Quantum Spintronics Design
(NV centers in diamond)

Eisuke Abe

RIKEN Center for Emergent Matter Science

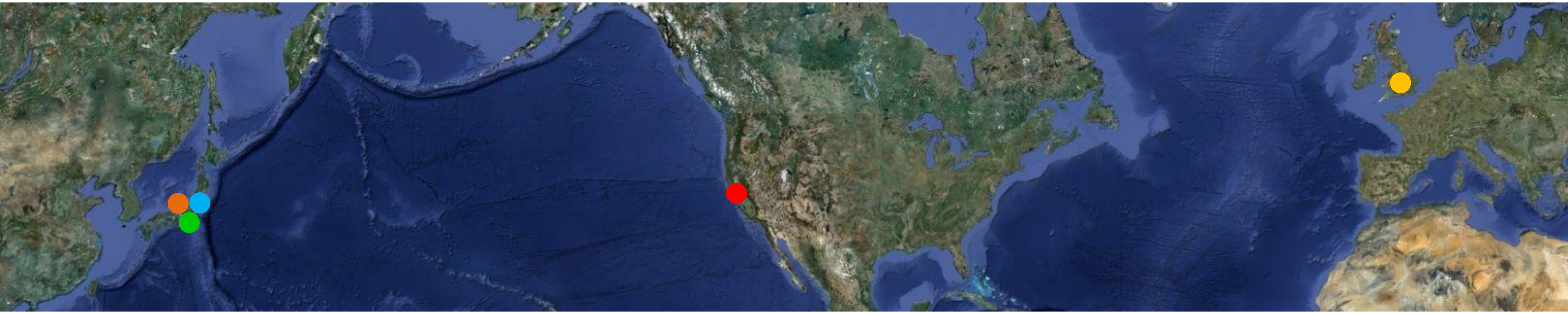
2020.02.19

CMD Spintronics Design Course

@Osaka University

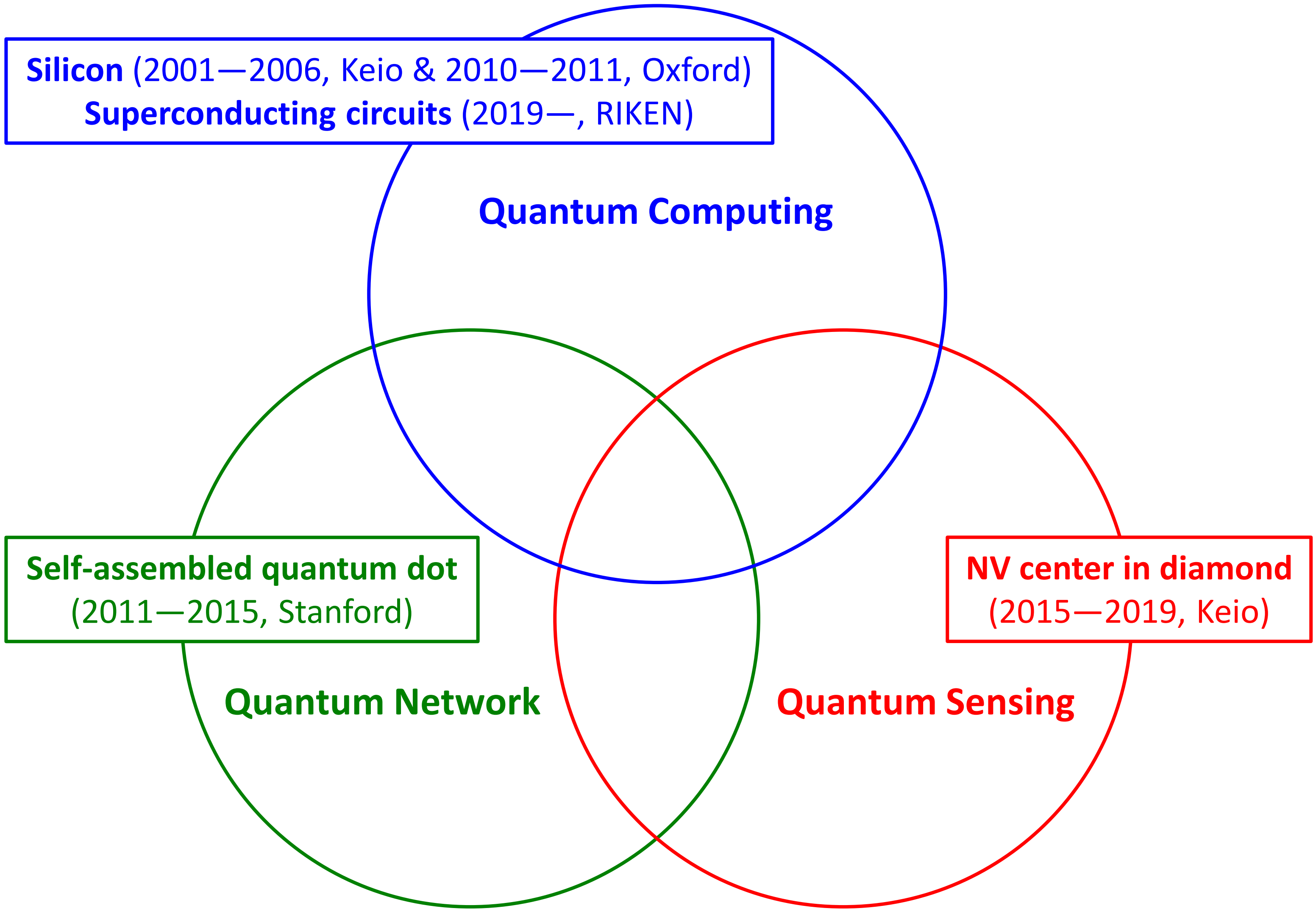
RIKEN

Short CV

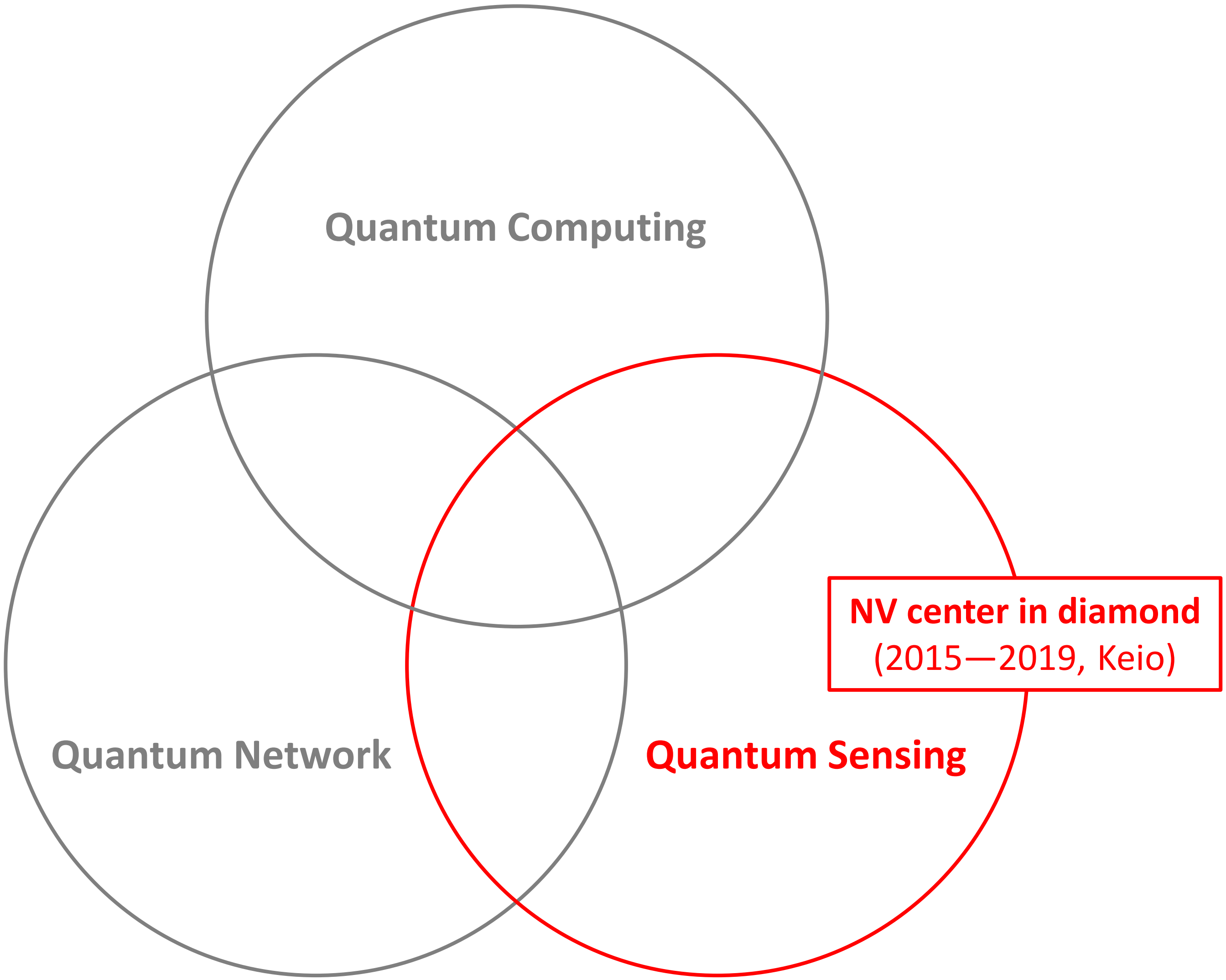


- **2001.4 – 2006.3 (Keio)** → Quantum computing (silicon)
- **2006.4 – 2009.12 (ISSP, UT)** → Quantum transport (GaAs QDs, Josephson)
- **2010.1 – 2011.6 (Oxford)** → Hybrid system (spin–cavity coupling)
- **2011.7 – 2015.3 (Stanford/RIKEN)** → Quantum network (InAs QDs)
- **2015.4 – 2019.1 (Keio)** → Quantum sensing (diamond)
- **2019.2 – Present (RIKEN)** → Quantum computing (Josephson)

Quantum technologies



Quantum technologies



Outline

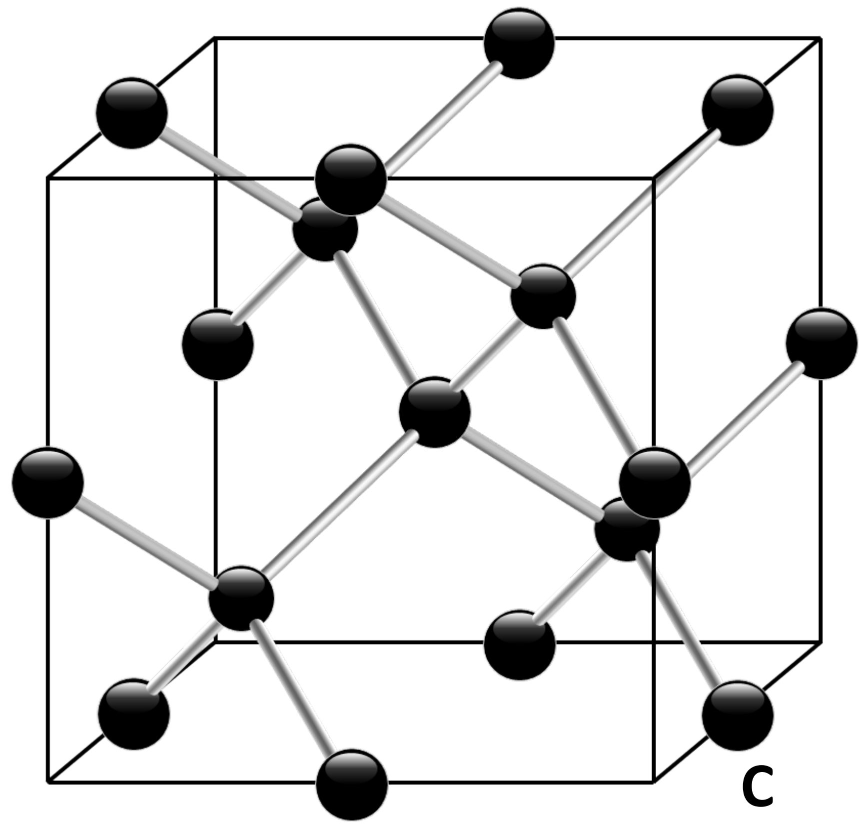
- **Basics of NV centers in diamond**
  - Structure
  - Optical properties
  - Spin properties and control
- **Quantum sensing**
  - Principle of AC magnetometry
  - Detection of proton spin ensemble
  - Detection and localization of a single ^{13}C nuclear spin
  - Ultrahigh resolution sensing

Outline

- **Basics of NV centers in diamond**
  - Structure
  - Optical properties
  - Spin properties and control

- **Quantum sensing**
  - Principle of AC magnetometry
  - Detection of proton spin ensemble
  - Detection and localization of a single ^{13}C nuclear spin
  - Ultrahigh resolution sensing

Diamond envy

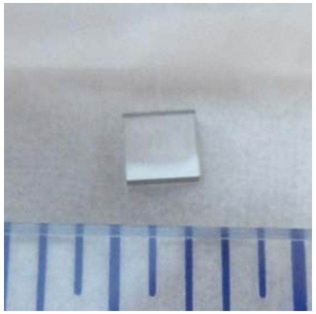


©GIA

$\rho_N = 1.77 \times 10^{23}\ cm^{-3}$

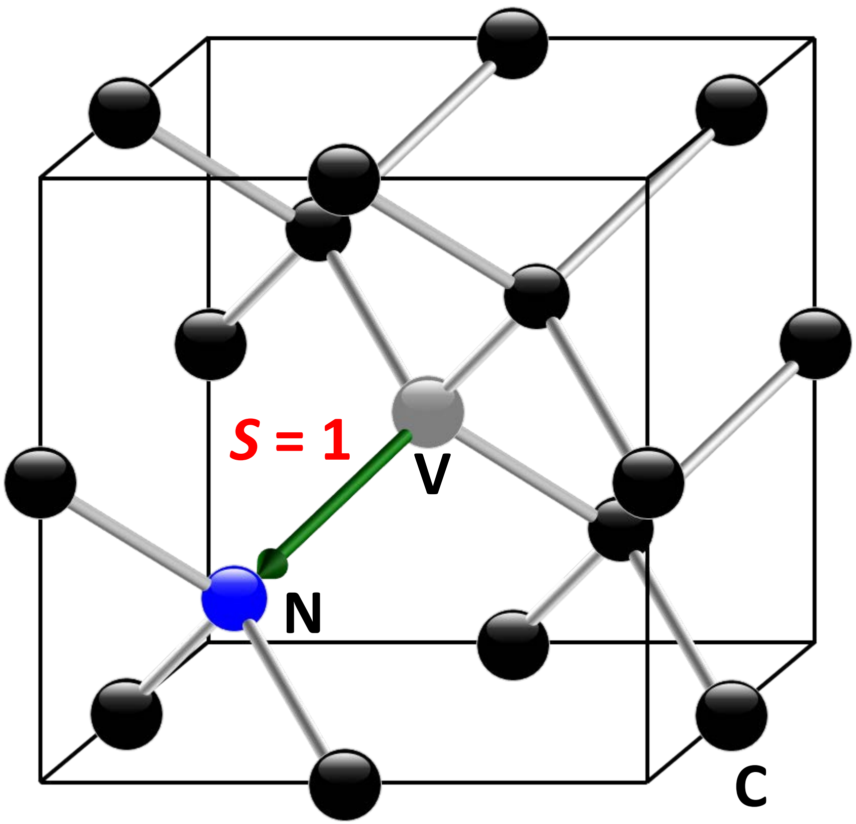
Diamond NV

Synthetic (CVD) diamond
2^2 x 0.5 mm^3, \$700 (E6)
[N] < 5 ppb, [NV] < 0.03 ppb



Not like…

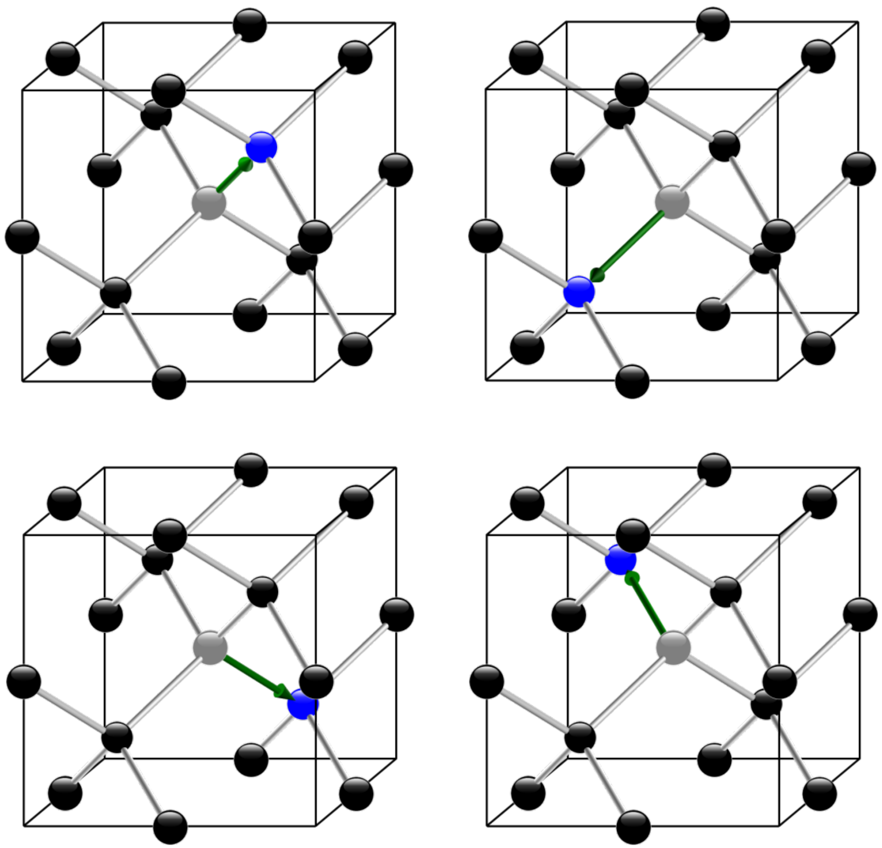
©GIA



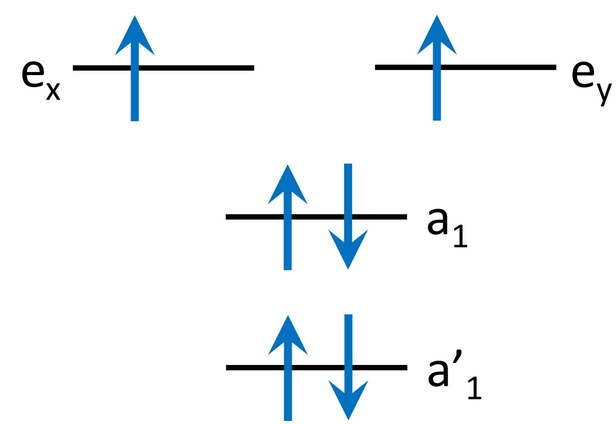
ρ_N = 1.77 x 10^{23} cm^{-3}

Crystal & energy level structures

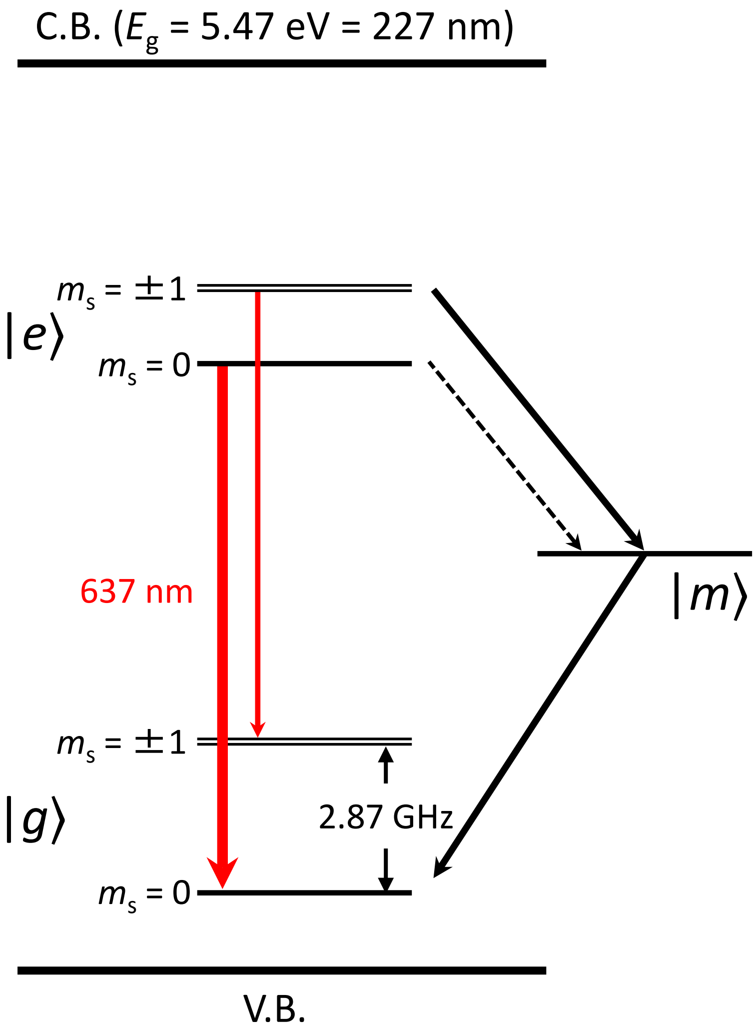
- Negatively-charged (NV^-)
- 4 sp^3 orbitals, 6 e^- (5 from the defect, 1 captured)
- C_{3v} (symmetry axis = quantization axis)



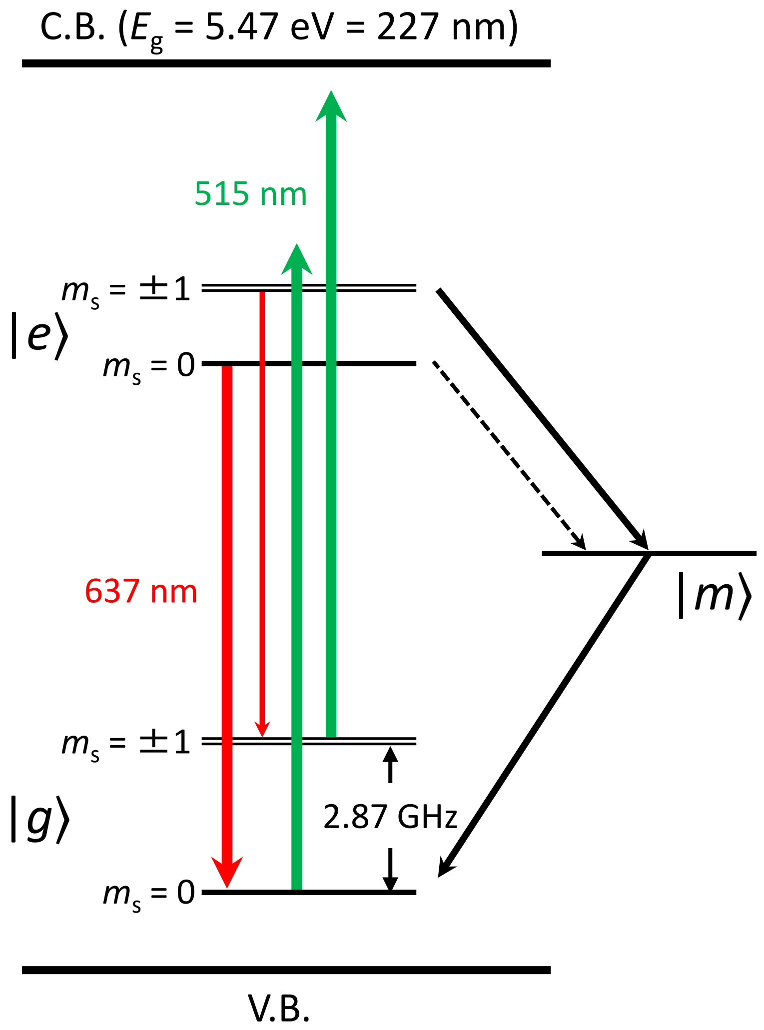
Effective spin-1 system
(e^2-hole spin-triplet)

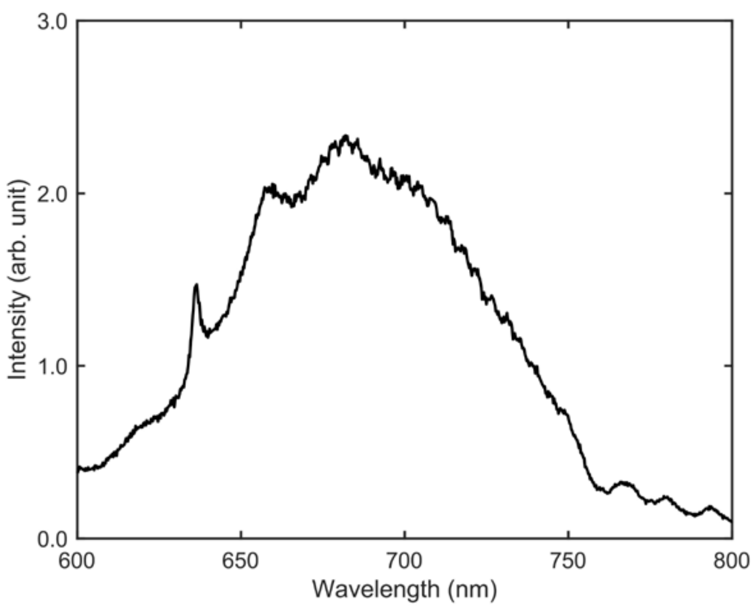


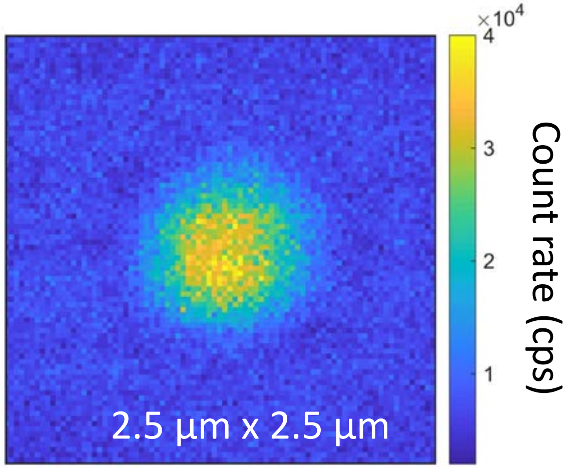
Energy levels



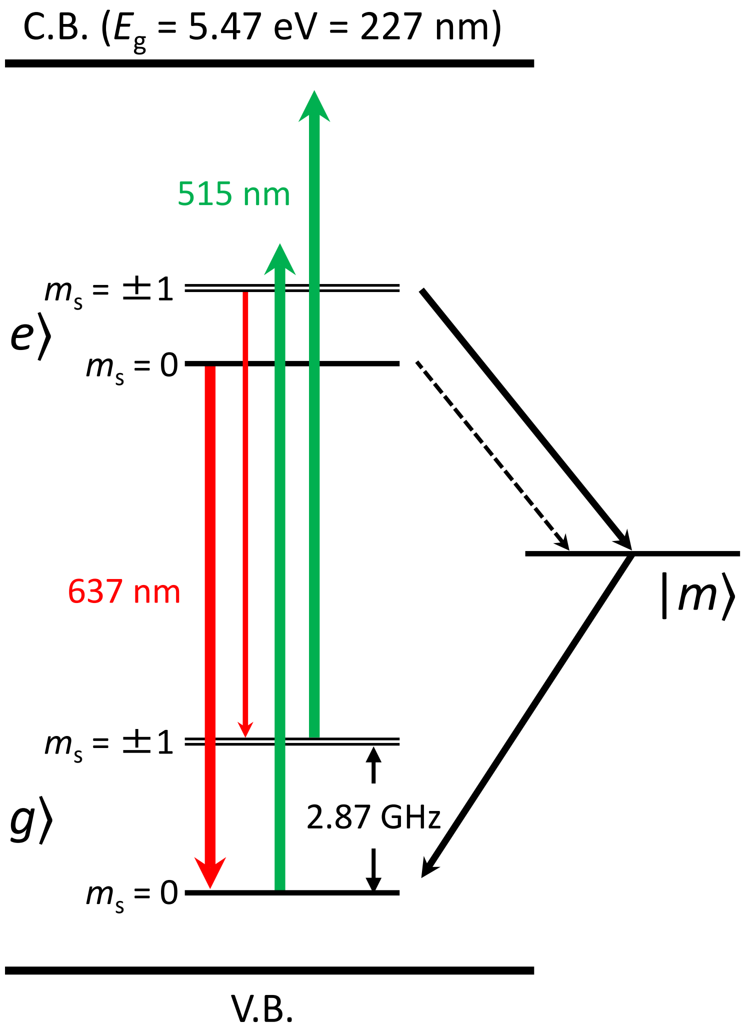
PL spectroscopy & imaging



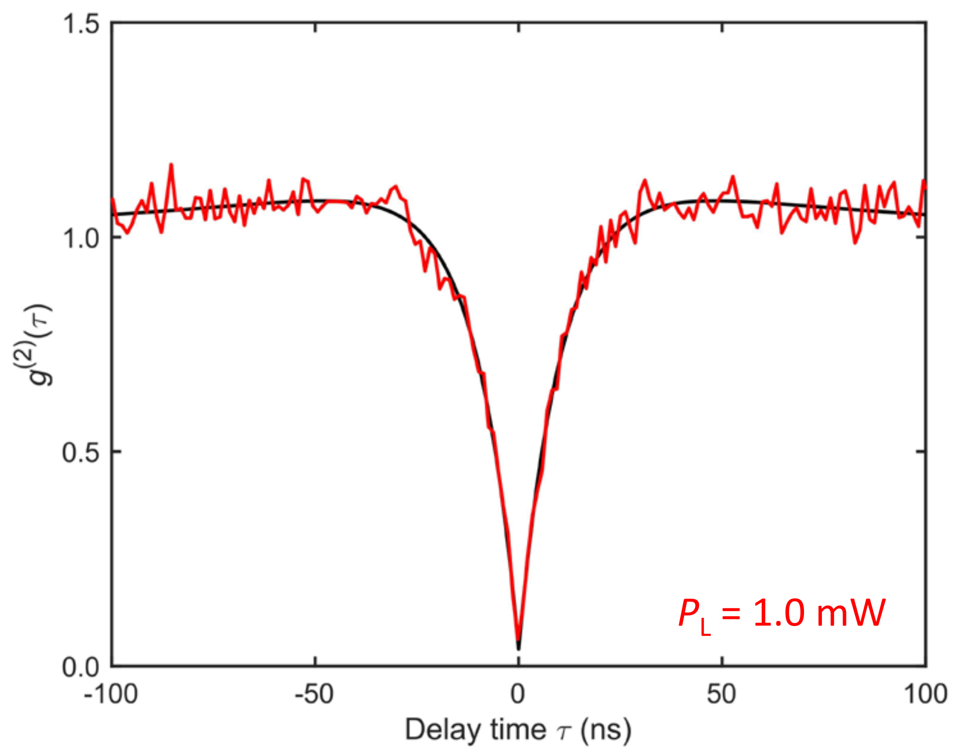




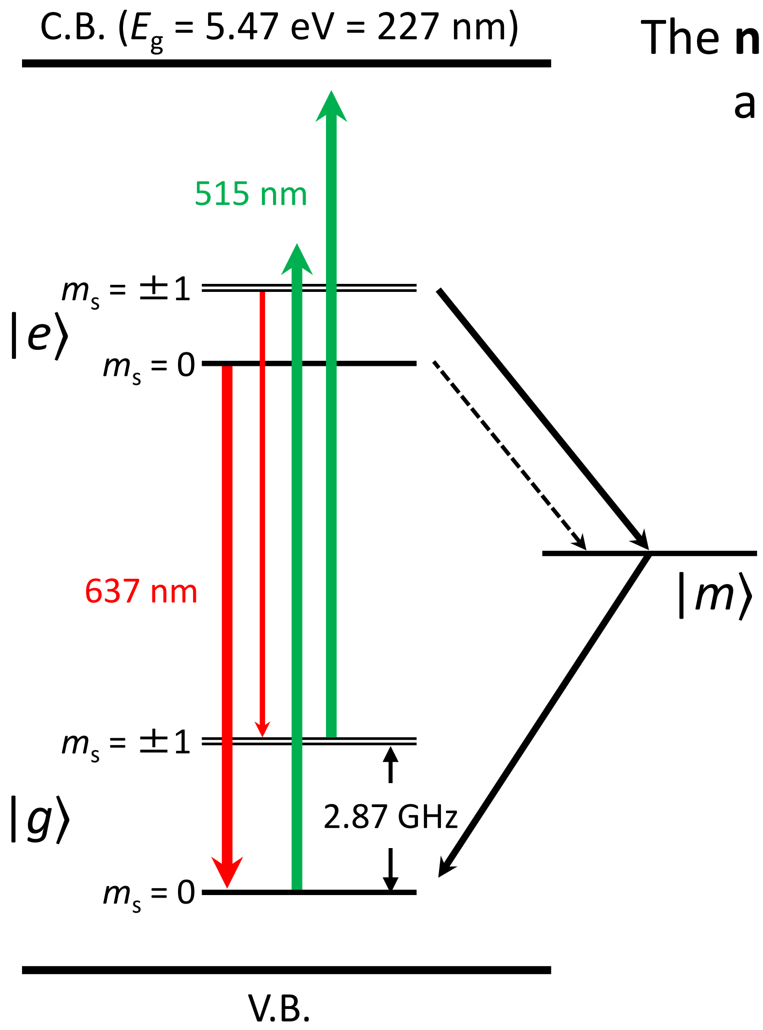
Photon statistics



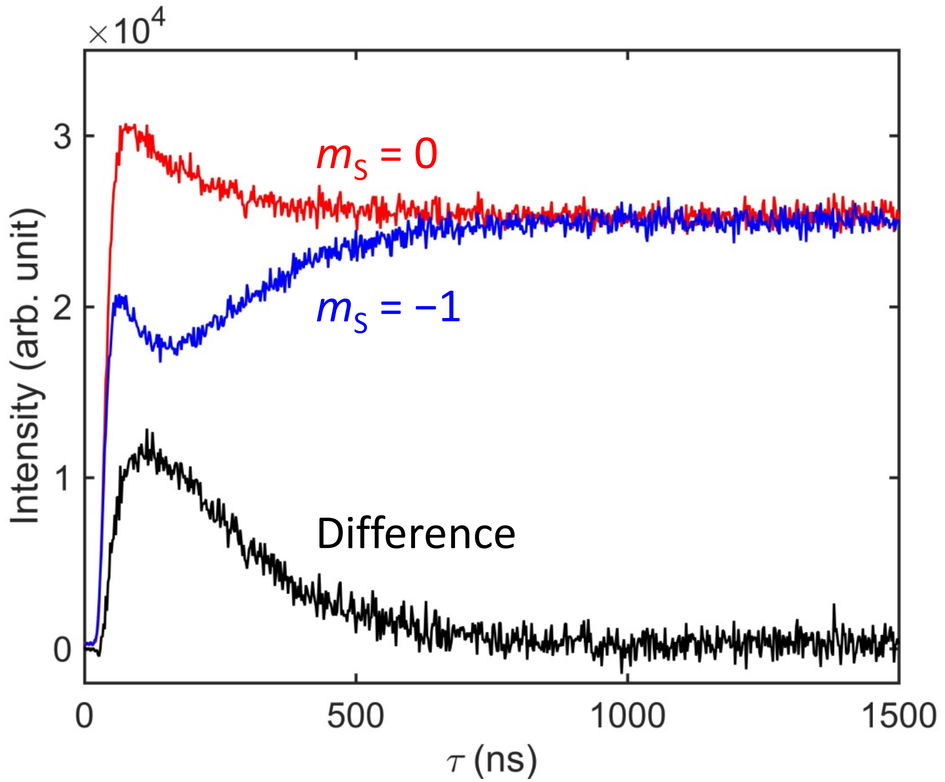
One photon at a time



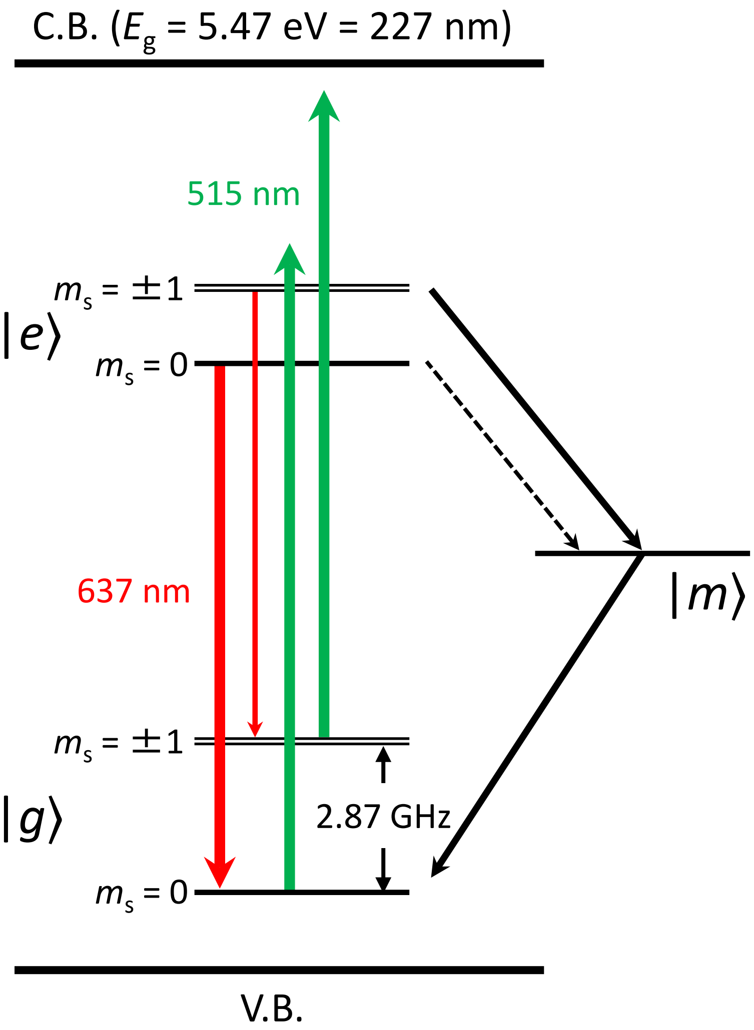
Time-resolved fluorescence



The **non-radiative** & **spin-selective** channel provides a means to **read out** & **initialize** the NV spin

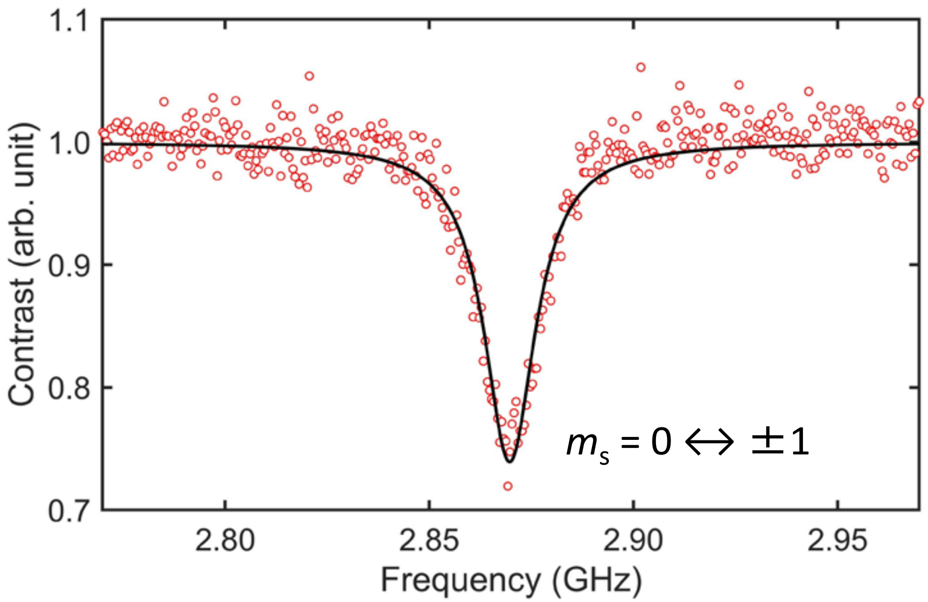


CW ODMR at $B_0 = 0$

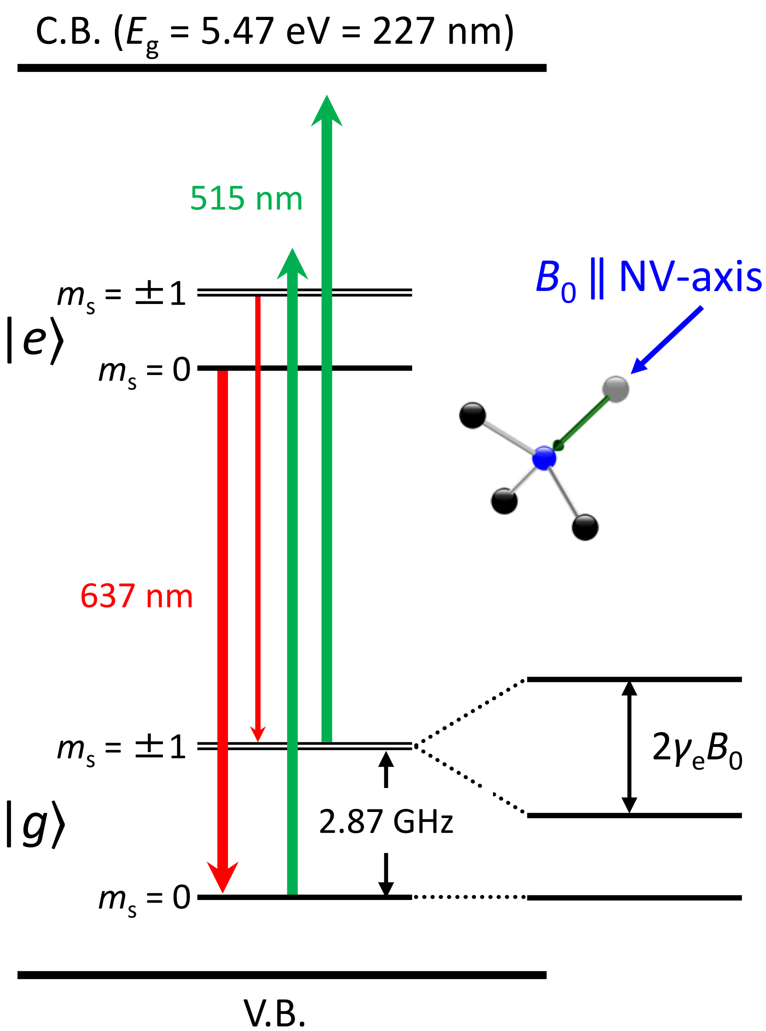


Zero-field splitting $H = DS_z^2$

D = 2.87 GHz

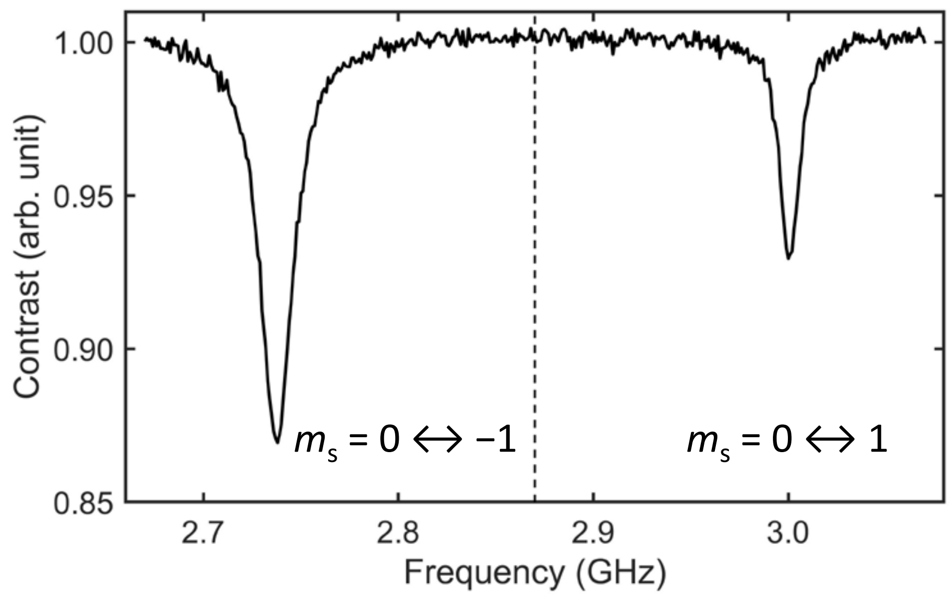


CW ODMR at $B_0 > 0$



Zeeman $H = DS_z^2 + \gamma_e B_0 S_z$

γ_e = 28 MHz/mT



B_0 = 4.7 mT (2.87±0.132 GHz)

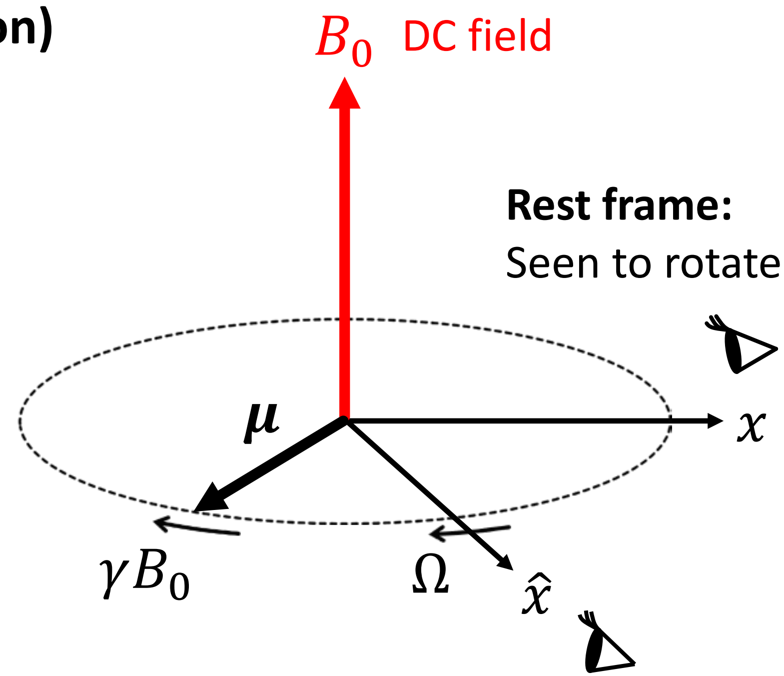
Magnetic resonance

Torque equation (Larmor precession)

$$\frac{d\boldsymbol{\mu}}{dt} = \boldsymbol{\mu} \times \gamma \boldsymbol{B}_0$$

Gyromagnetic ratio

Magnetic moment: $\boldsymbol{\mu} = \gamma \boldsymbol{J}$



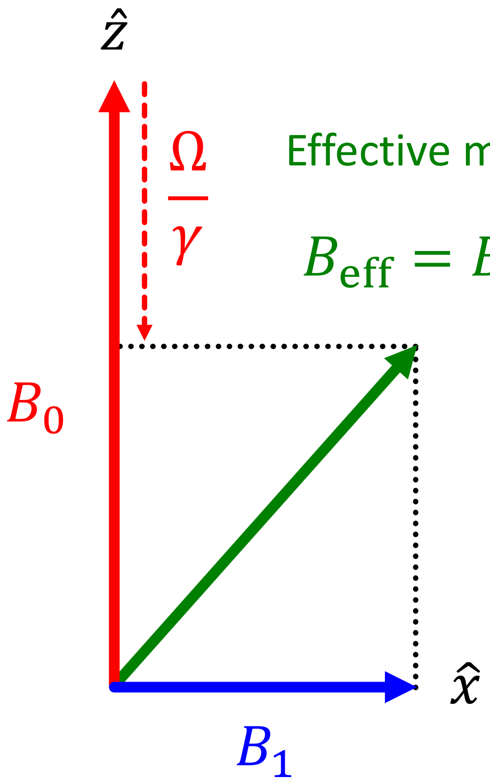
Rest frame:
Seen to rotate at γB_0

Frame rotating at angular velocity $\boldsymbol{\Omega}$:
Rotate slower…why?

⇓

DC field along the z direction becomes weaker

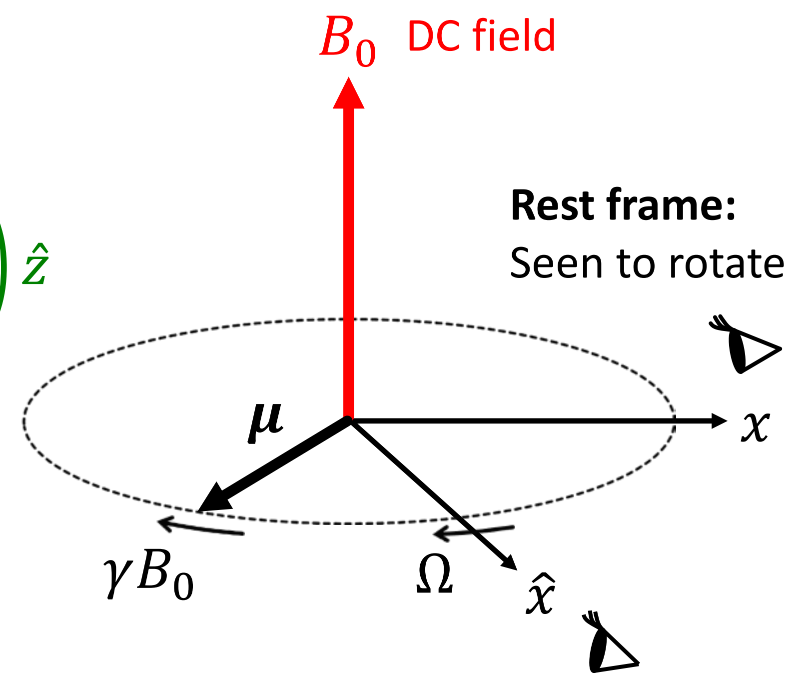
Magnetic resonance



AC field rotating in the xy plane at Ω

Effective magnetic field

$$B_{\text{eff}} = B_1\hat{x} + \left(B_0 - \frac{\Omega}{\gamma}\right)\hat{z}$$



Rest frame:
Seen to rotate at γB_0

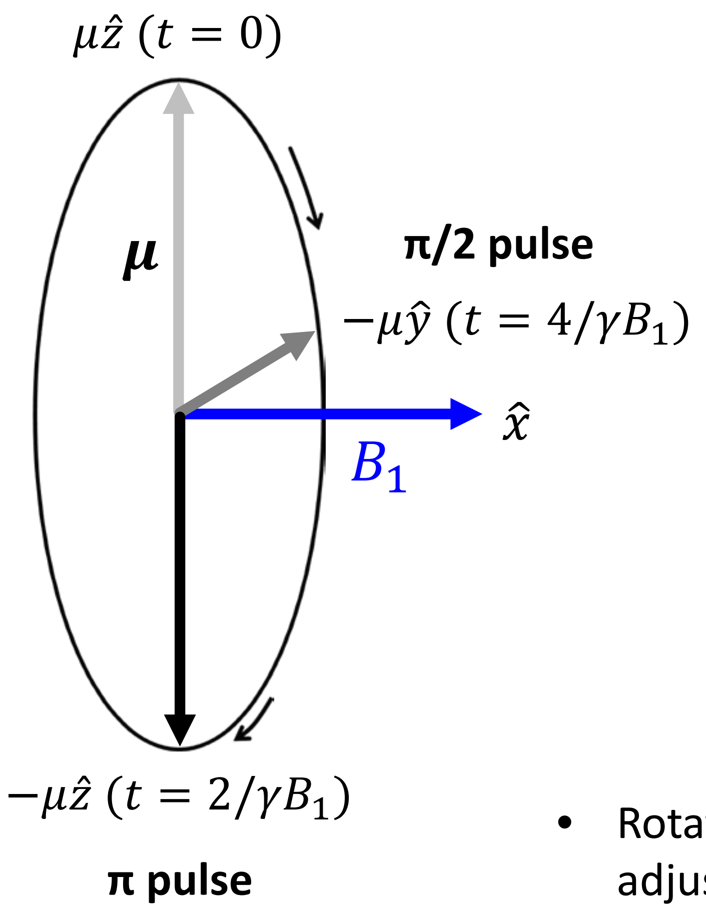
Frame rotating at angular velocity Ω:
Rotate slower…why?

⇩

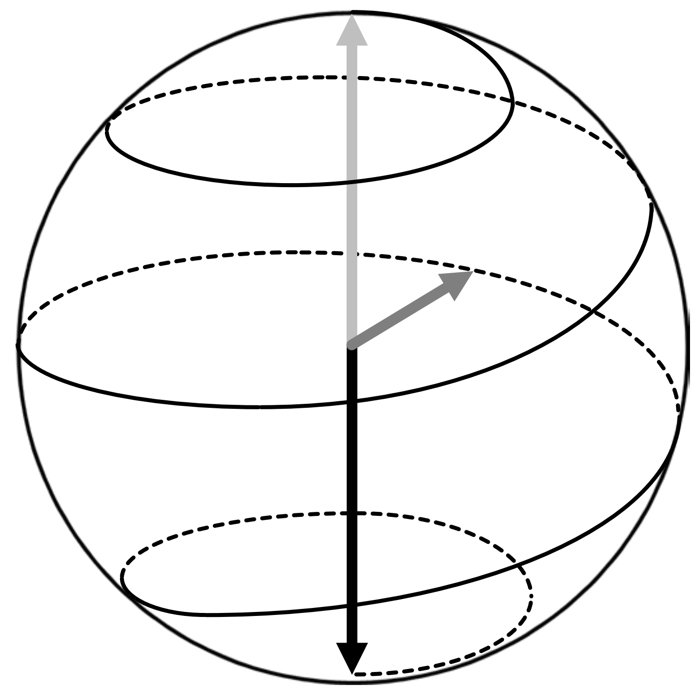
DC field along the z direction becomes weaker

Magnetic resonance

Frame rotating at $\Omega = \gamma B_0$



Rest (non-resonant) frame



- Rotations about the $\pm\hat{x}, \pm\hat{y}$ axes are realized by adjusting the microwave phases
- Rotation about the $\hat{z}$ axis is superposed when observed from the rest (non-resonant) frame

Quantum bit

Qubit, spin-1/2 (NV is spin-1!)

$$\begin{cases} |"0"\rangle \equiv |m_s = 0\rangle \\ |"1"\rangle \equiv |m_s = -1\rangle \end{cases}$$

Superposition state

$$|\psi\rangle = \alpha|0\rangle + \beta|1\rangle \qquad |\alpha|^2 + |\beta|^2 = 1$$

⇩

$$|\psi\rangle = e^{i\gamma}\left(\cos\frac{\theta}{2}|0\rangle + e^{i\phi}\sin\frac{\theta}{2}|1\rangle\right)$$

Global phase

$$0 \le \theta \le \pi$$
$$0 \le \gamma, \phi < 2\pi$$

⇩

$$|\psi\rangle = \cos\frac{\theta}{2}|0\rangle + e^{i\phi}\sin\frac{\theta}{2}|1\rangle$$

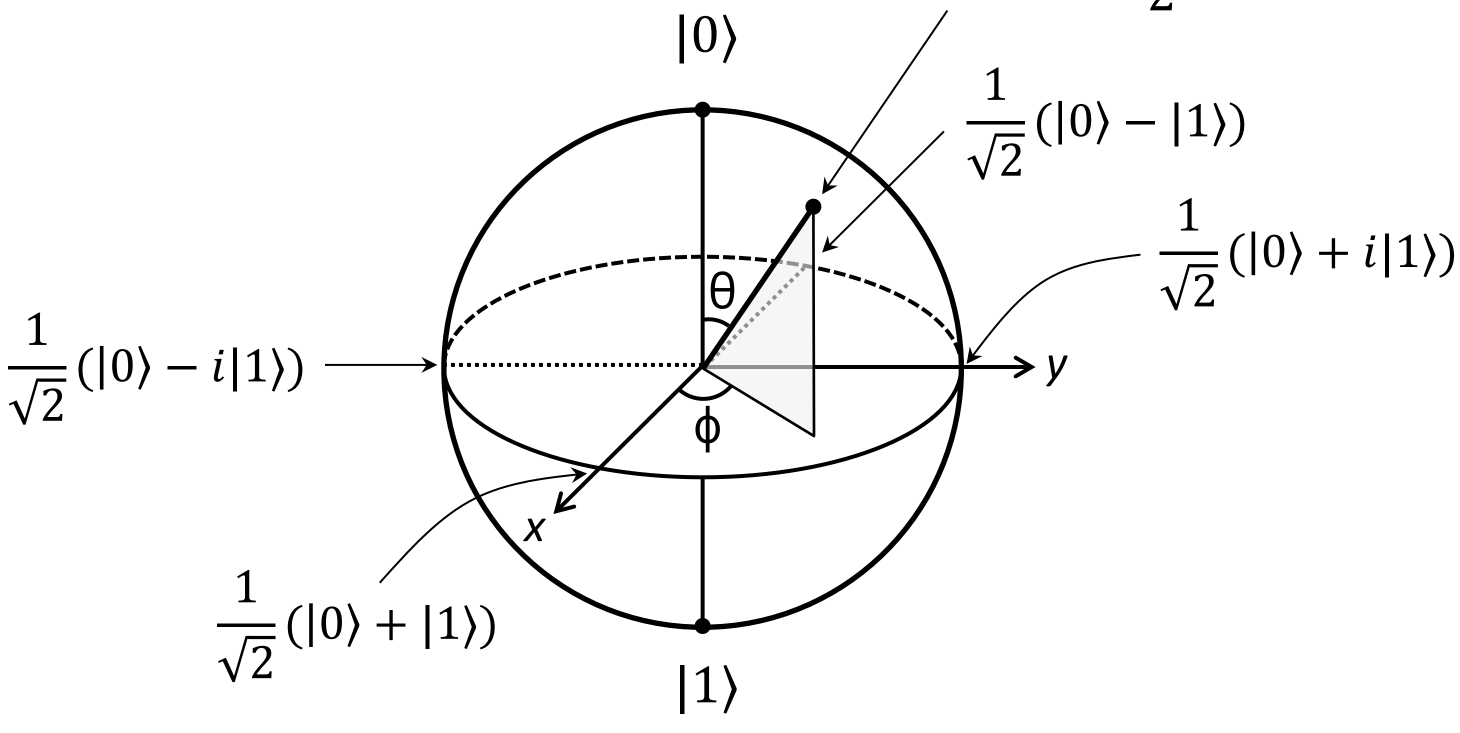
$$0 \le \theta \le \pi$$
$$0 \le \phi < 2\pi$$

Bloch sphere

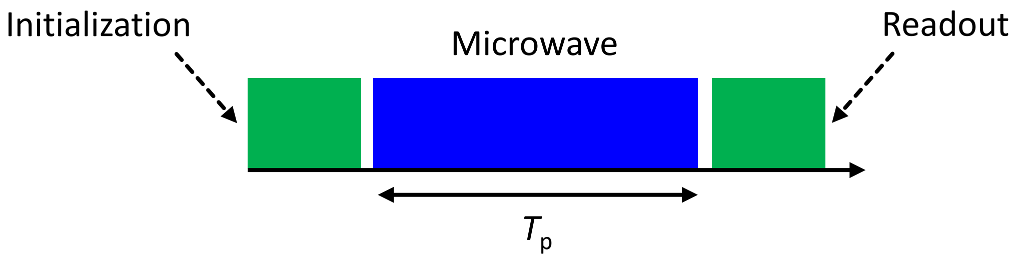
Qubit, spin-1/2 (NV is spin-1!)

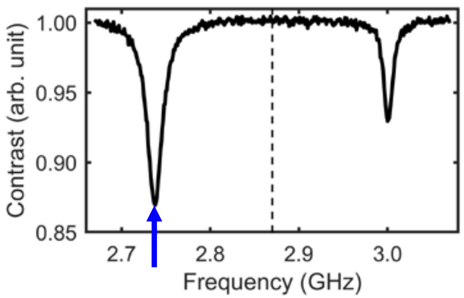
$$\begin{cases} |"0"\rangle \equiv |m_s = 0\rangle \\ |"1"\rangle \equiv |m_s = -1\rangle \end{cases}$$

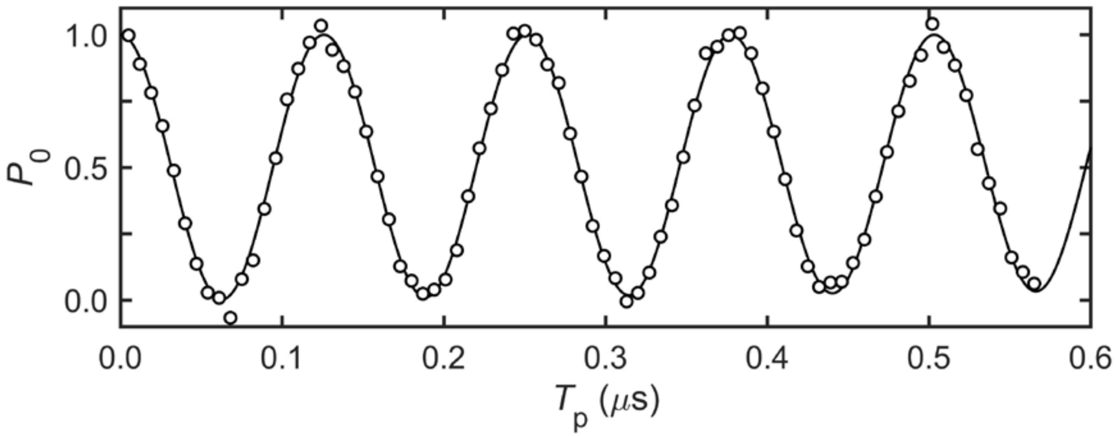
$$|\psi\rangle = \cos\frac{\theta}{2}|0\rangle + e^{i\phi}\sin\frac{\theta}{2}|1\rangle$$

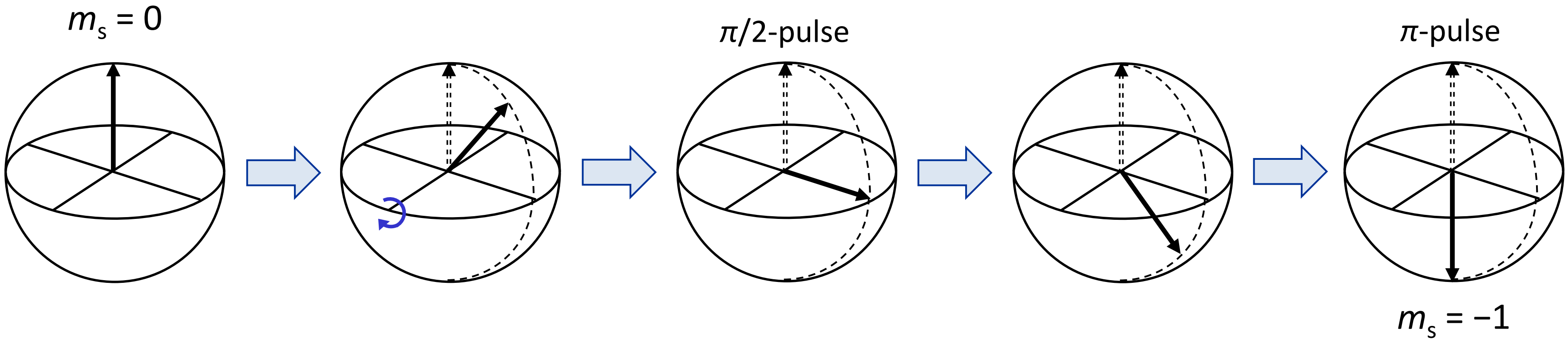


Rabi oscillation

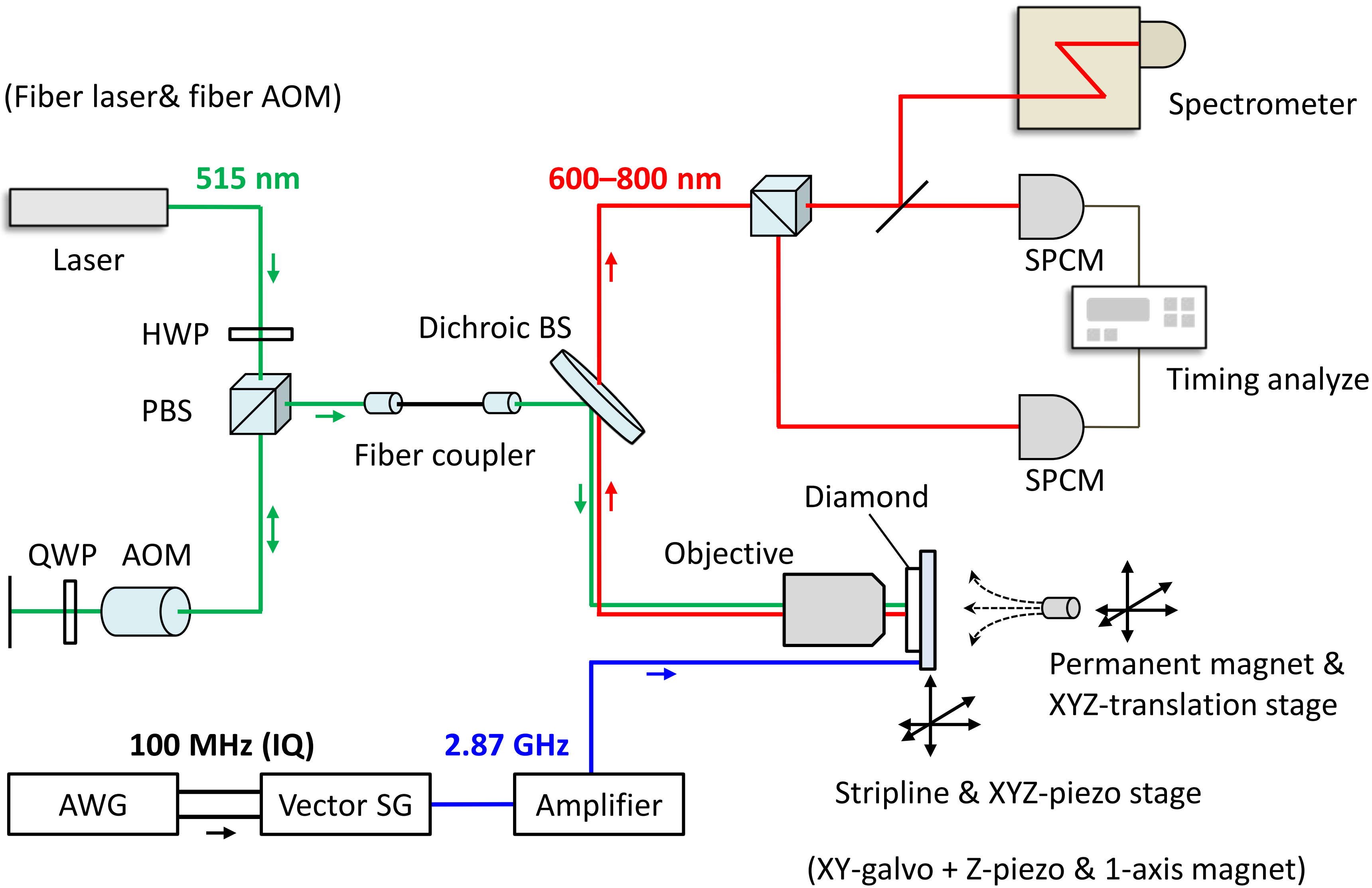




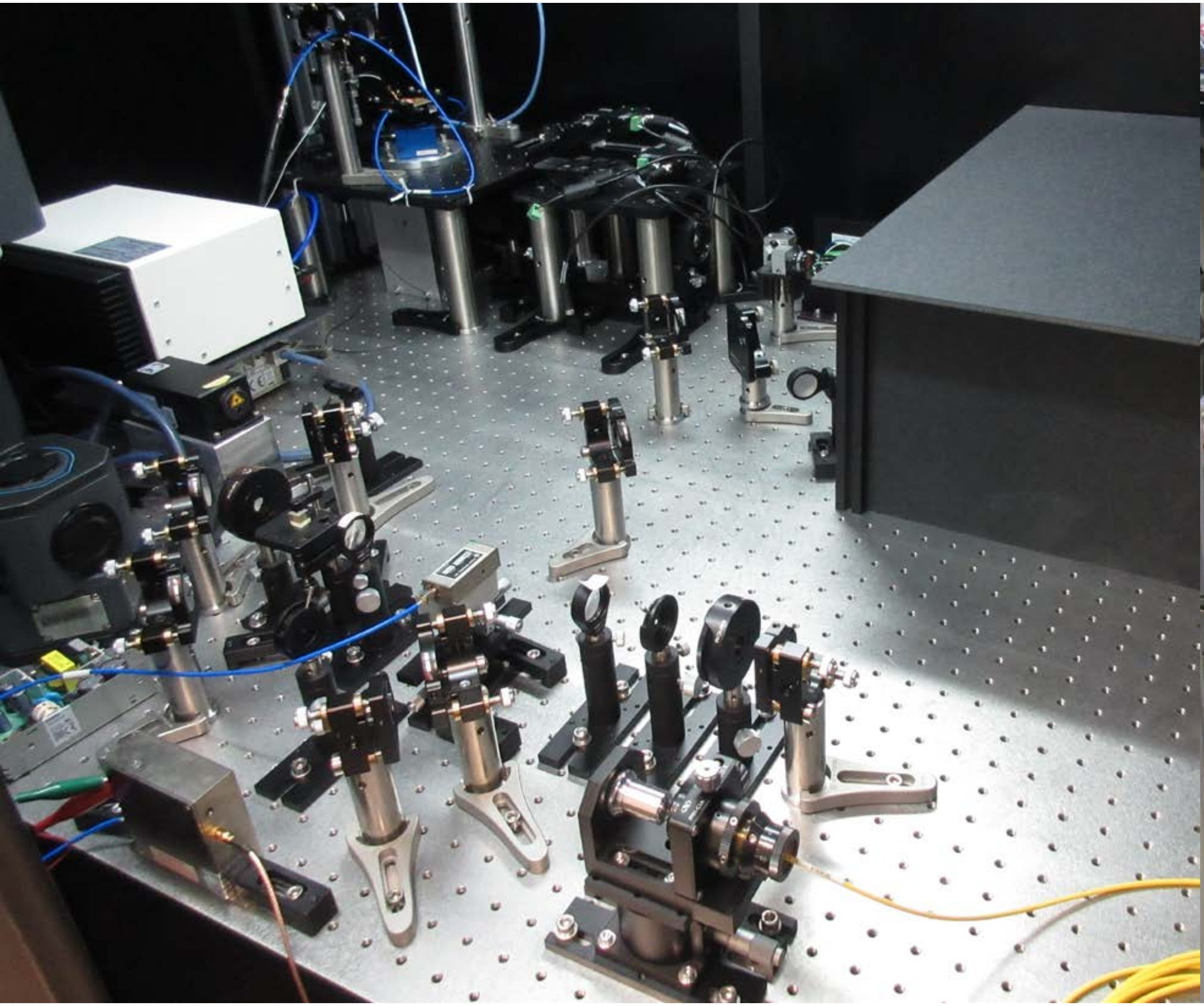


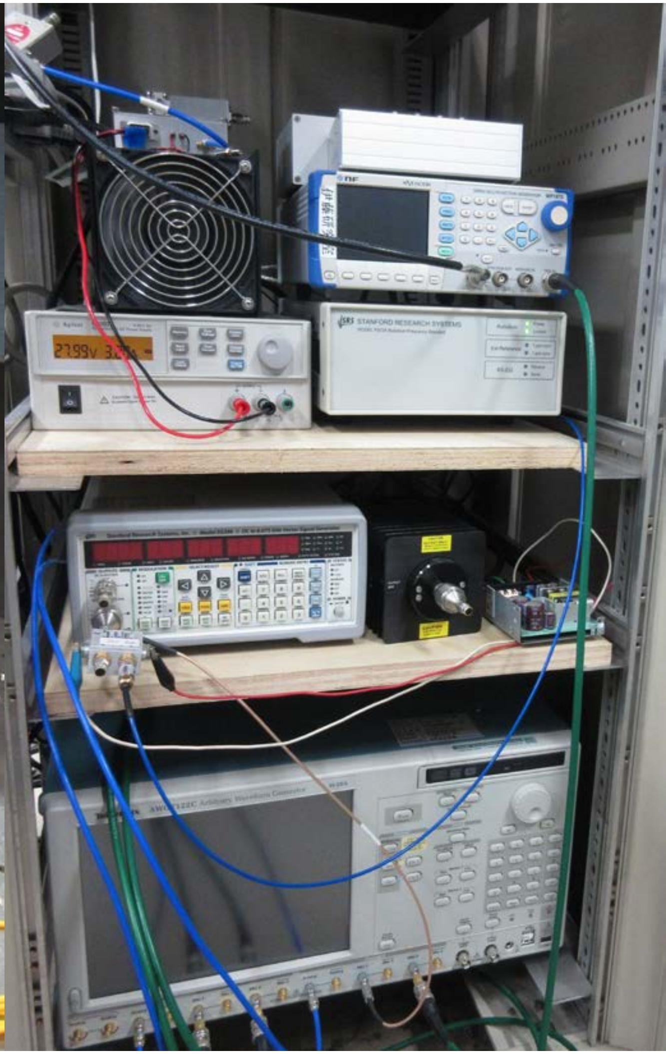


Experimental setup

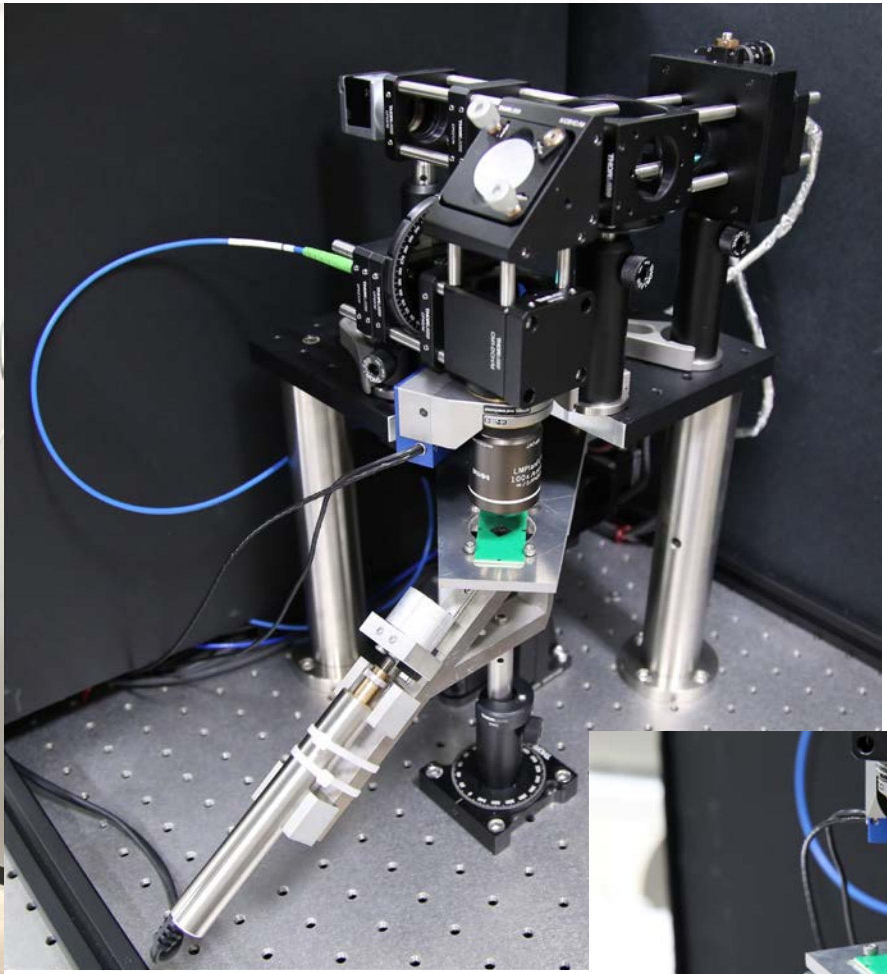


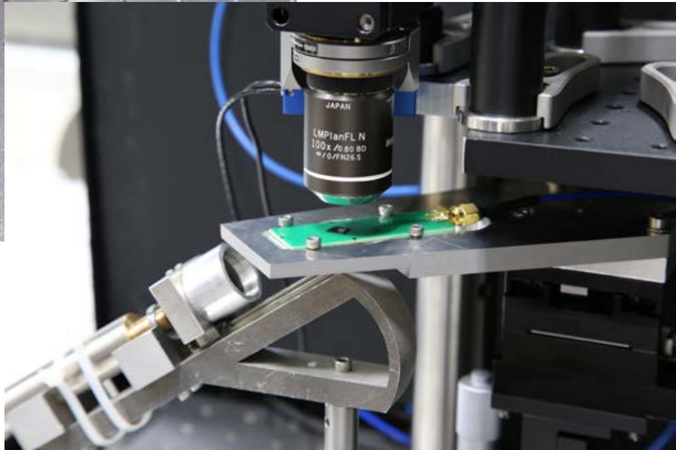
Experimental setup





Experimental setup





AIP Advances **10**, 025206 (2020)
Misonou *et al.*

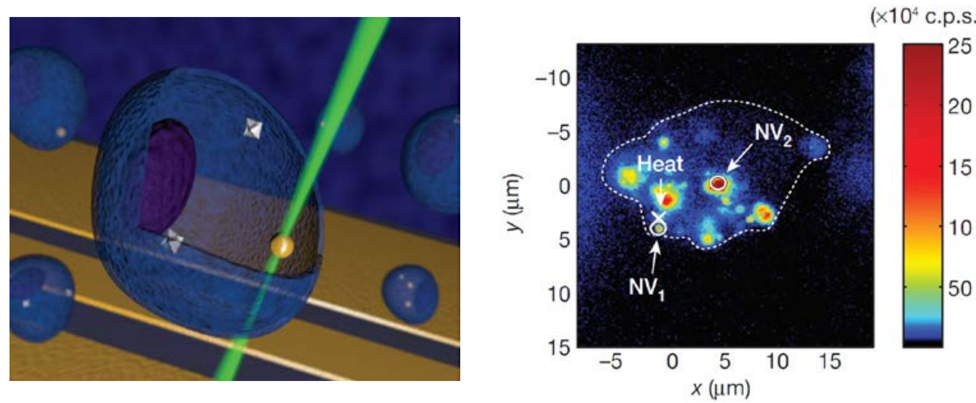
Outline

- **Basics of NV centers in diamond**
  - Structure
  - Optical properties
  - Spin properties and control
- **Quantum sensing**
  - Principle of AC magnetometry
  - Detection of proton spin ensemble
  - Detection and localization of a single ^{13}C nuclear spin
  - Ultrahigh resolution sensing

Quantum sensing with NV centers

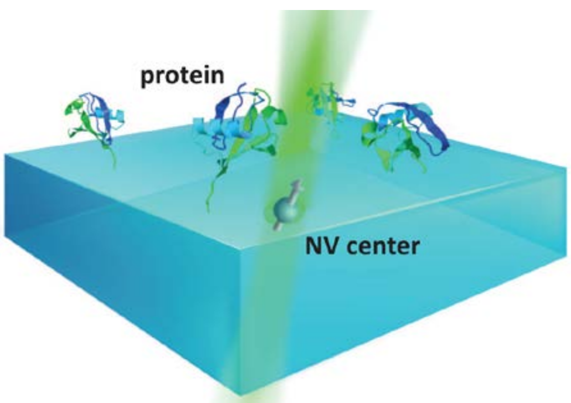
- *B*, *E*, *T*, *S*...
- DC & AC modes
- Wide temperature range
- Nondestructive
- High spatial resolution
- Various modalities

Nanodiamond & biology



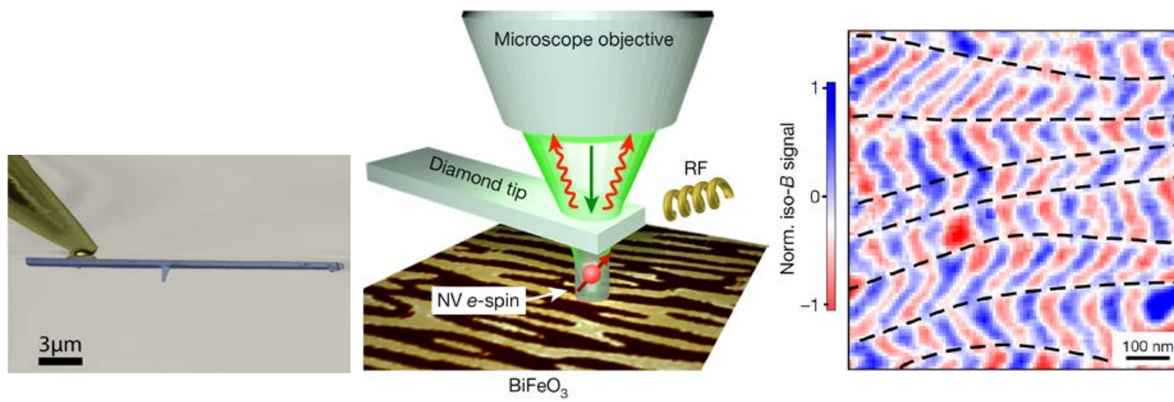
Nature **500**, 54 (2013)

Near-surface NV center & NMR



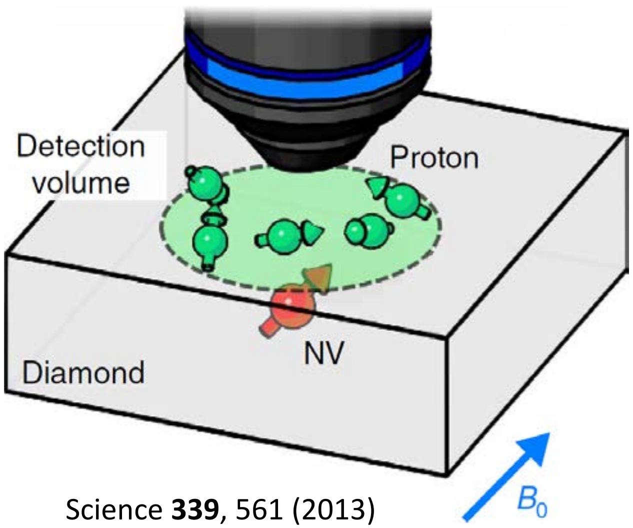
Science **351**, 836 (2016)

Scanning probe & condensed matter

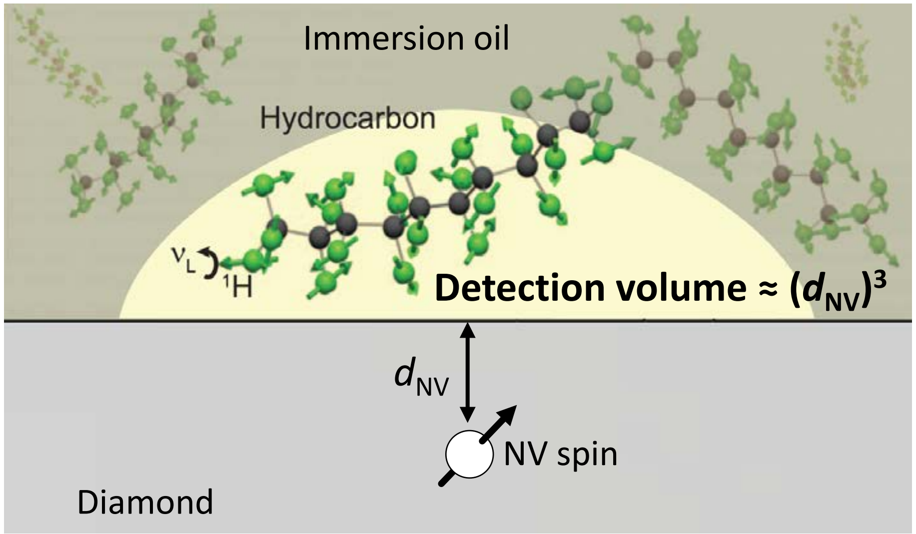


Rev. Sci. Instrum. **87**, 063703 (2016); Nature **549**, 252 (2017)

Nuclear spin sensing



Science **339**, 561 (2013)



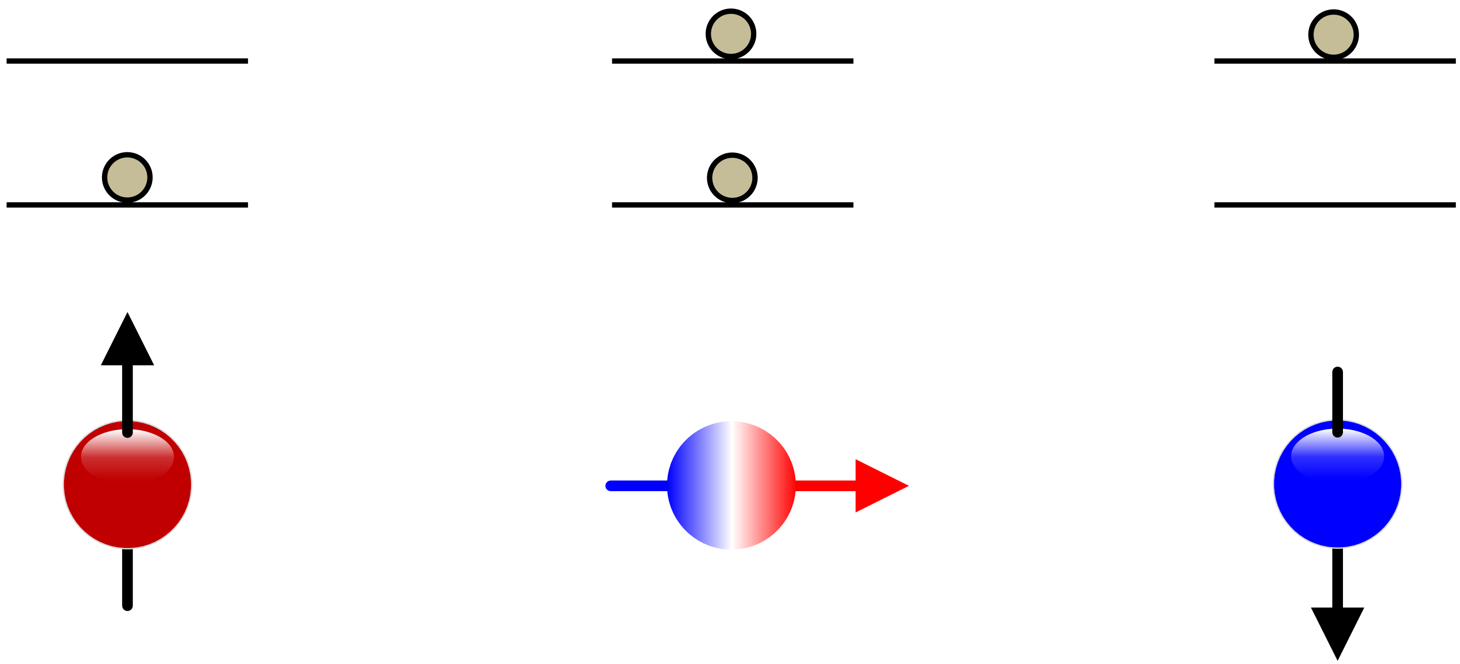
Nature Commun. **6**, 8527 (2015)

Nuclear spins **precess** at f_{ac} = a few kHz–MHz under B_0

⇨ **Weak AC magnetic field** on the NV spin

⇨ Detect using **quantum coherence**

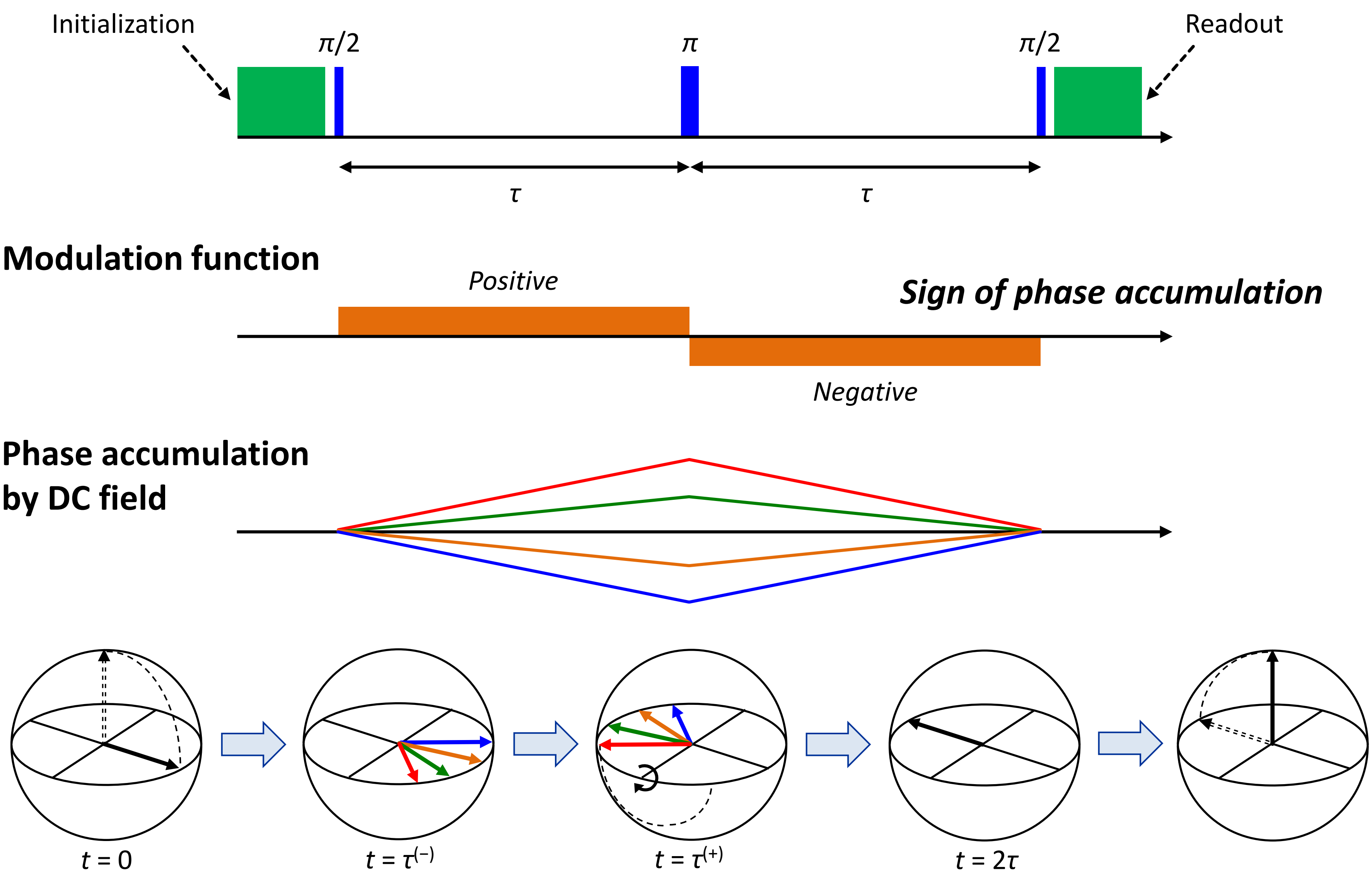
Quantum coherence



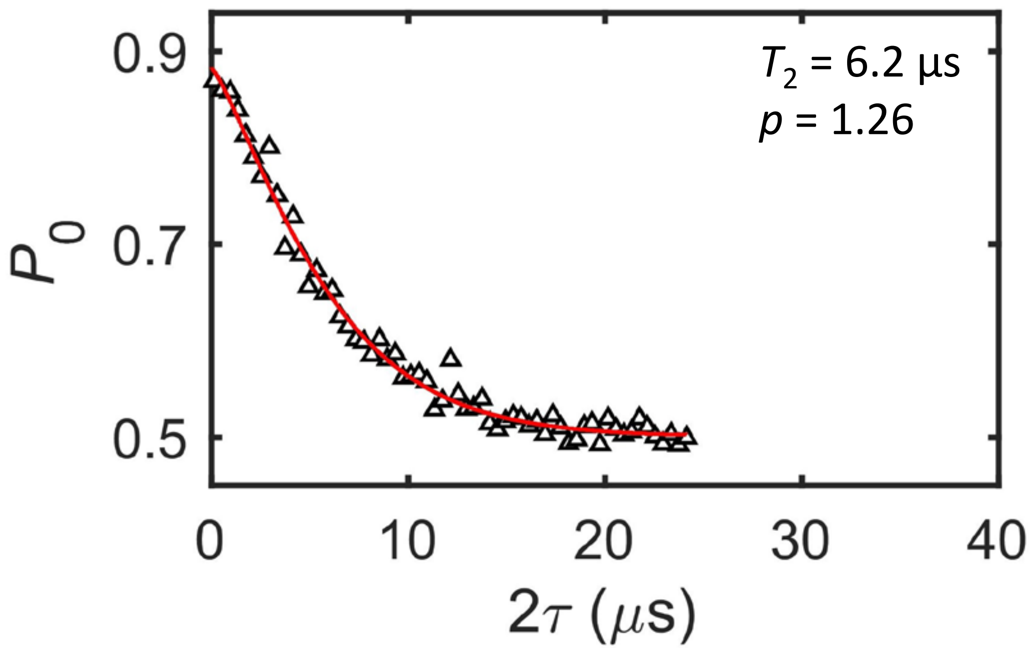
$|0\rangle \equiv |m_s = 0\rangle$ $\quad$ $|\Psi\rangle = \alpha|0\rangle + \beta|1\rangle$ $\quad$ $|1\rangle \equiv |m_s = -1\rangle$

T_2: measure of how long a superposition state is preserved

Spin echo


Initialization
π/2
π
π/2
Readout
τ
τ
Modulation function
Positive
Sign of phase accumulation
Negative
Phase accumulation
by DC field
t = 0
t = τ(−)
t = τ(+)
t = 2τ

Coherence time



Stretched exponential decay

$$\exp\left[-\left(\frac{2\tau}{T_2}\right)^p\right]$$

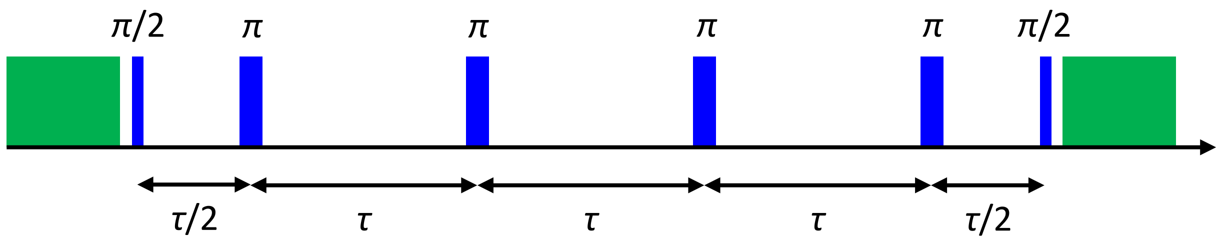
Near-surface NV center

- N^+ implantation into ^{12}C (I = 0) layer
- d_{NV} = 6.26 nm
- B_0 = 23.5 mT

AIP Advances **10**, 025206 (2020) Misonou *et al.*

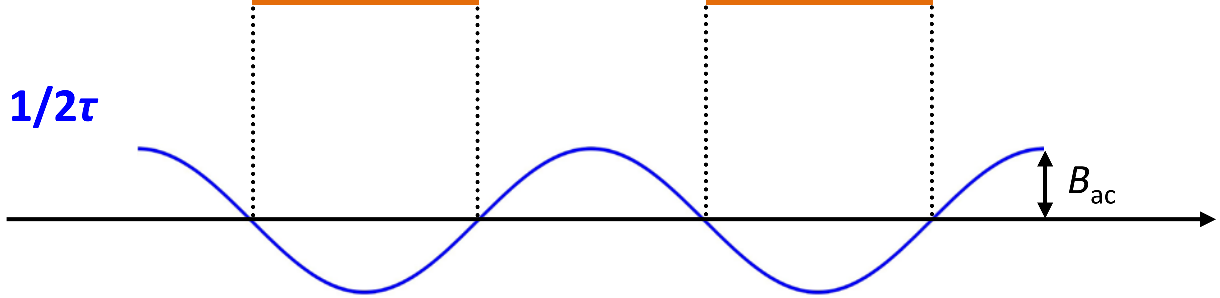
AC magnetometry

CP (*N* = 4)



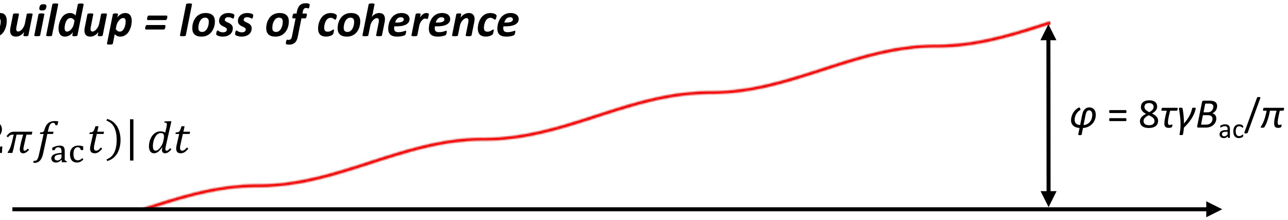
Modulation function

AC field at $f_{ac} = 1/2\tau$

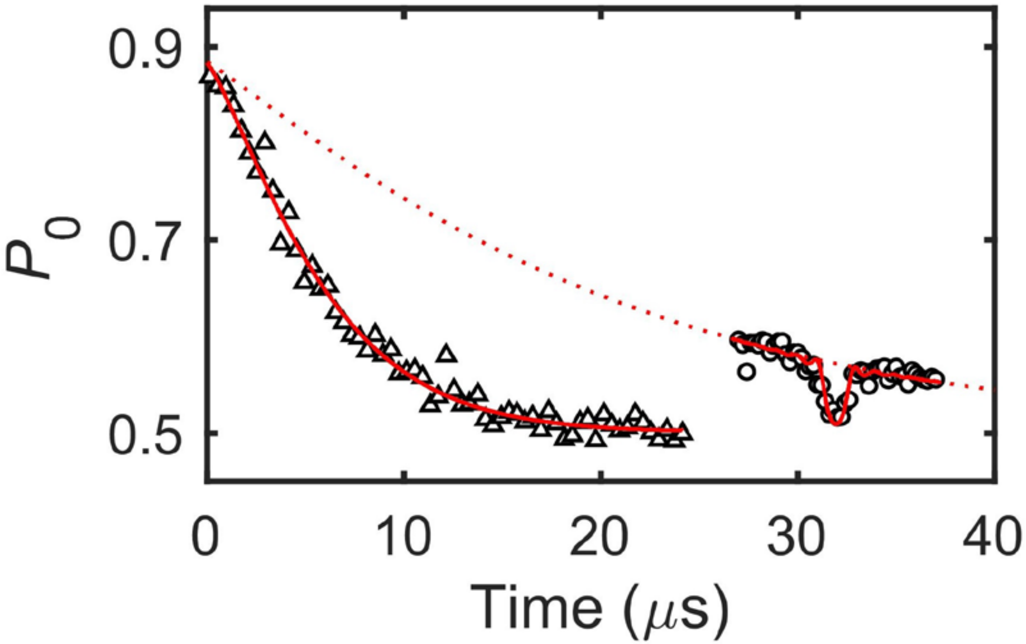


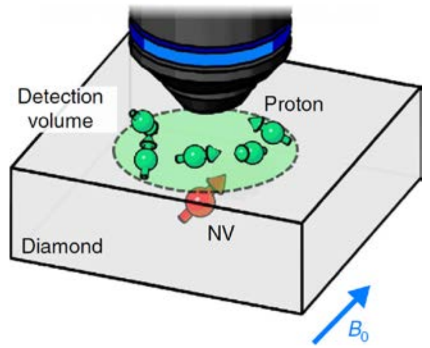
Sensor phase buildup = loss of coherence

$$\gamma B_{\mathrm{ac}} \int_0^t |\cos(2\pi f_{\mathrm{ac}} t)| \, dt$$



Nuclear spin sensing



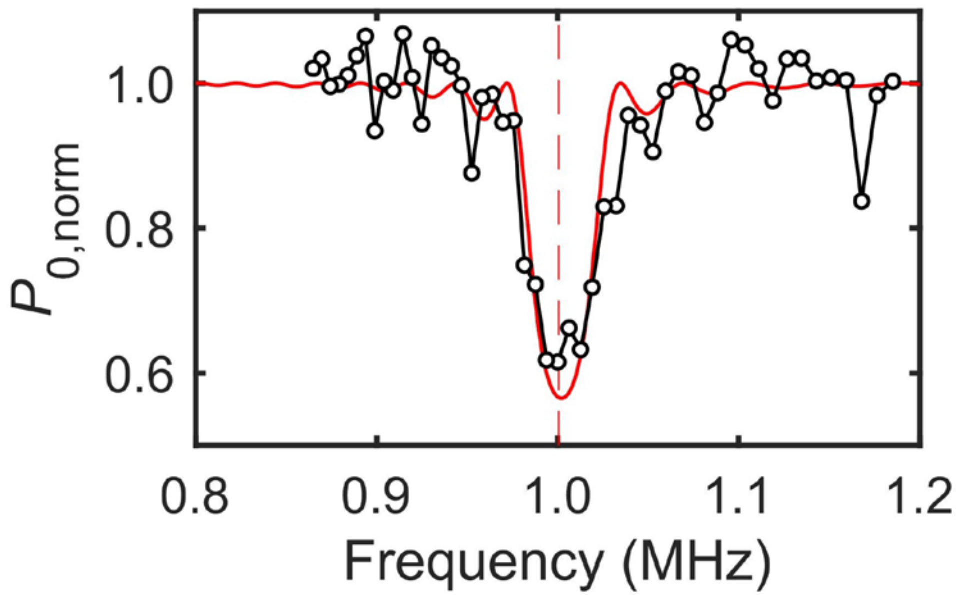


- T_2 = 6.2 μs @B_0 = 23.5 mT
- N = 64 (XY16)
- $(2\tau)^{-1}$ = 64/(2 x 32 μs) = 1 μs

  → $\gamma_H B_0$ = (42.577 kHz/mT) x B_0 = 1.00 MHz

AIP Advances **10**, 025206 (2020) Misonou *et al.*

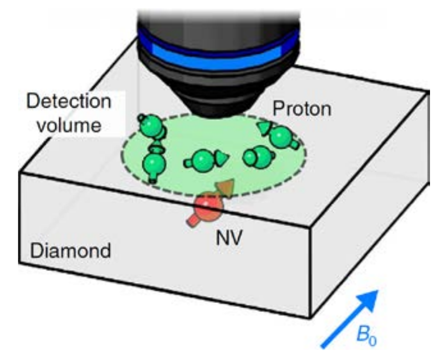
Nuclear spin sensing



$$C(\tau) = f(B_{\text{rms}})$$

$$B_{\text{rms}} = \frac{\mu_0}{4\pi} h\gamma_{\text{H}} \sqrt{\frac{5\pi\rho}{96 d_{\text{NV}}^3}}$$

Phys. Rev. B **93**, 045425 (2016)



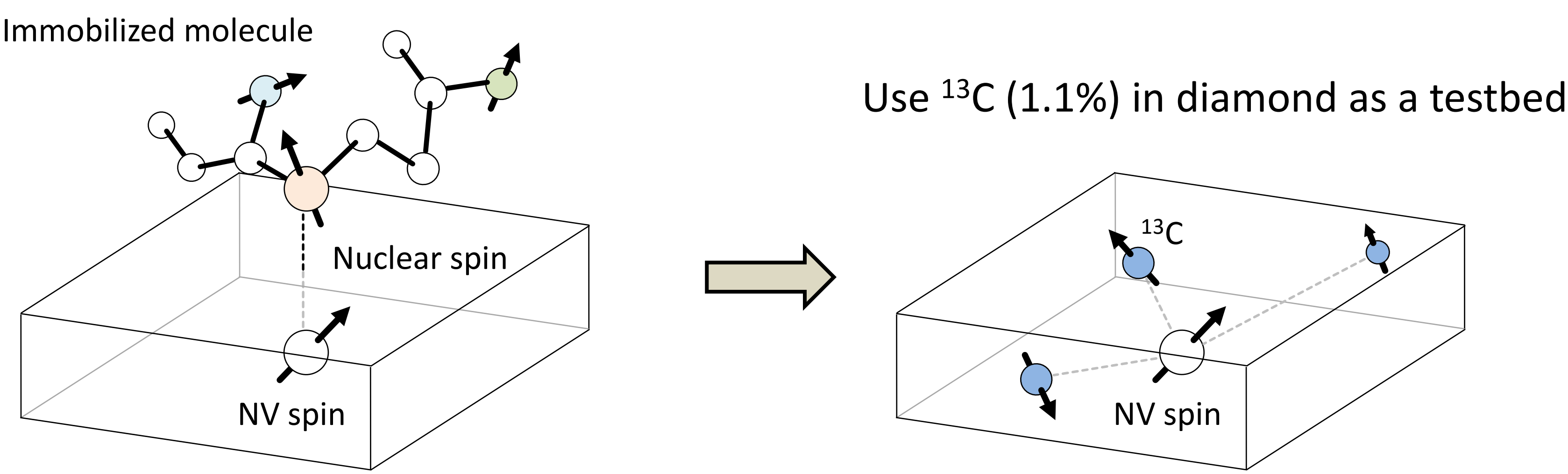
- Proton density ρ = 6 x 10^{28} m^{-3} (known)
- d_{NV} = 6.26 nm
- B_{rms} ≈ 560 nT
- Detection volume $(d_{\text{NV}})^3$ ≈ 0.25 zL (zepto = 10^{-21})
- # of proton $\rho(d_{\text{NV}})^3$ ≈ 1500
- Thermal pol. (10^{-7}) vs. statistical pol. $(1500)^{0.5}$ ≈ 39

AIP Advances **10**, 025206 (2020) Misonou *et al.*

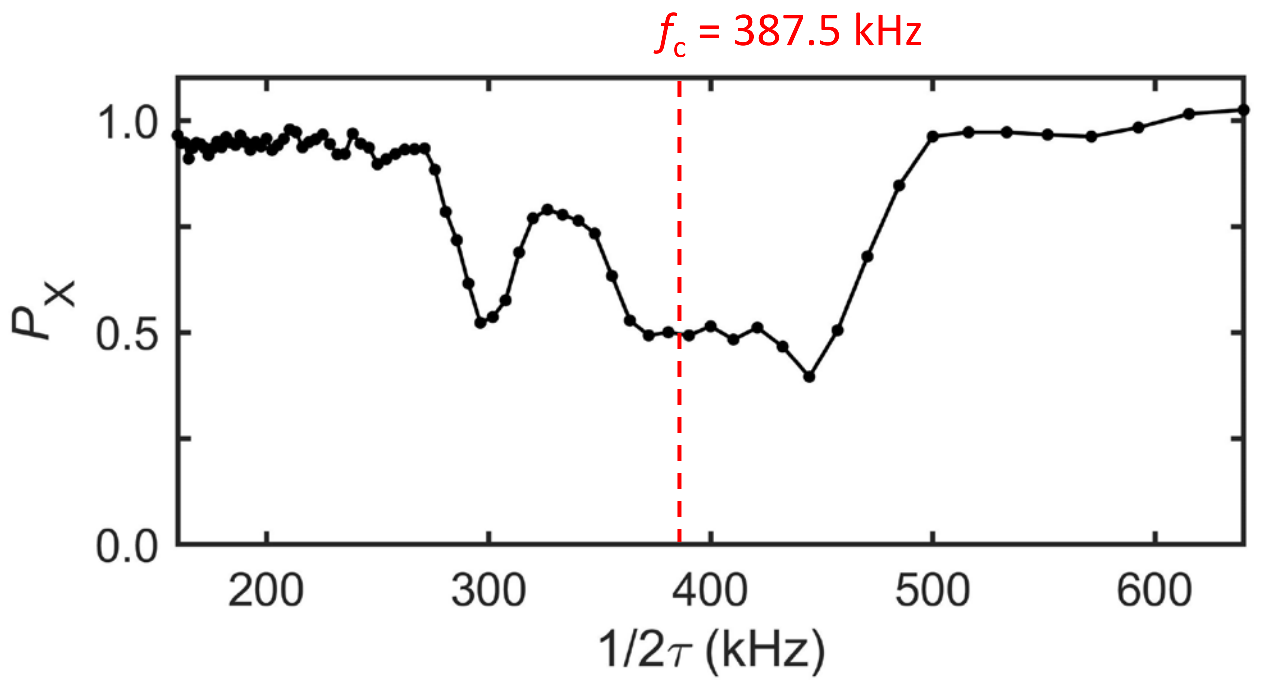
Toward single-molecular imaging

- **Strategy**
  → Detect **individual nuclear spins** contained in a single molecule
  → Determine their **nuclear species (& chemical shifts)** and **positions**

- **Practical issues**
  → Preparation of high-quality near-surface NV centers
  → Accurate positioning of single molecules/proteins near the sensor



Nuclear spin sensing

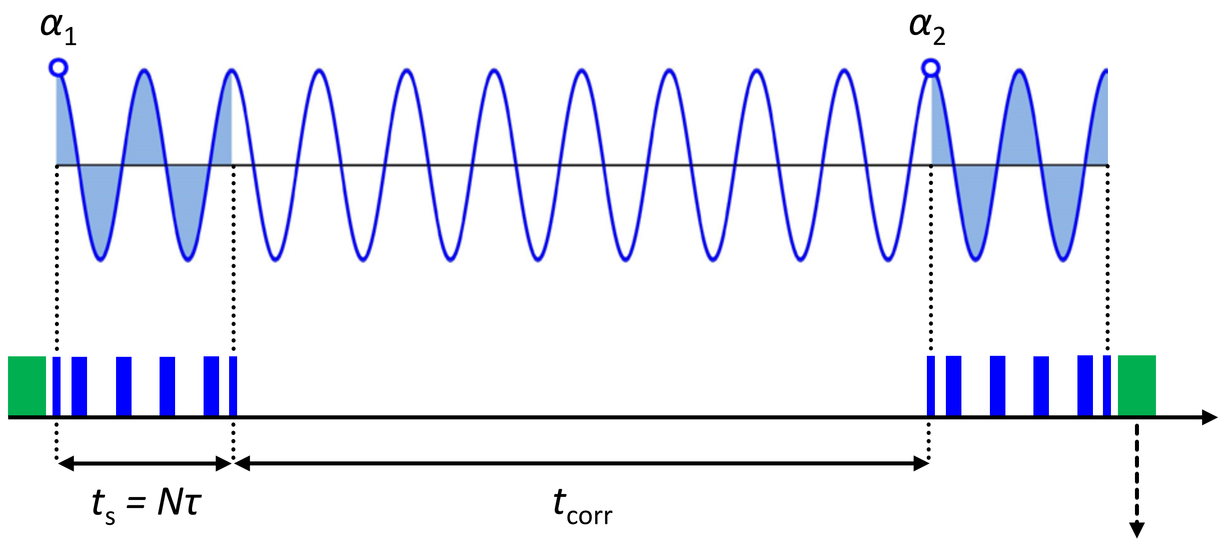


- Single NV in bulk ([^{13}C] = 1.1%, $d_{NV} \approx 50$ μm)
- $N = 16$
- $f_c = \gamma_C B_0$ = 10.705 kHz/mT x 36.2 mT

Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

Correlation spectroscopy

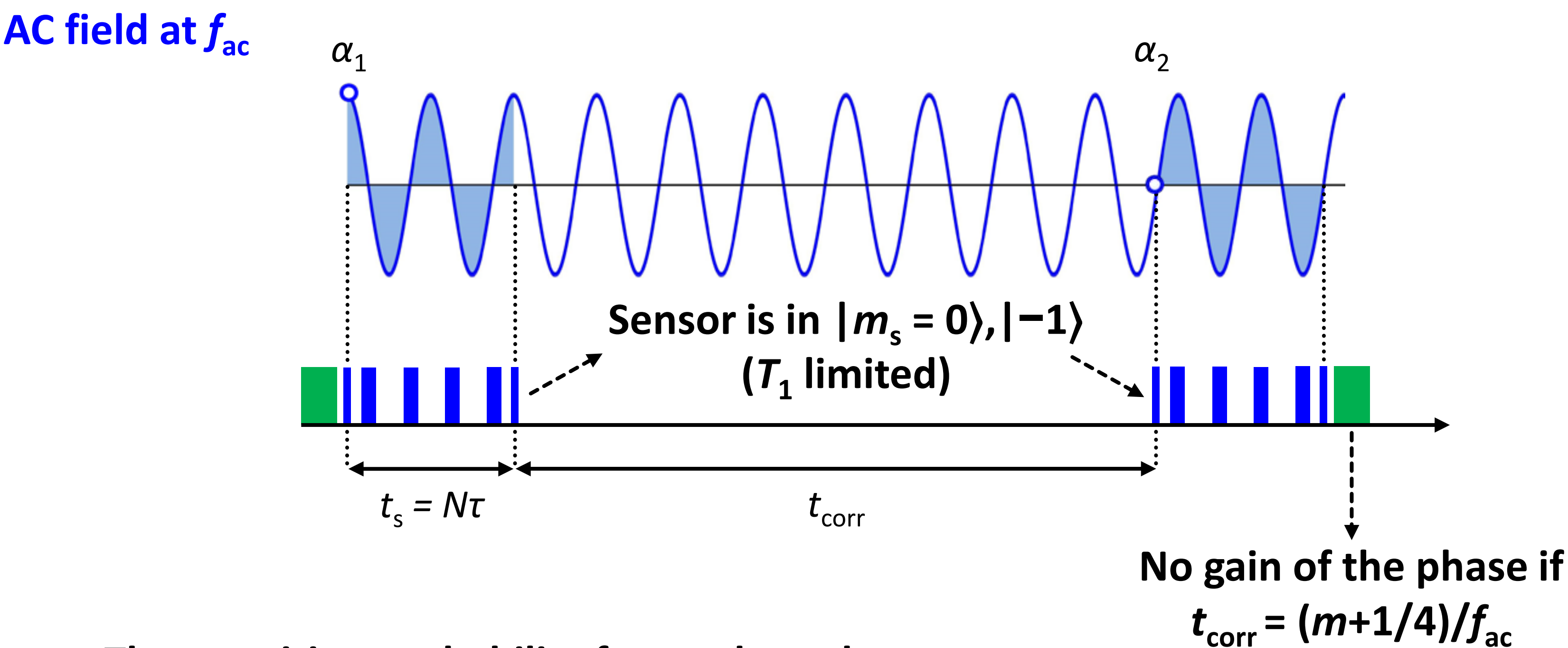
AC field at f_{ac}



Accumulate more phase
if $t_{corr} = m/f_{ac}$

Nature Commun. **4**, 1651 (2013) Laraoui *et al.*
Phys. Rev. Appl. **4**, 024004 (2015) Kong *et al.*
Nature Commun. **6**, 8527 (2015) Staudacher *et al.*
Phys. Rev. Lett. **116**, 197601 (2016) Boss *et al.*

Correlation spectroscopy

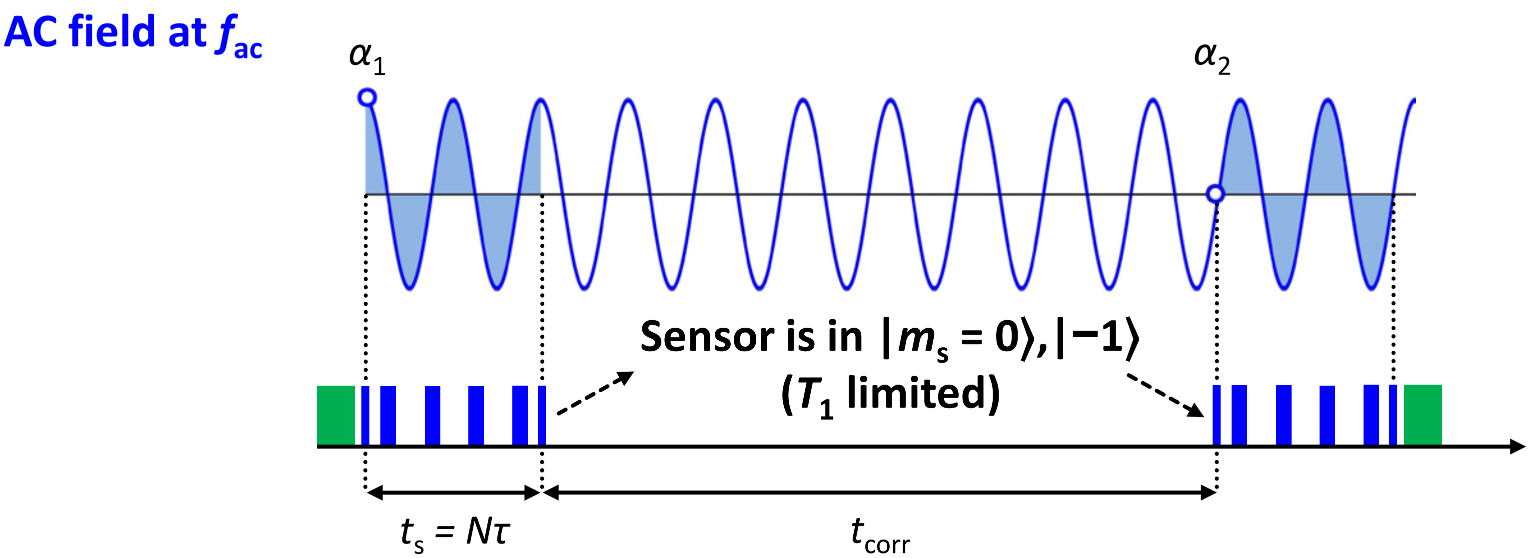


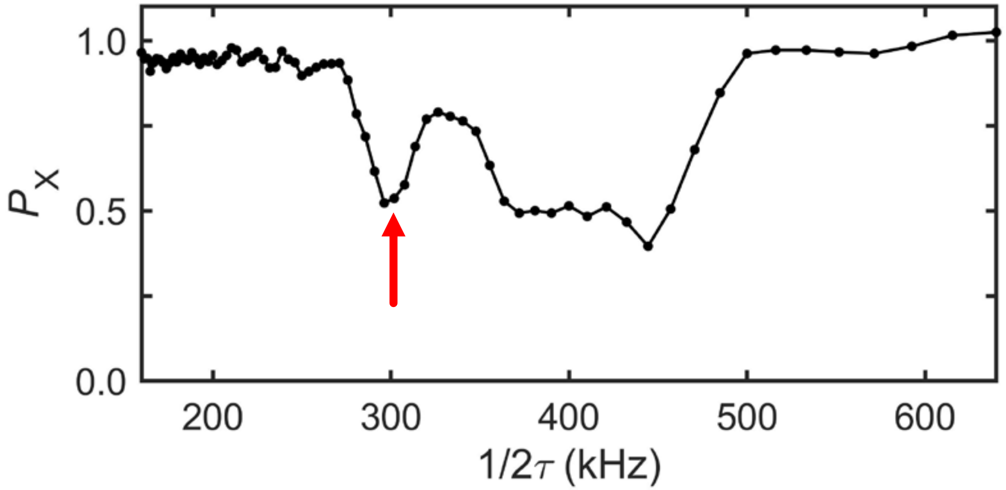
The transition probability for random phases

$$p(t_1) \approx \frac{1}{2}\left\{1 - \frac{1}{2}\left(\frac{\gamma B_{ac} t_s}{\pi}\right)^2 \cos(2\pi f_{ac} t_{corr})\right\}$$

Nature Commun. **4**, 1651 (2013) Laraoui *et al.*
Phys. Rev. Appl. **4**, 024004 (2015) Kong *et al.*
Nature Commun. **6**, 8527 (2015) Staudacher *et al.*
Phys. Rev. Lett. **116**, 197601 (2016) Boss *et al.*

Correlation spectroscopy



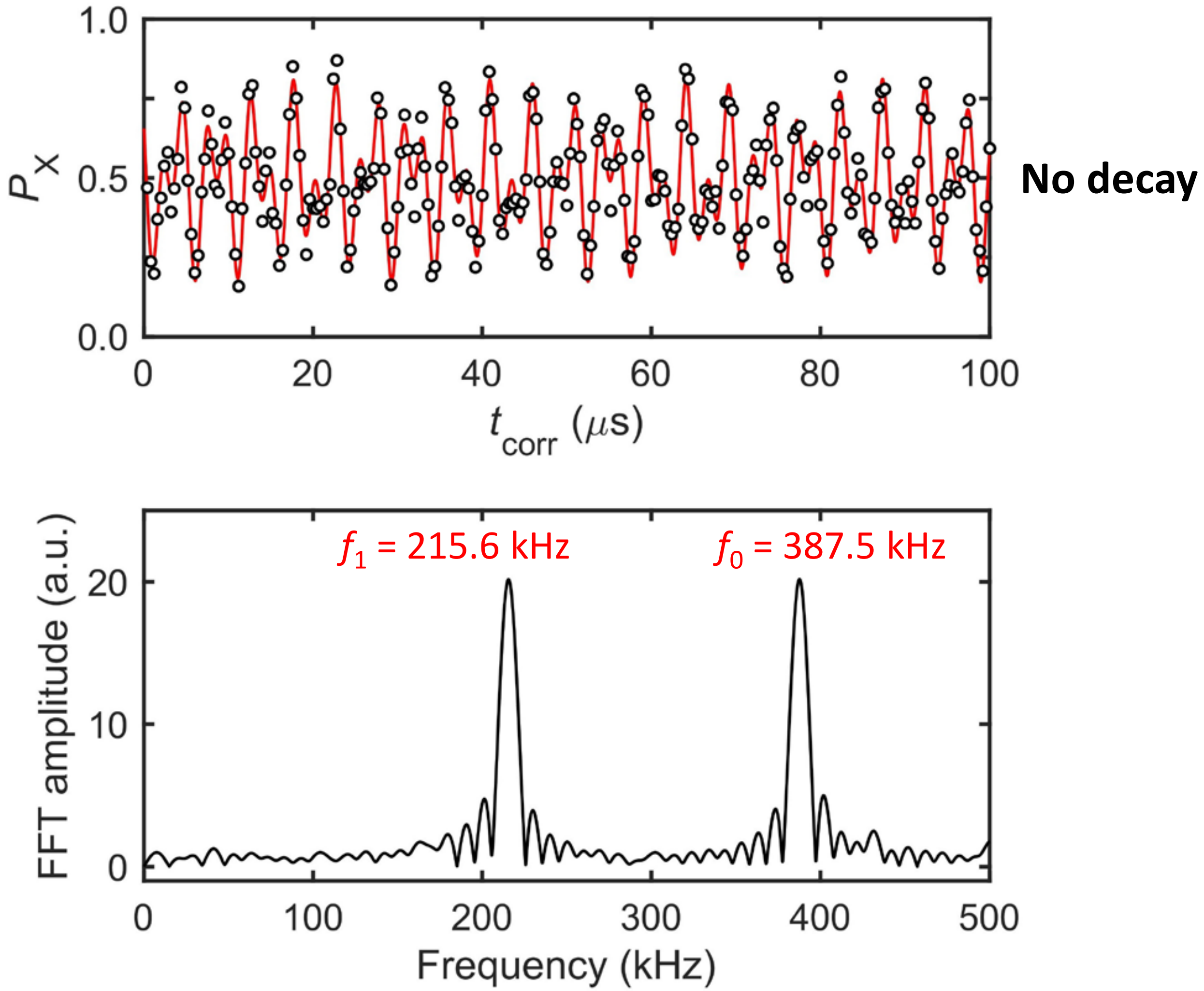


Where to look at?

- $f_t = 1/2\tau = 301.6$ kHz
- $\tau = 1.7875$ μs

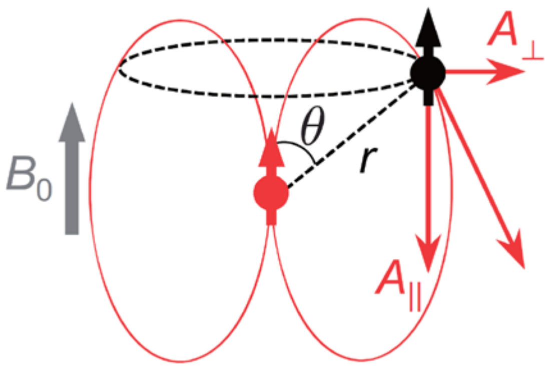
Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

Correlation spectroscopy of a nucleus



Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

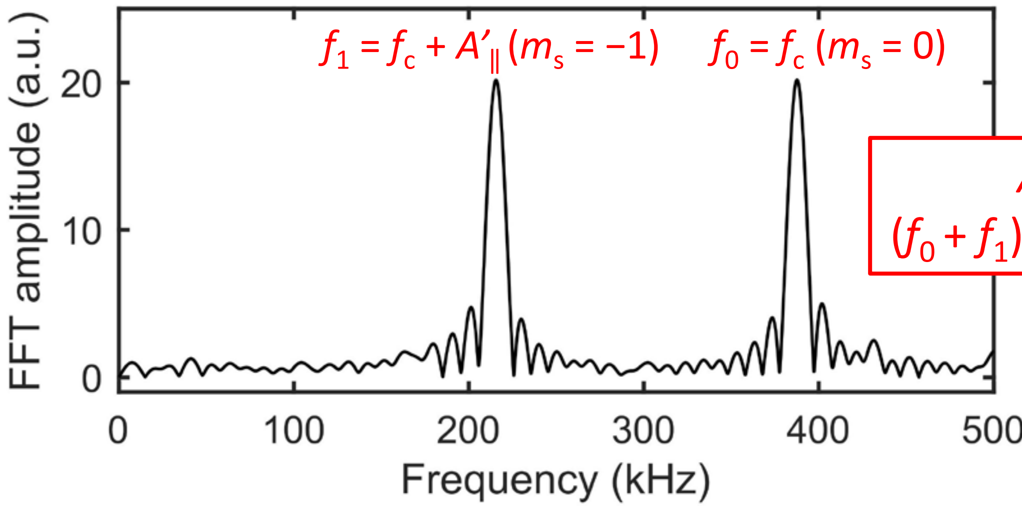
Correlation spectroscopy of a nucleus



Hamiltonian of NV–[13]C coupled system

$$H = f_c I_z + |m_s = -1\rangle\langle -1|(A_\parallel I_z + A_\perp I_x)$$

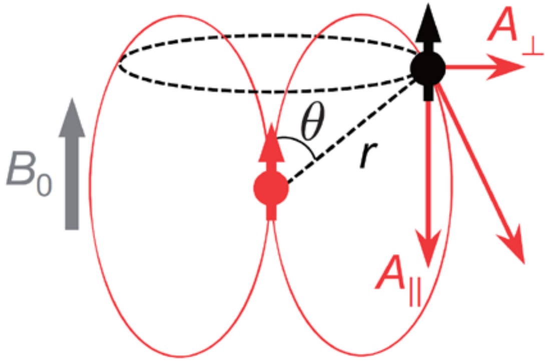
→ No hyperfine field when $|m_s = 0\rangle$



$A'_\parallel$ = −171.9 kHz
$(f_0 + f_1)/2$ = 301.55 kHz → dip

Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

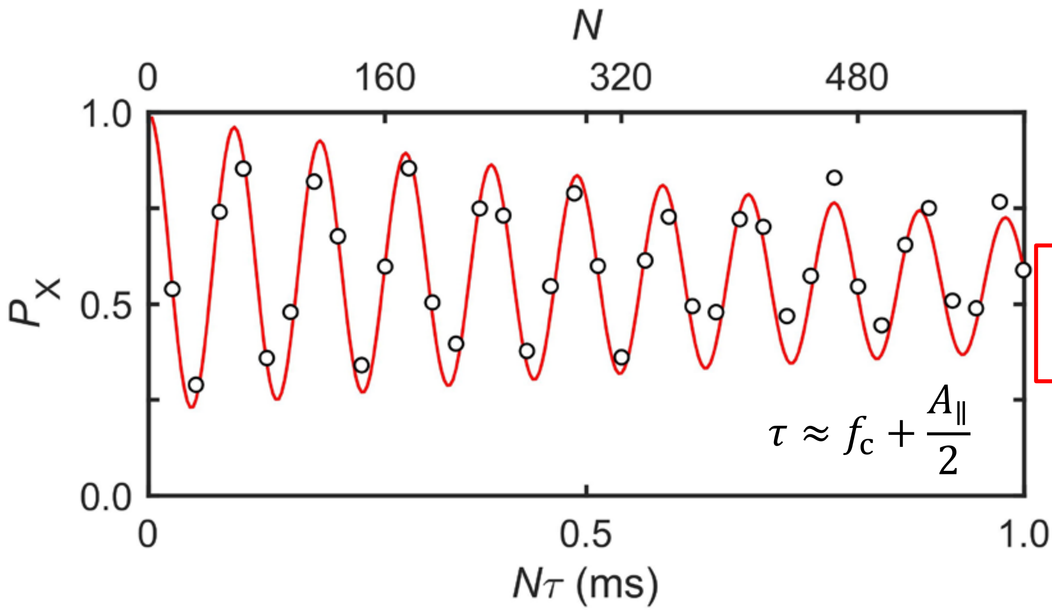
Coherent control of a nuclear spin



Hamiltonian of NV–[13]C coupled system

$$H = f_c I_z + |m_s = -1\rangle\langle -1|(A_\parallel I_z + A_\perp I_x)$$

→ The single [13]C *n*-spin rotates about the $A_\perp$ axis

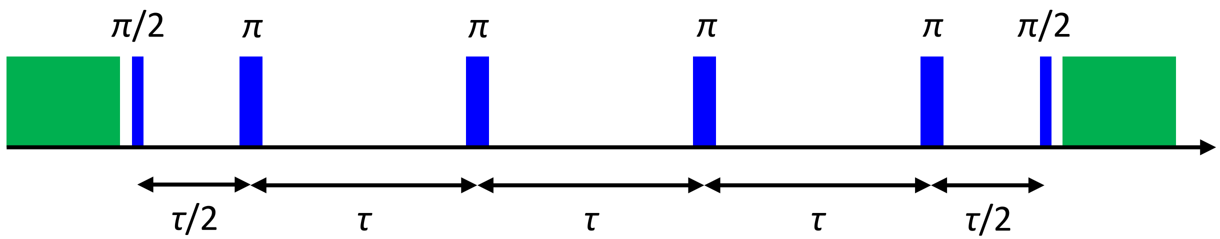


f_{osc} = 10.2 kHz ≈ $A'_\perp/2$
$P_X < 0.5$ → single

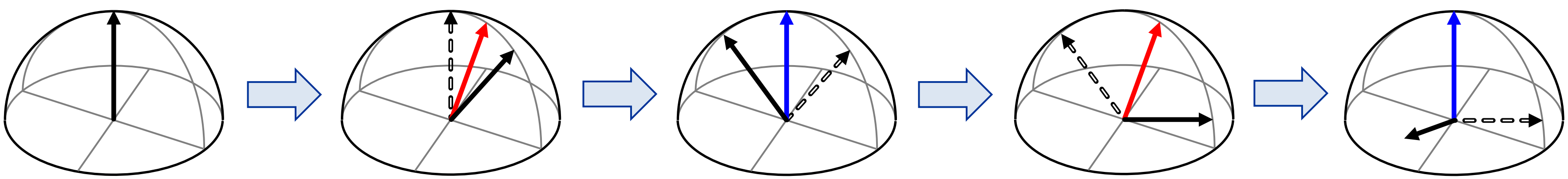
Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

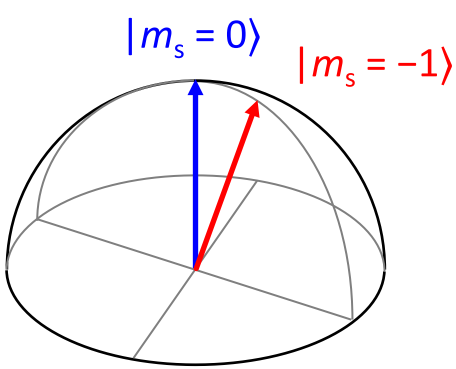
Conditional rotation of a nuclear spin

CP (N = 4)



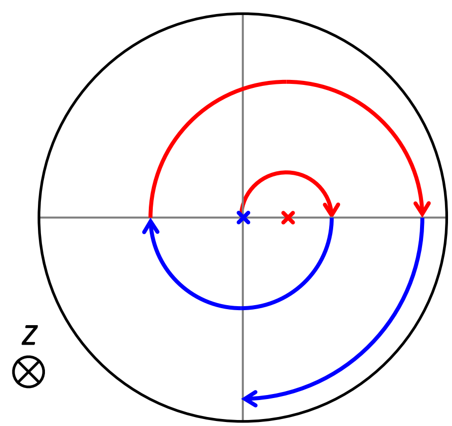
Evolution of *n*-spin vector



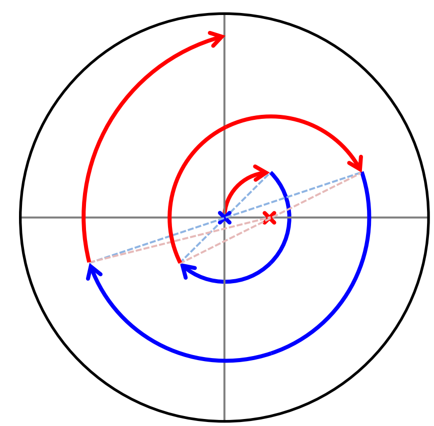


Q-axis of *n*-spin

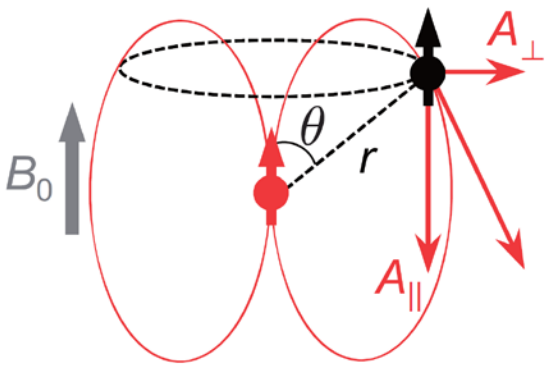
Start from $|m_s = 0\rangle$



Start from $|m_s = -1\rangle$



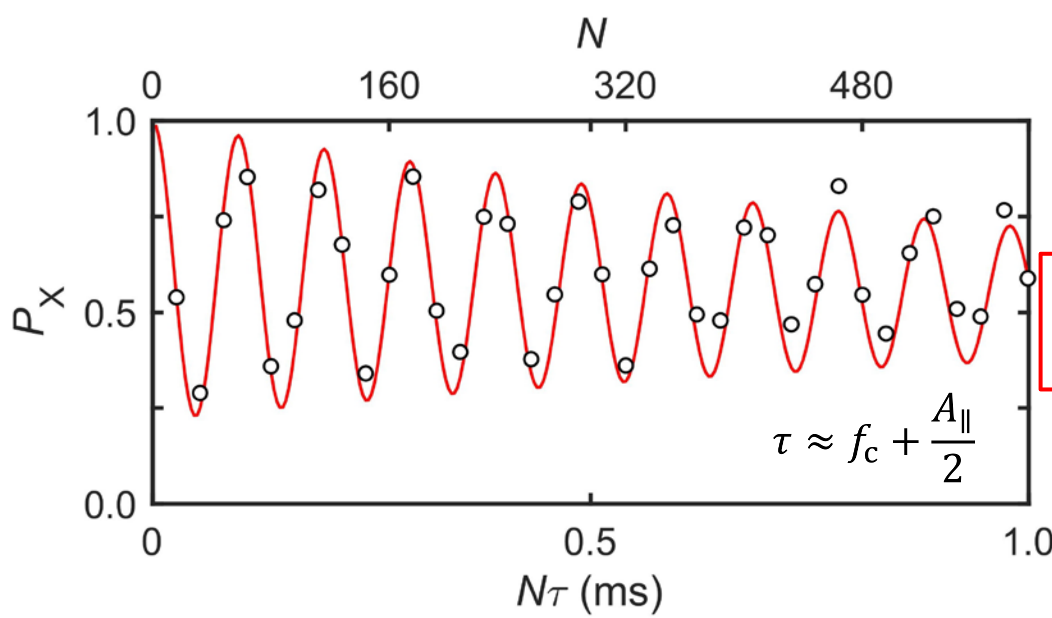
Coherent control of a nuclear spin



Transition probability of the NV spin

$$P_X = 1 - \frac{1}{2}(1 - \underbrace{\boldsymbol{n}_0 \cdot \boldsymbol{n}_{-1}}_{-1}) \sin^2 \frac{N\phi_{cp}}{2}$$

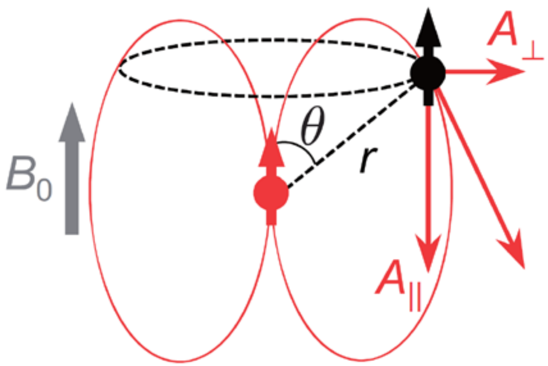
Phys. Rev. Lett. **109**, 137602 (2012) Taminiau *et al.*



f_{osc} = 10.2 kHz ≈ $A'_\perp/2$
$P_X < 0.5$ → single

Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

Determination of hf constants



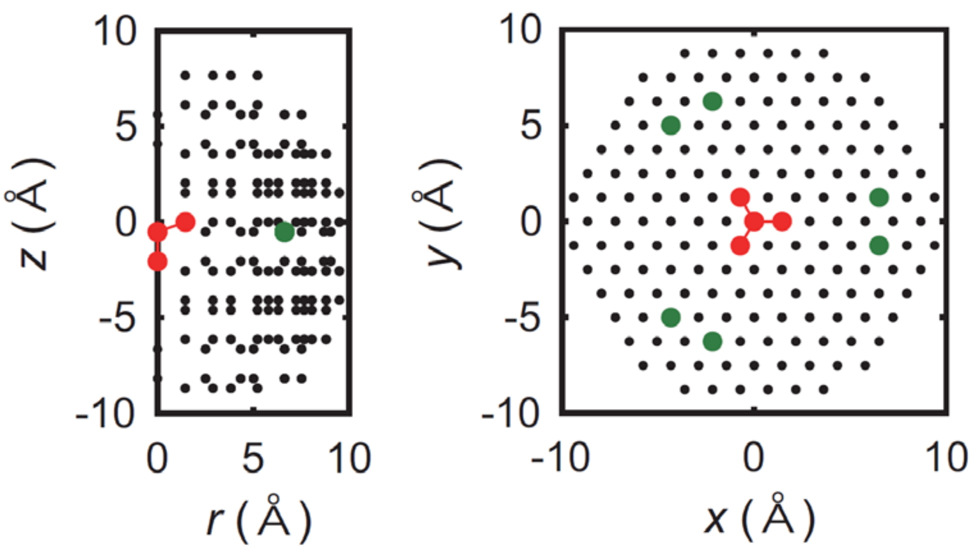
Magnetic dipole int. **+ contact hf int.**

$$A_\parallel \propto \frac{3\cos^2\theta - 1}{r^3} \qquad A_\perp \propto \frac{3\cos\theta\sin\theta}{r^3}$$

$A_\parallel$ = −173.1 kHz
$A_\perp$ = 22.3 kHz

$A_\parallel$ = −175.1±2.1kHz
$A_\perp$ = 21.9±0.2 kHz

DFT: New J. Phys. **20**, 023022 (2018) Nizovtsev *et al.*

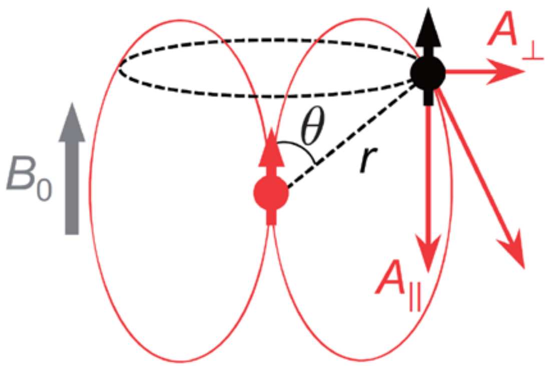


(r, θ) = (6.84 Å, 94.8°)

Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

How to determine ϕ?

(azimuthal angle)

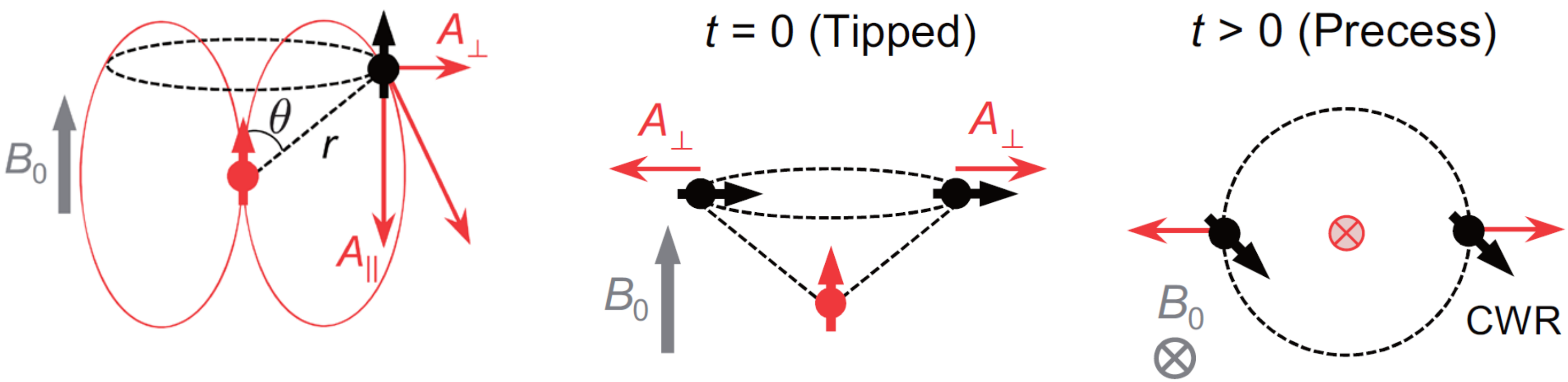


Magnetic dipole int.

$$A_\parallel \propto \frac{3\cos^2\theta - 1}{r^3} \qquad A_\perp \propto \frac{3\cos\theta\sin\theta}{r^3}$$

Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

How to determine ϕ?



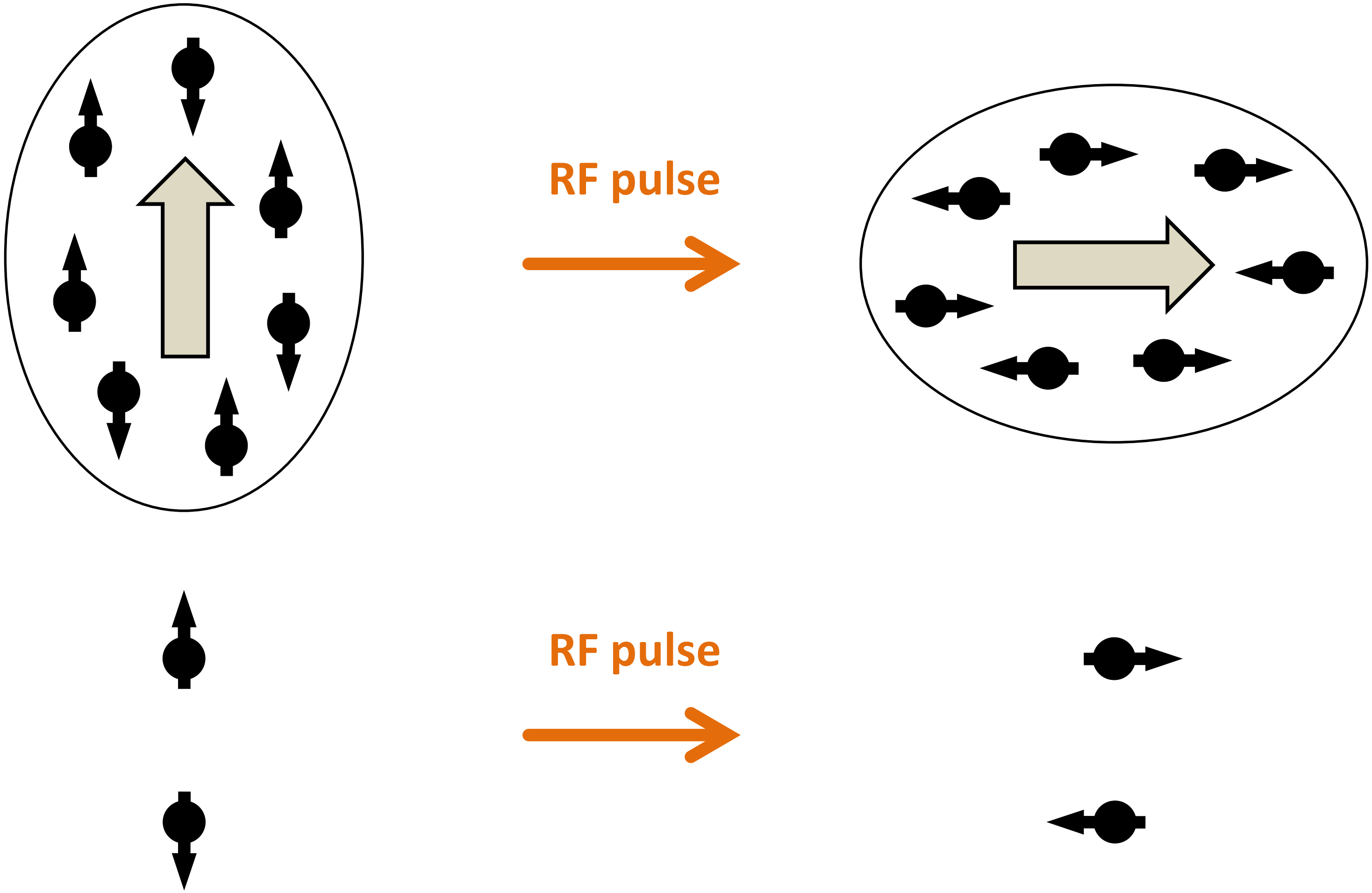
Transition probability of the NV spin after the detection of a single nuclear spin

$$P_Y = \frac{1}{2} - \frac{1}{2}\cos(\phi - \phi_n)\sin N\phi_{cp}$$

Azimuthal angle of the nuclear Bloch vector: $2\pi f_p t + \phi_n(0)$

Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

Ensemble vs. single

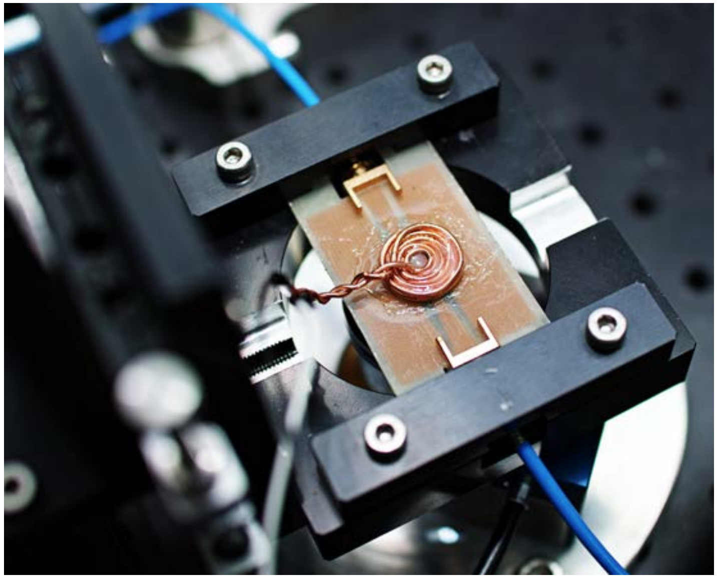


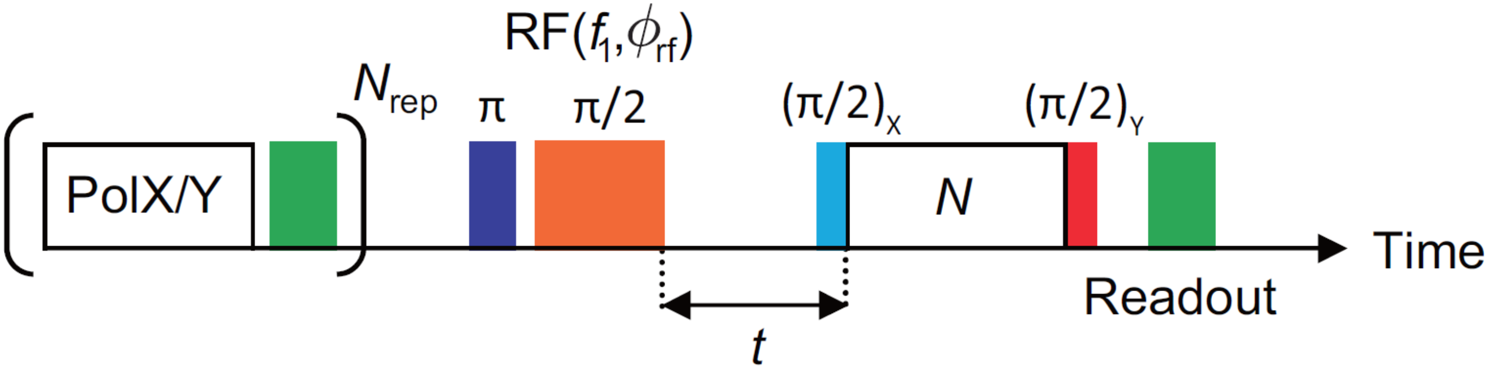
The initial state matters

→ Dynamic nuclear polarization (DNP)

Determination of ϕ of a ^{13}C *n*-spin

1. **DNP (PulsePol)**
2. **RF pulse@m_s = −1**
3. **Wait *t* (*n*-spin precesses)**
4. **AC sensing**

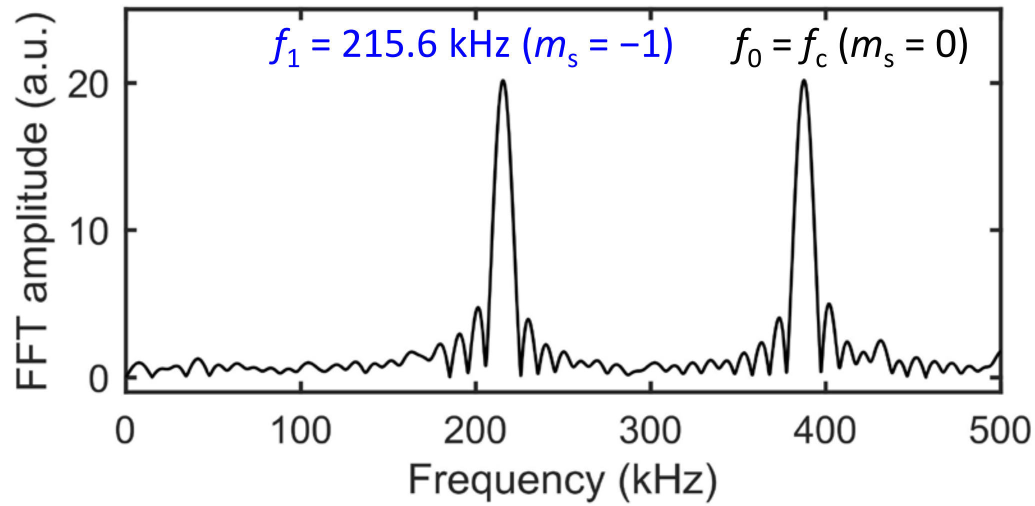


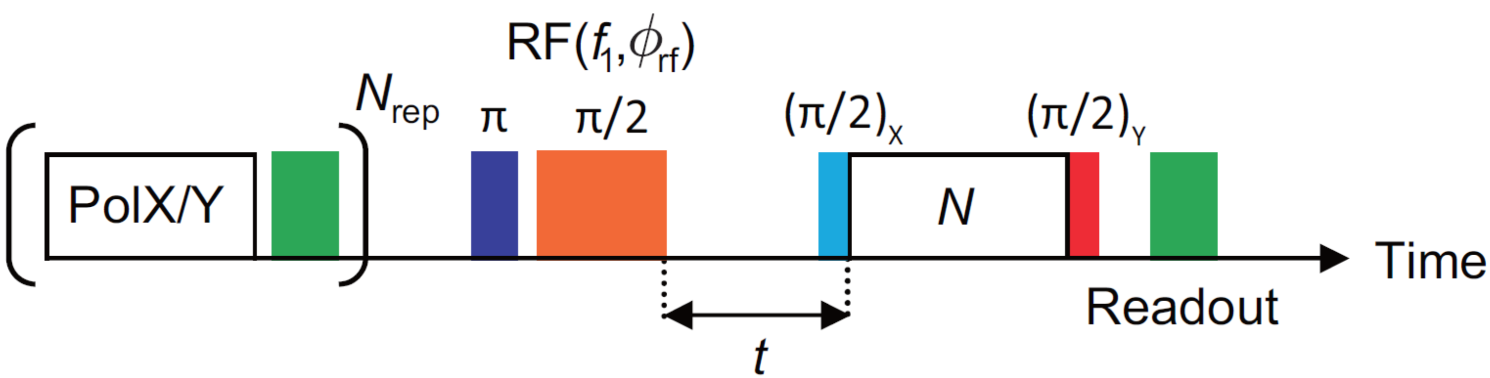


Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

Determination of ϕ of a ^{13}C *n*-spin

1. **DNP (PulsePol)**
2. **RF pulse@m_s = −1**
3. **Wait *t* (*n*-spin precesses)**
4. **AC sensing**



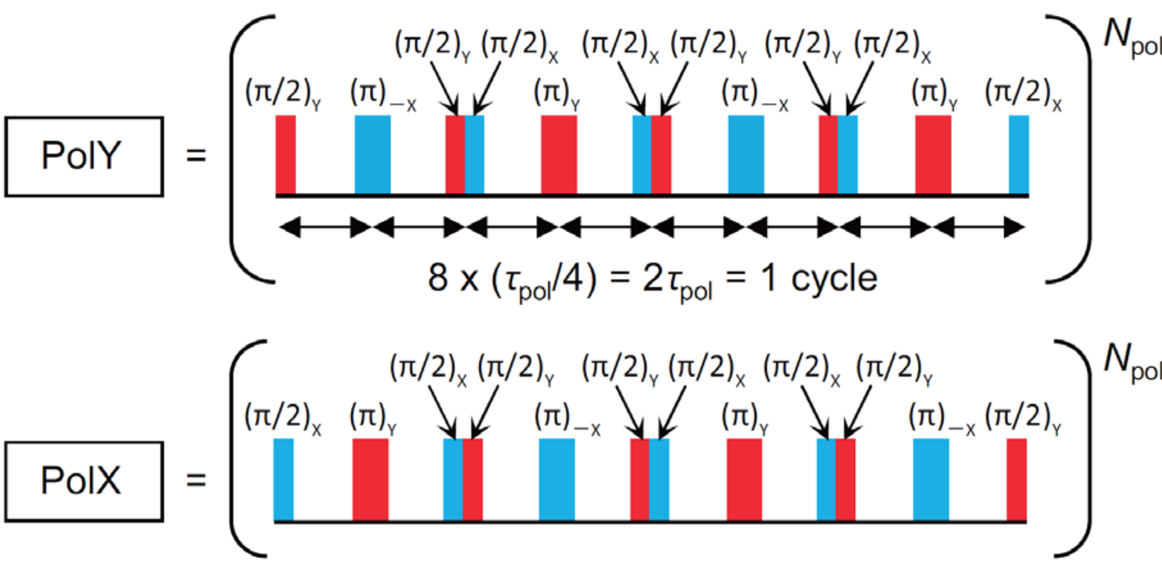


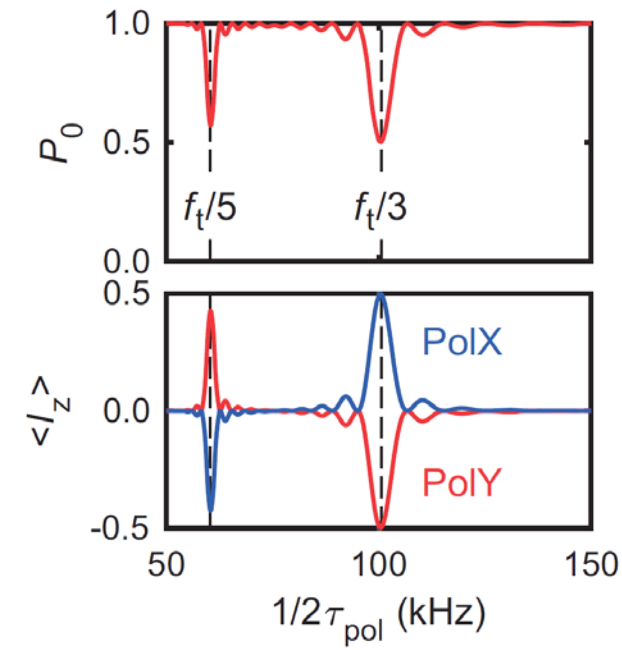
Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

PulsePol

Hamiltonian engineering

- Average Hamiltonian $\propto S_+I_- + S_-I_+, \propto S_+I_+ + S_-I_-$
- DNP condition: $1/(2\tau_{pol}) = f_n/k$ (f_n: n-precession frequency, k: odd)

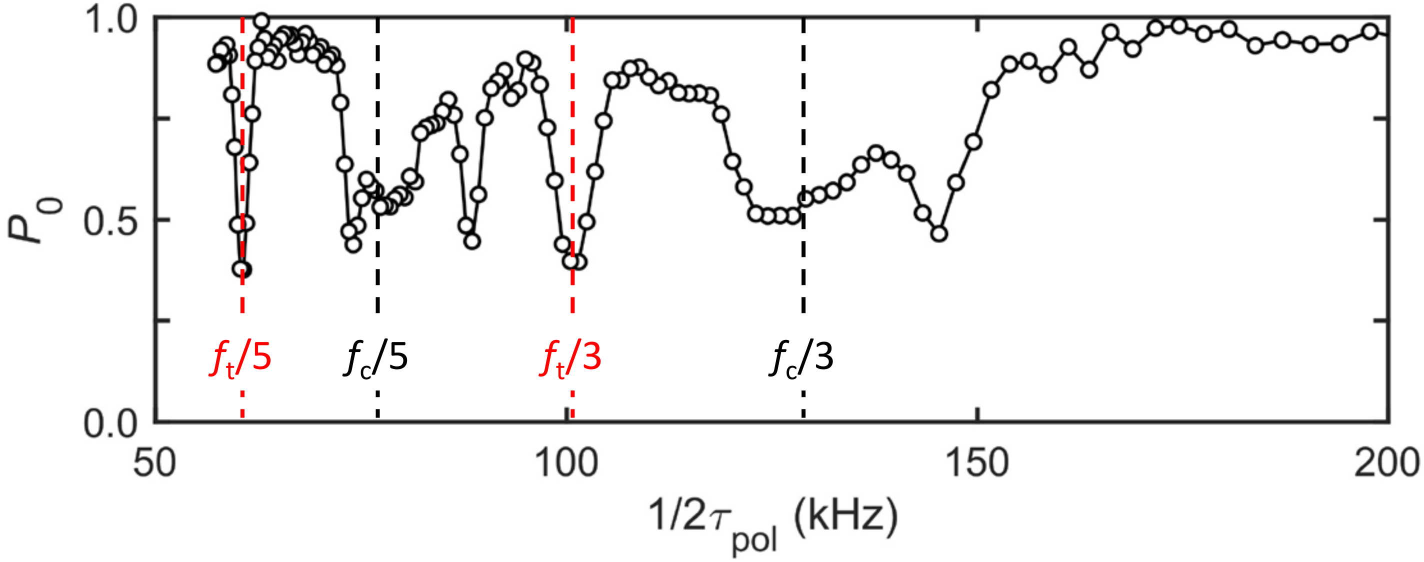


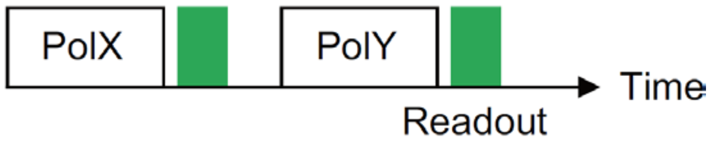


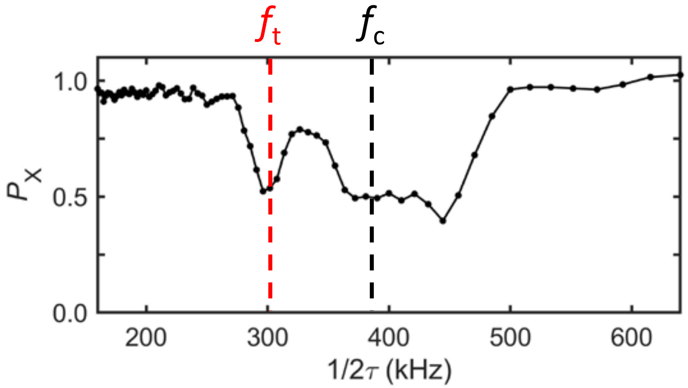
Sci. Adv. **4**, eaat8978 (2018) Schwartz *et al.*

Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

PulsePol

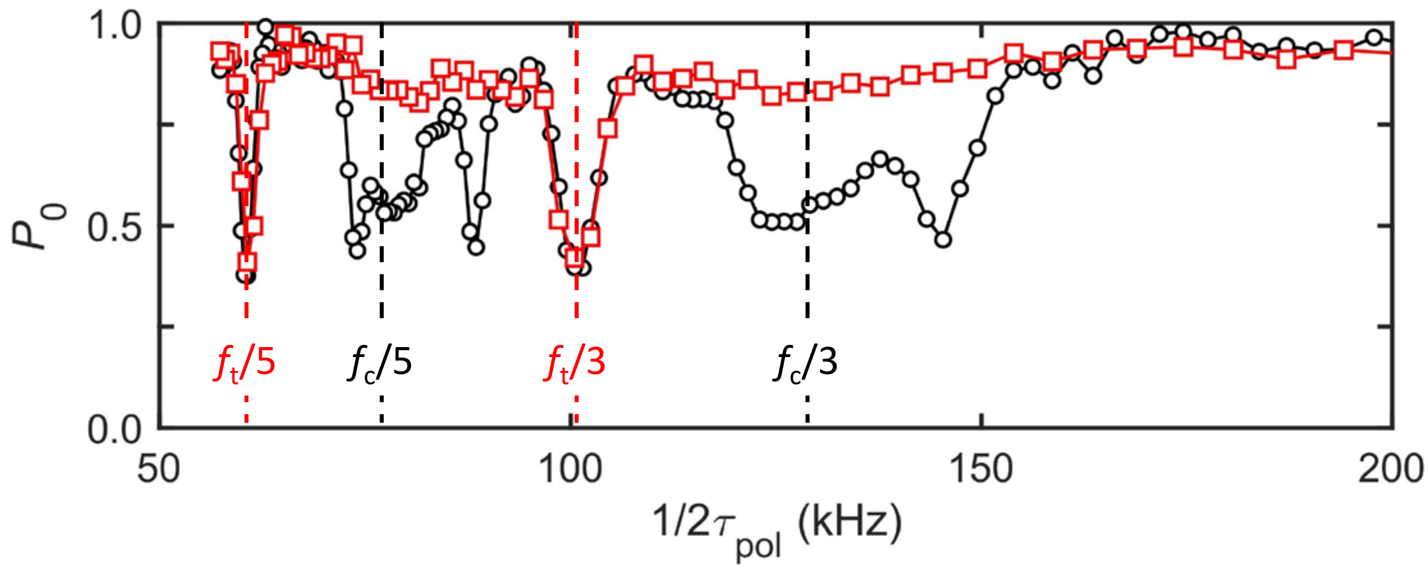


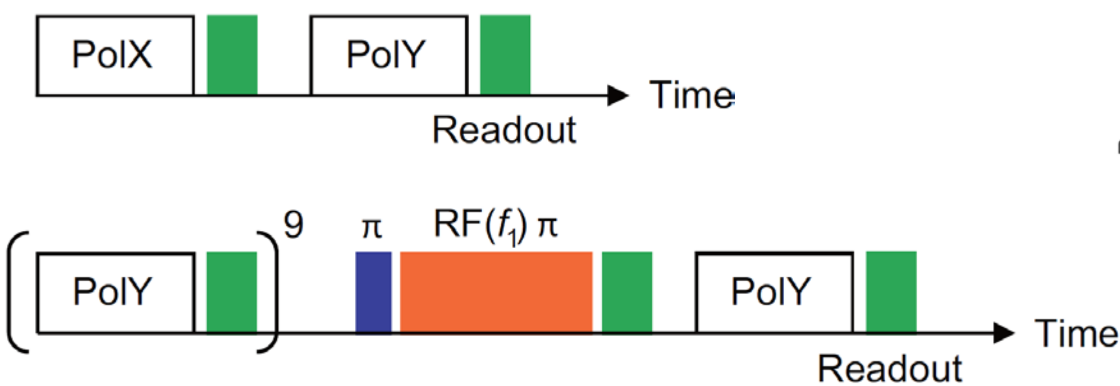


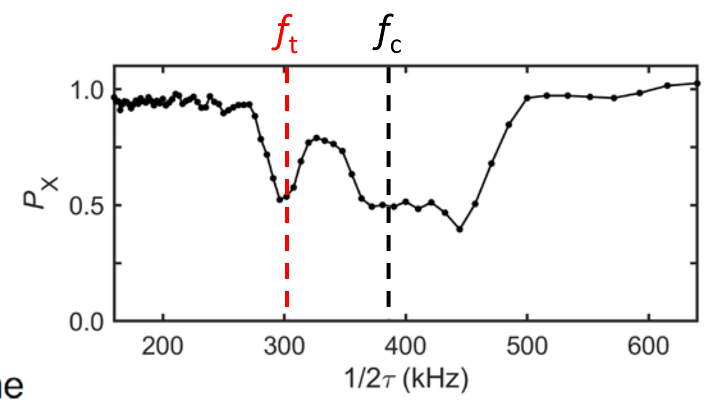


Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

PulsePol

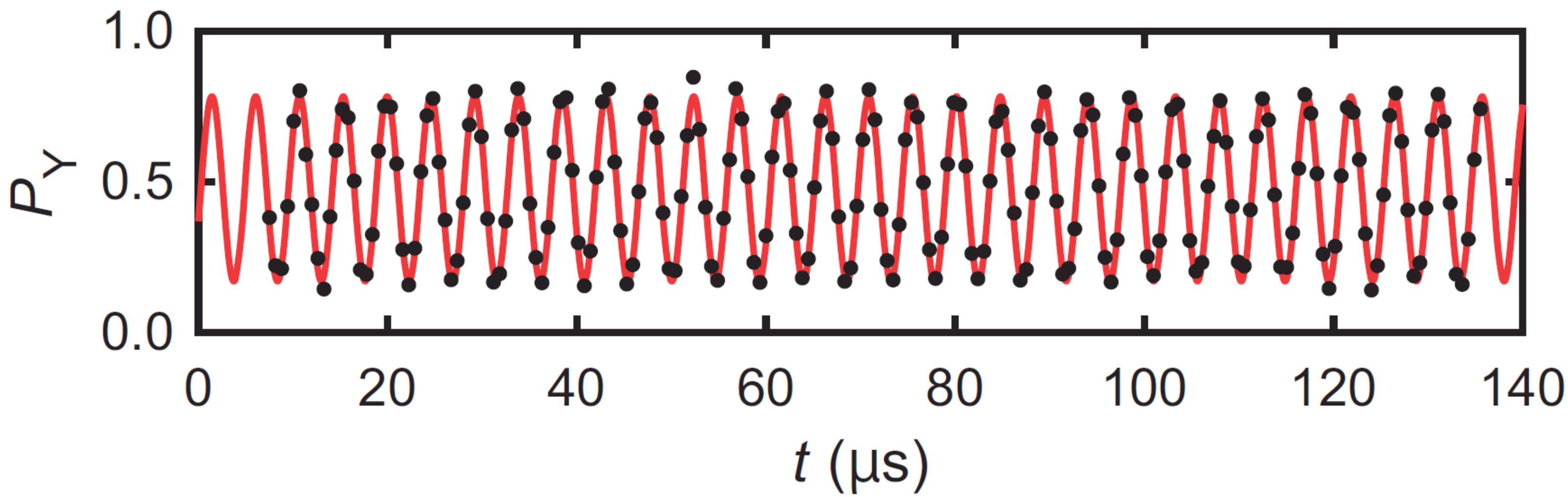


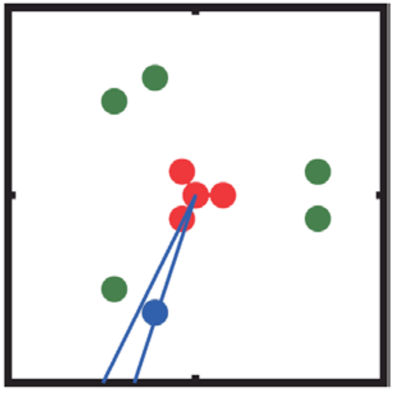




Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

Determination of ϕ of a ^{13}C n-spin





- ✓ $t \rightarrow 1$ ms (undersampling)
- ✓ $f_p = 215.79$ kHz $\approx f_1 = 215.6$ kHz
- ✓ $\phi - \phi_n(0) = 334.0^o$
- ✓ $\phi_n(0) = 89.2^o$ (Real-space n-spin trajectory)

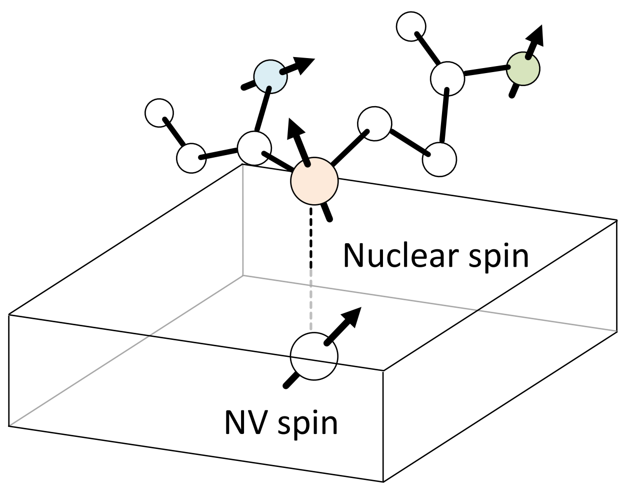
$\rightarrow \phi = 247.8 \pm 4.1^o$

Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

Toward single-molecular imaging

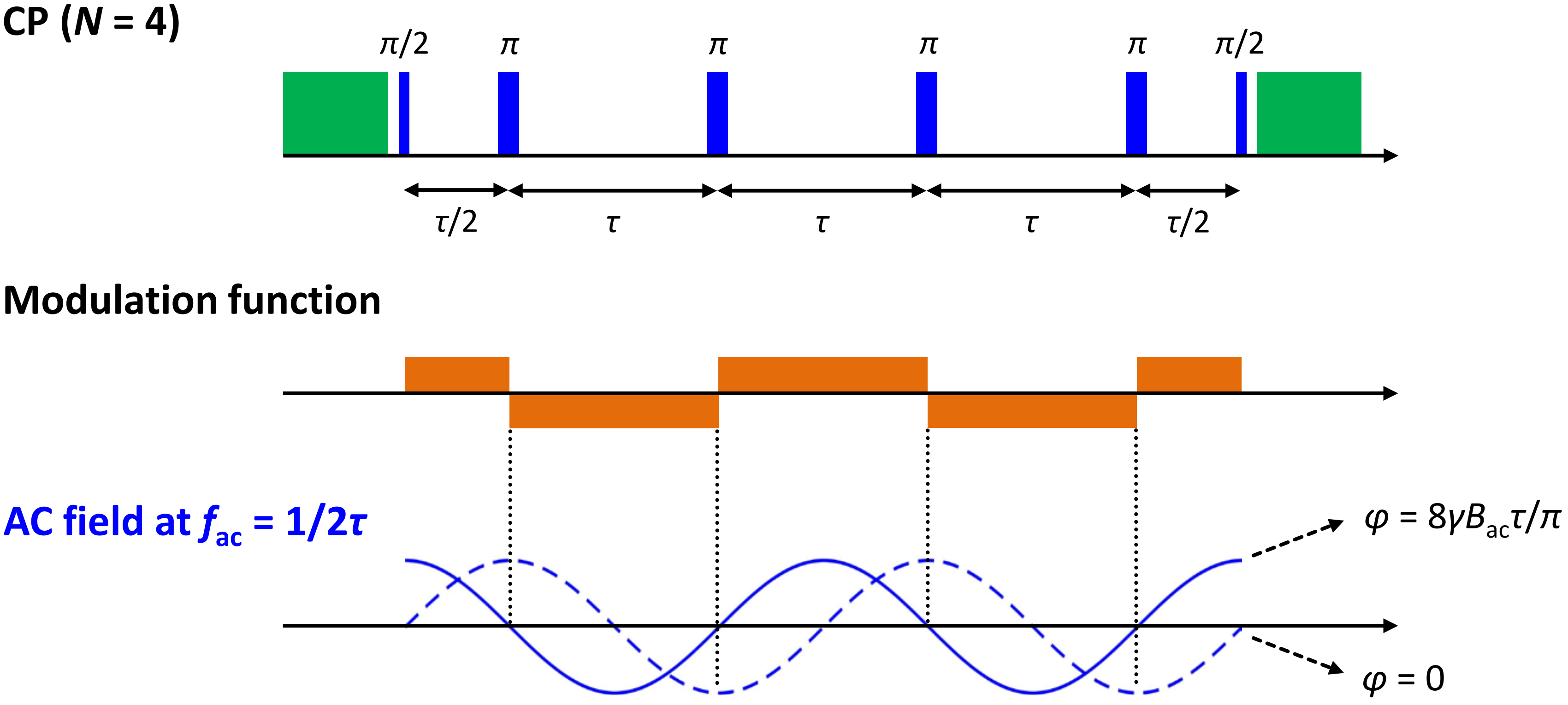
- **Information of the positions of the individual nuclei**
  → Accurate measurement of *e*–*n* int. const's $(A_{\parallel}, A_{\perp}) \approx (r, \theta)$
  → Lack of information on the azimuthal angle ϕ

- **Spectral resolution**
  → Easy to resolve isotopes
  → Need to measure *J*-couplings & chemical shifts (ppm!)
  → Limited by sensor/memory lifetimes $(T_{2e/n}, T_{1e/n})$



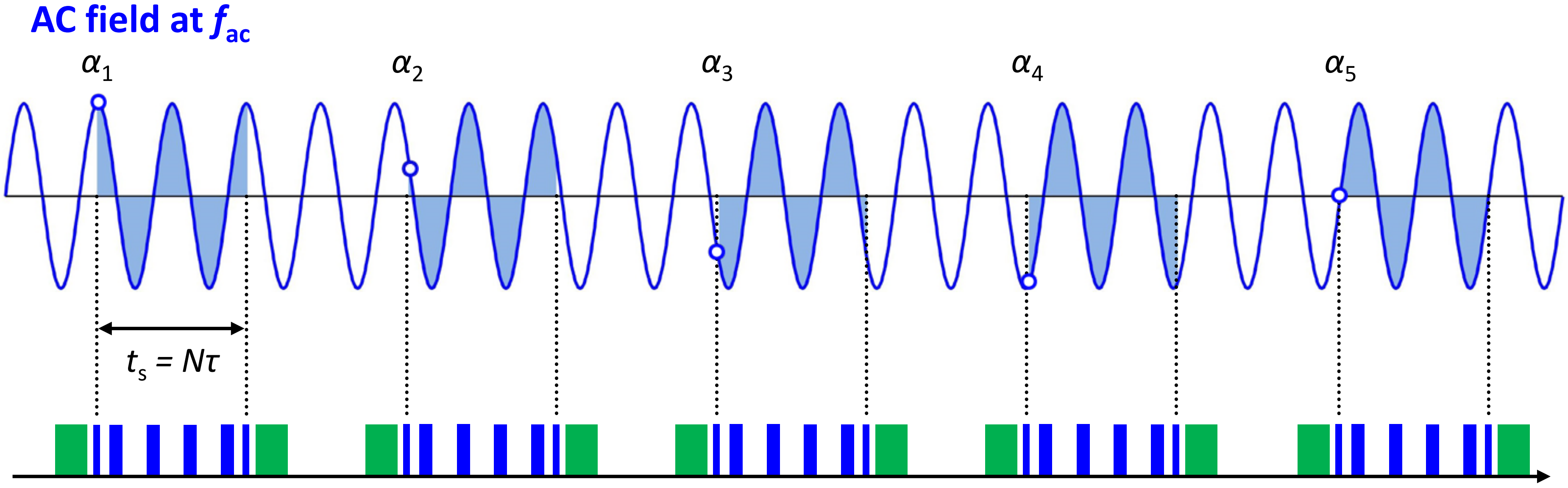
AC magnetometry

CP (N = 4)



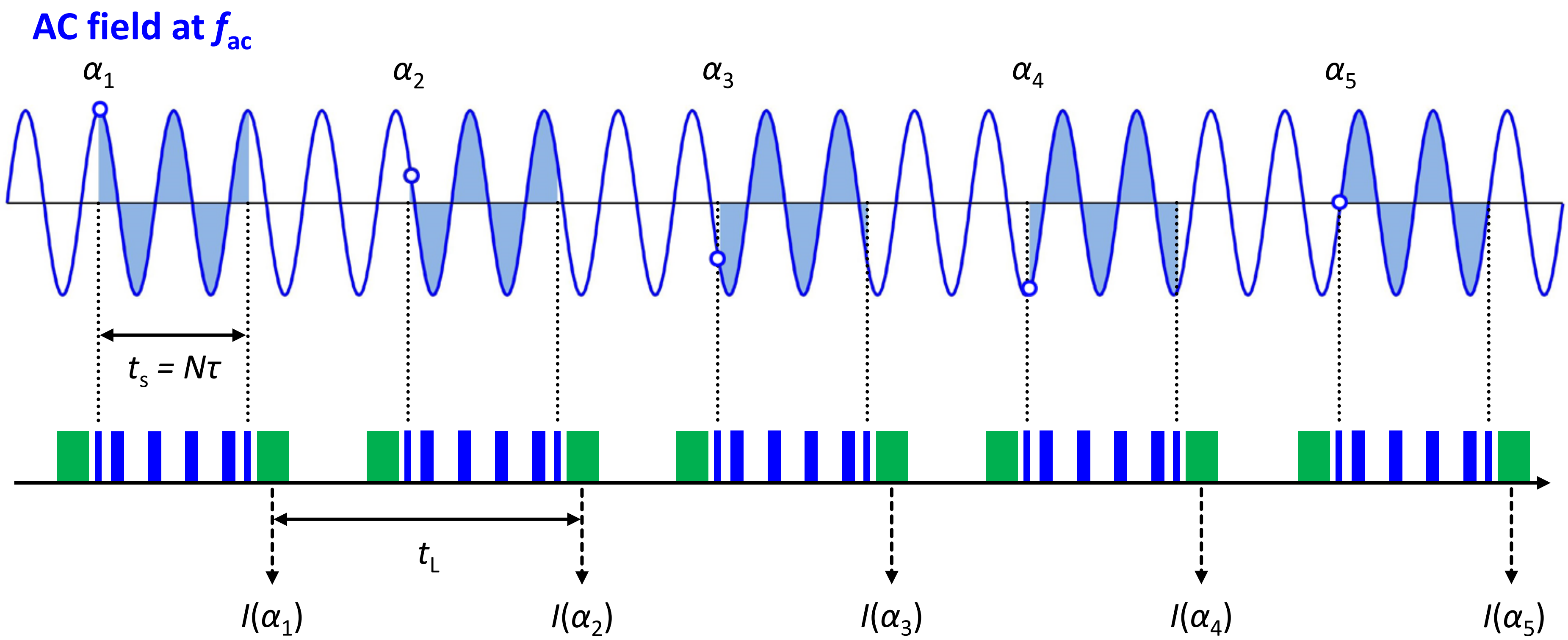
- φ depends on the **initial phase α of the AC field** ($\varphi \propto \cos\alpha$)

AC magnetometry



- φ depends on the **initial phase $\boldsymbol{\alpha}$ of the AC field** ($\varphi \propto \cos \alpha$)
- Average over **random $\boldsymbol{\alpha}$**

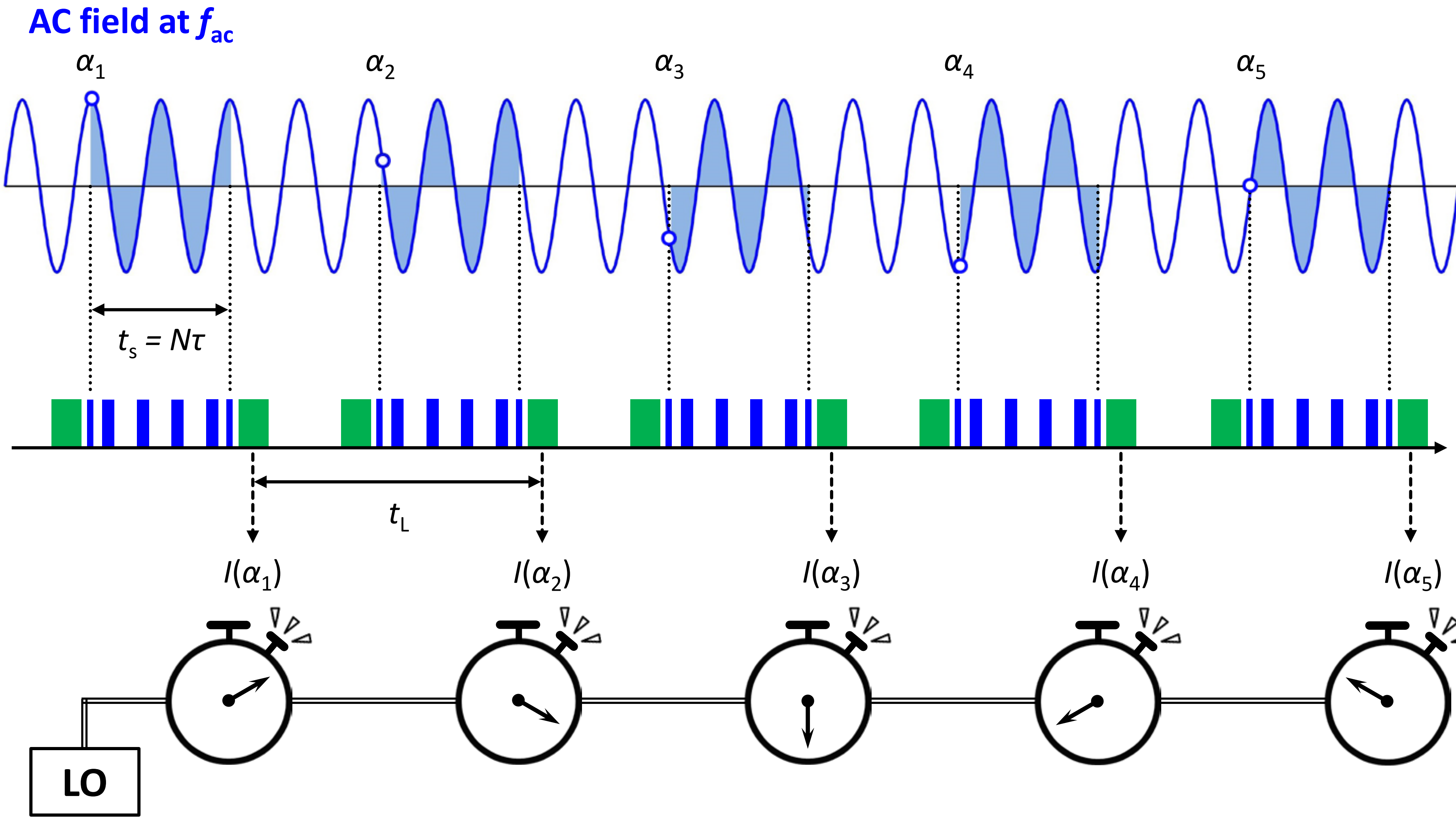
Ultrahigh resolution sensing



- φ depends on the **initial phase $\boldsymbol{\alpha}$ of the AC field** ($\varphi \propto \cos \alpha$)
- Average over **random $\boldsymbol{\alpha}$**
- **If the data acq. is periodic,** adjacent α's are related by $\alpha_{k+1} = 2\pi f_{ac} t_L + \alpha_k$

Science **356**, 832 (2017) Schmitt *et al.*; Science **356**, 837 (2017) Boss *et al.*; Nature **555**, 351 (2018) Glenn *et al.*

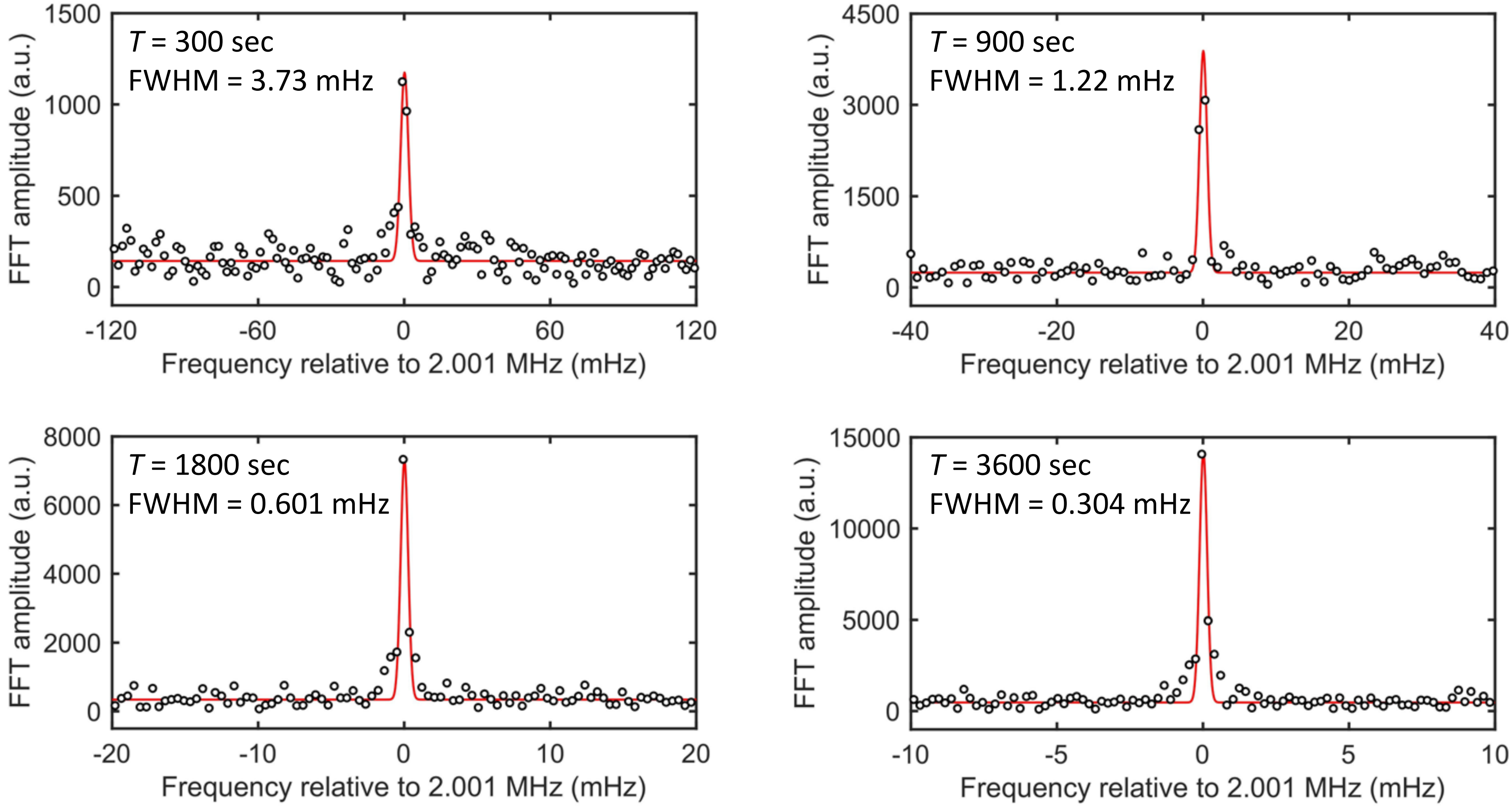
Ultrahigh resolution sensing



Science **356**, 832 (2017) Schmitt *et al.*; Science **356**, 837 (2017) Boss *et al.*; Nature **555**, 351 (2018) Glenn *et al.*

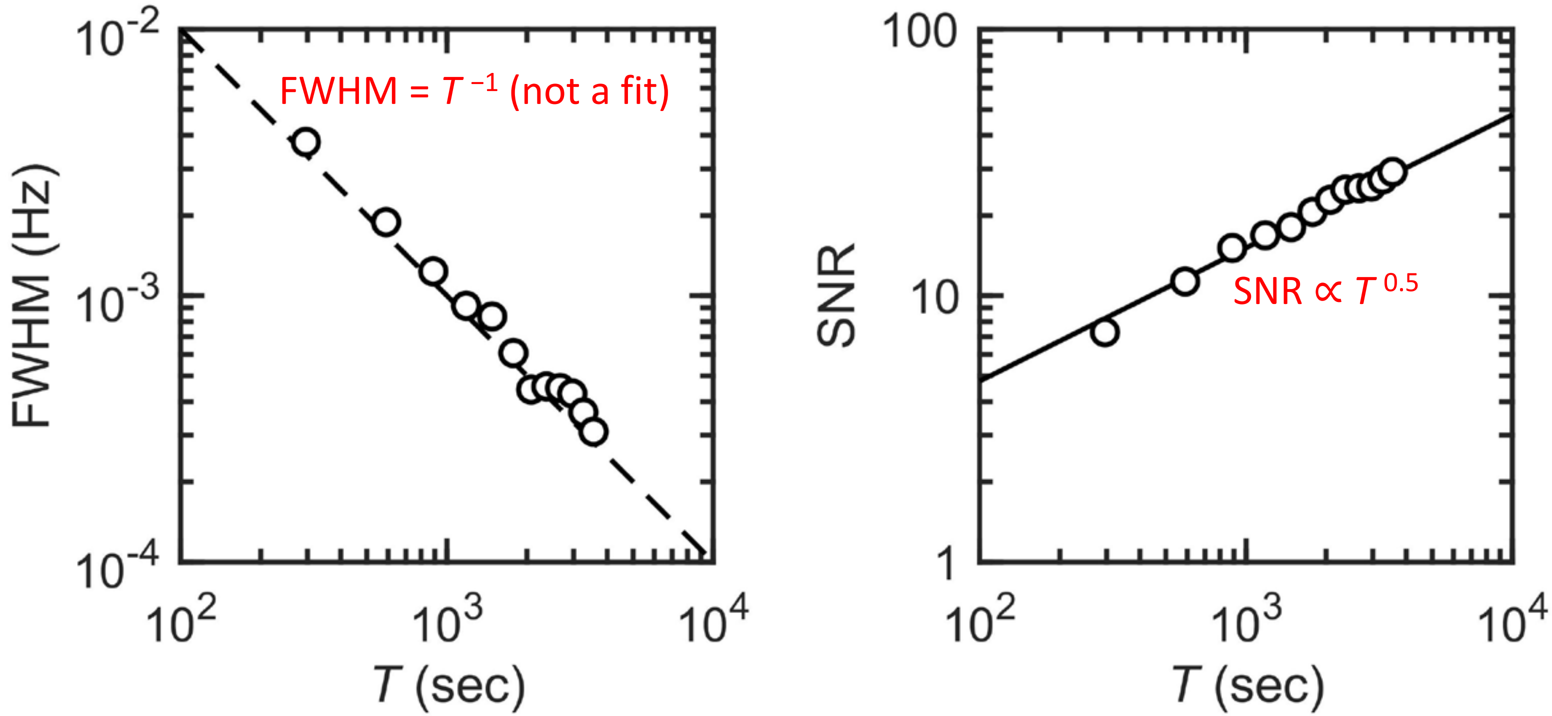
Ultrahigh resolution sensing

B_{ac} = 96.5 nT & f_{ac} = 2.001 MHz applied from a coil, detected by a single NV center



J. Appl. Phys. **123**, 161101 (2018) Abe & Sasaki

Ultrahigh resolution sensing

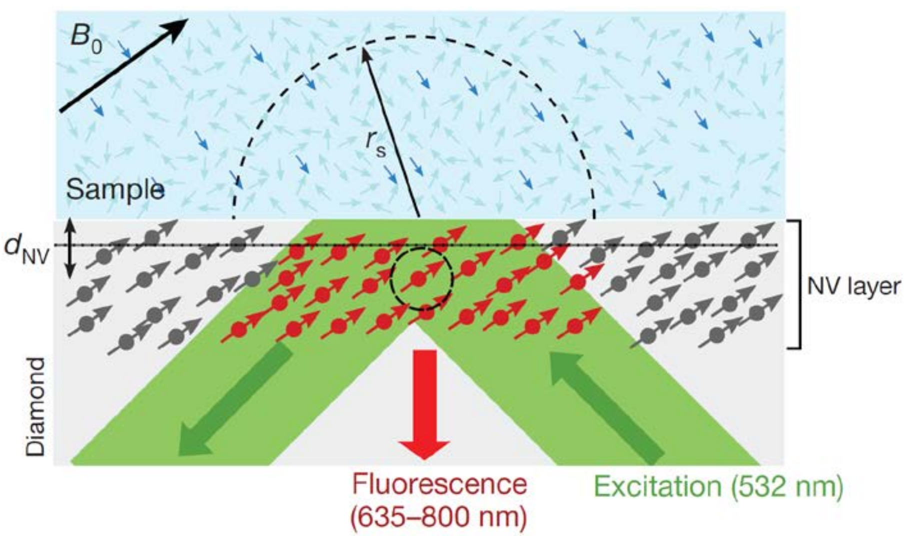


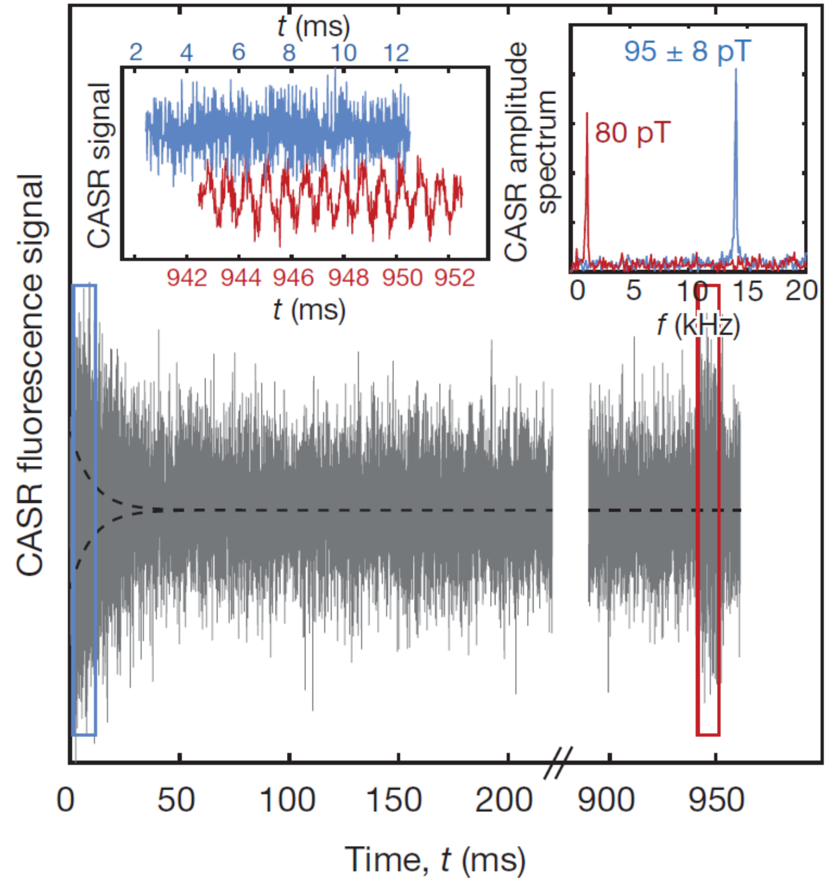
- Spectral resolution not limited by sensor/memory lifetimes ($T_{2e/n}$, $T_{1e/n}$)
- Only limited by the stability of LO (essentially infinite)
- Resolution = T^{-1} & SNR $\propto T^{0.5}$ → Precision $\propto T^{-1.5}$

J. Appl. Phys. **123**, 161101 (2018) Abe & Sasaki

NMR spectroscopy

Data from Harvard: Nature **555**, 351 (2018) Glenn *et al.*





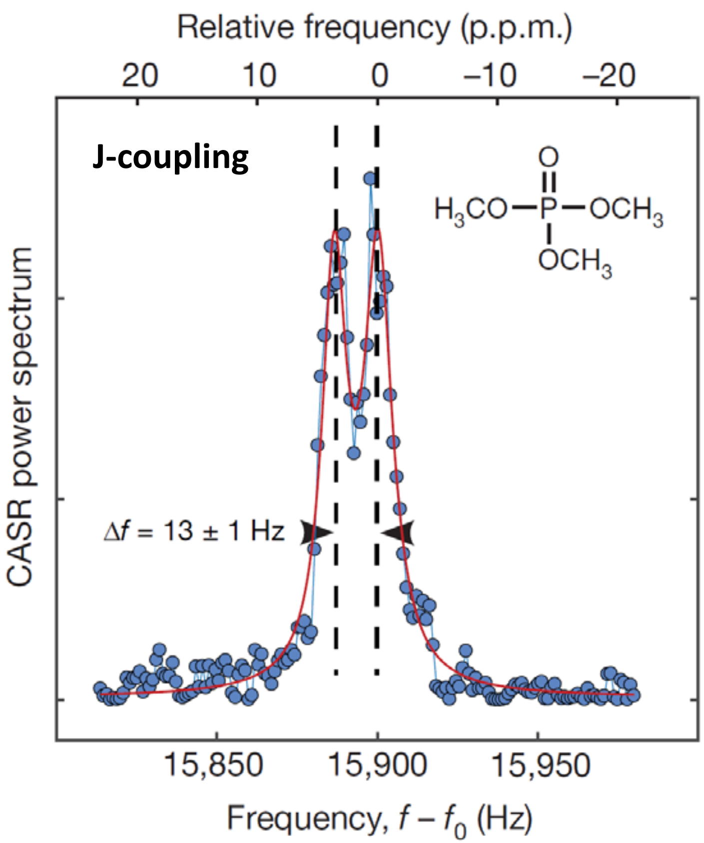
- $[NV] \approx 3 \times 10^{17}$ cm^{-3}
- # of NV ≈ 5×10^9
- $V_{detect} \approx 25$ pL
- # of protons ≈ 2.5×10^{15}
- RF pulse → FID

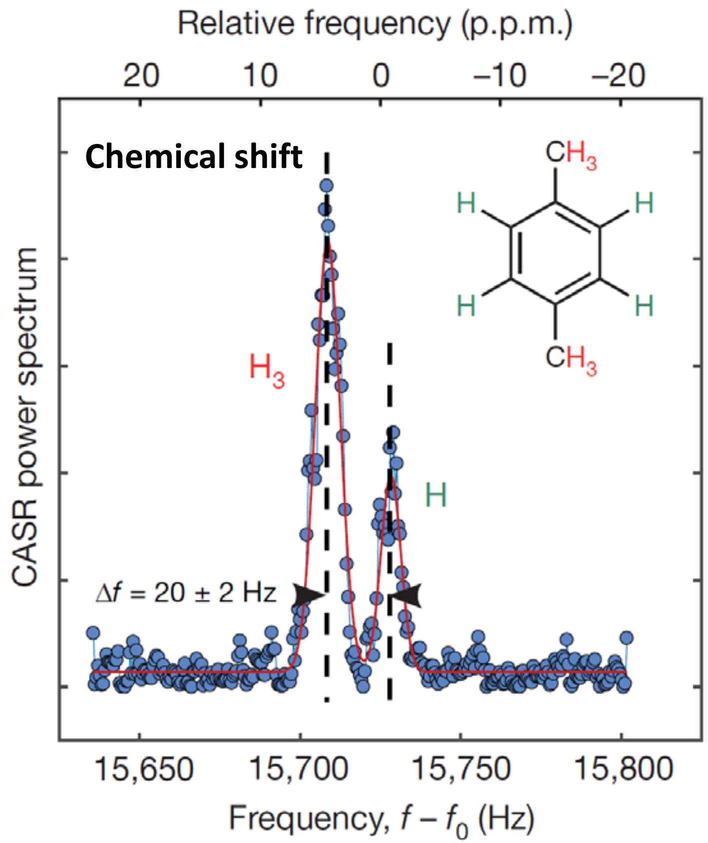
See also: Science **357**, 67 (2017) Aslam *et al.* (Wrachtrup, Stuttgart)

[B_0 = 3 T, f_e = 87 GHz, T_{1n} = 260 s]

NMR spectroscopy

Data from Harvard: Nature **555**, 351 (2018) Glenn *et al.*





See also: Science **357**, 67 (2017) Aslam *et al.* (Wrachtrup, Stuttgart)

[B_0 = 3 T, f_e = 87 GHz, T_{1n} = 260 s]

Summary

- **Tools for single-molecule imaging/structural analysis are being developed**
  - → Determination of the position of individual *n*-spins[1,2,3]
  - → Ultrahigh resolution sensing[4,5,6], resolving chemical shifts[6,7] & suppression of backaction from *n*-spins[8,9]

[1] Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.* (Keio)
[2] Phys. Rev. Lett. **121**, 170801 (2018) Zopes *et al.* (ETH)
[3] Nature **576**, 411 (2019) Abobeih *et al.* (Delft)
[4] Science **356**, 832 (2017) Schmitt *et al.* (Ulm)
[5] Science **356**, 837 (2017) Boss *et al.* (ETH)
[6] Nature **555**, 351 (2018) Glenn *et al.* (Harvard)
[7] Science **357**, 67 (2017) Aslam *et al.* (Stuttgart)
[8] Nature Commun. **10**, 594 (2019) Pfender *et al.* (Stuttgart)
[9] Nature **571**, 230 (2019) Cujia *et al.* (ETH)