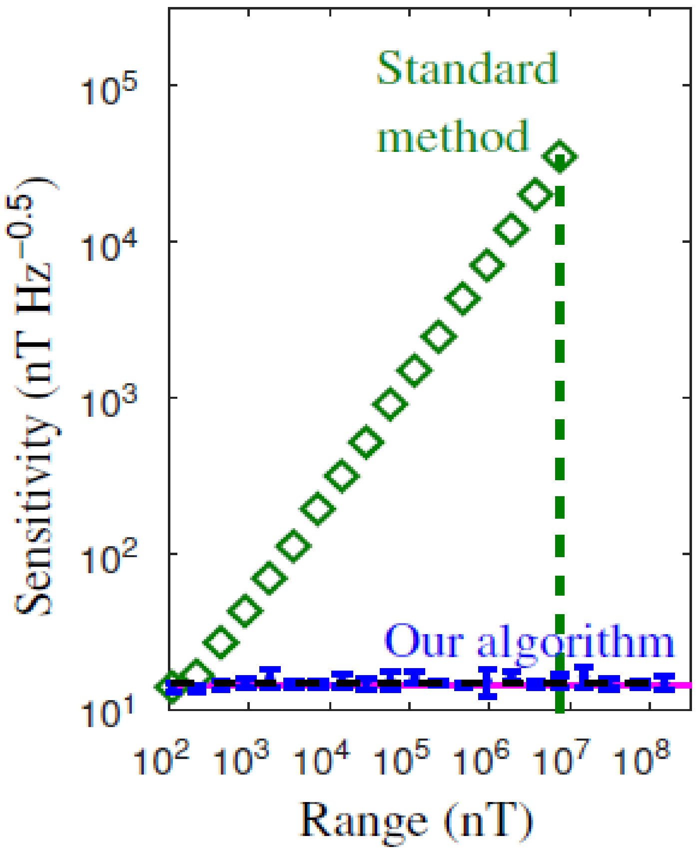
Results





Algorithm: The measurement resulting from different areas combined via Bayes' theorem.

Dynamic range of about 10^7 retaining high sensitivity. Two orders of magnitude over the previous best (Bonato et al., *Nat. Nanotechnol.*, 11, 247 (2015).).

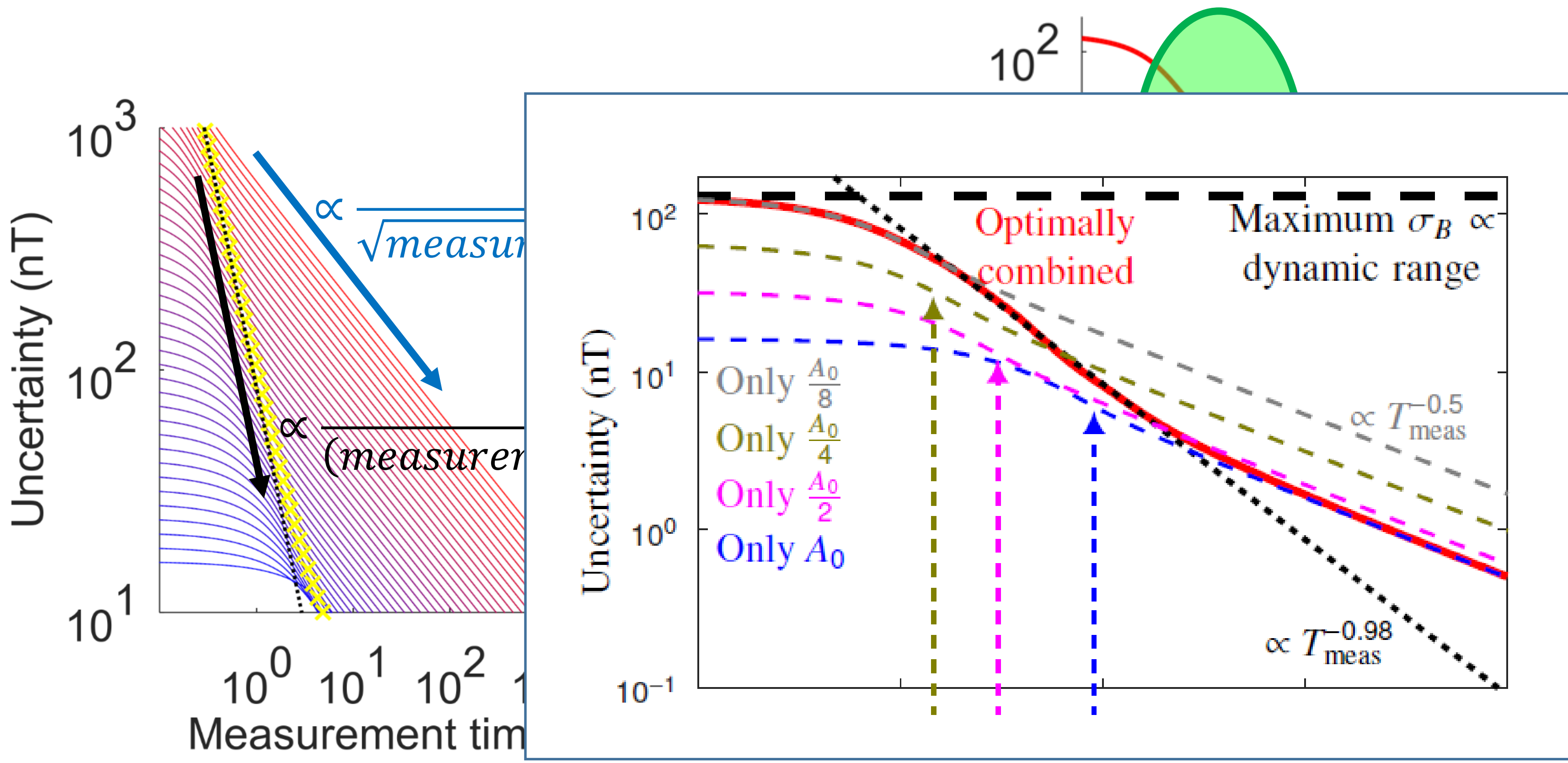


Applicable for other modulo-limited sensors. Important for entanglement-based sensors.

The enhancement of dynamic range will lead to expanding the area of the measurement space.

Algorithm – scaling: time dependence

steep region



We showed the mechanism of Heisenberg-like scaling (T^{-2}).

Short Summary of last part

- Dynamic range of about 10^7 retaining high sensitivity was demonstrated. Two orders of magnitude over the previous best.
- Applicable for other modulo-limited sensors. Important for entanglement-based sensors.
- The enhancement of dynamic range will lead to expanding the area of the measurement space.
- We showed the mechanism of Heisenberg-like scaling (T^{-2}).

"Ultra-high dynamic range quantum measurements retaining its sensitivity",
E. D. Herbschleb, H. Kato, T. Makino, S. Yamasaki, N. Mizuochi,
Nature Communications, 12, 306 (2021)

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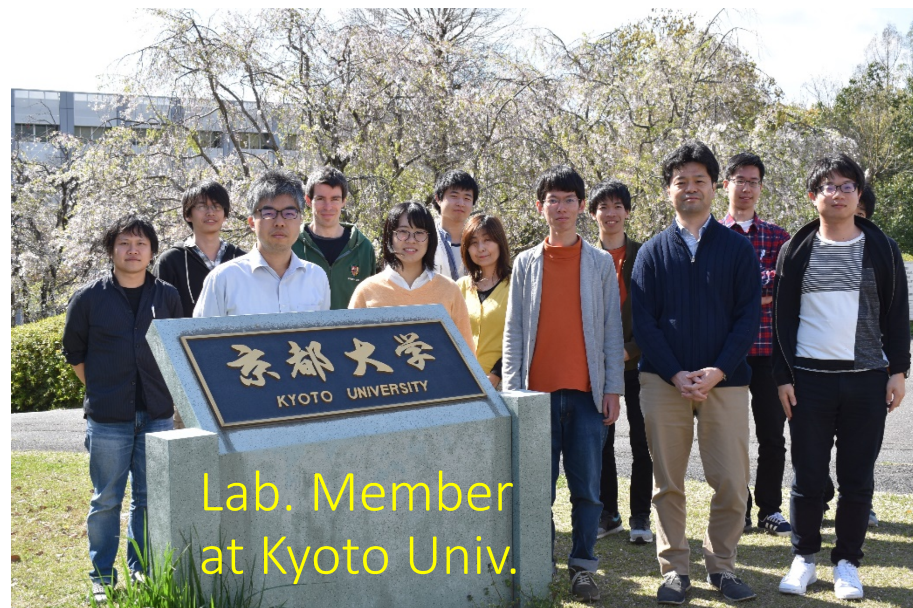
Kyoto Univ.

Dr. Morishita, Dr. Fujiwara, Dr. Herbschleb,
Dr. Ohki, Dr. Hayashi

科研費 KAKENHI

Q-LEAP



Summary

1. Overview: Quantum sensor, NV center in diamond
2. Characteristics of NV centers for sensor
   ～ Why can we improve sensitivity and spatial resolution? ～
3. How to measure? (Magnetic field, electric field, temperature)
4. Expected applications
5. Our recent studies