# Quantum Spintronics Design
## (NV centers in diamond)

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***RIKEN Center for Emergent Matter Science***

2021.02.24

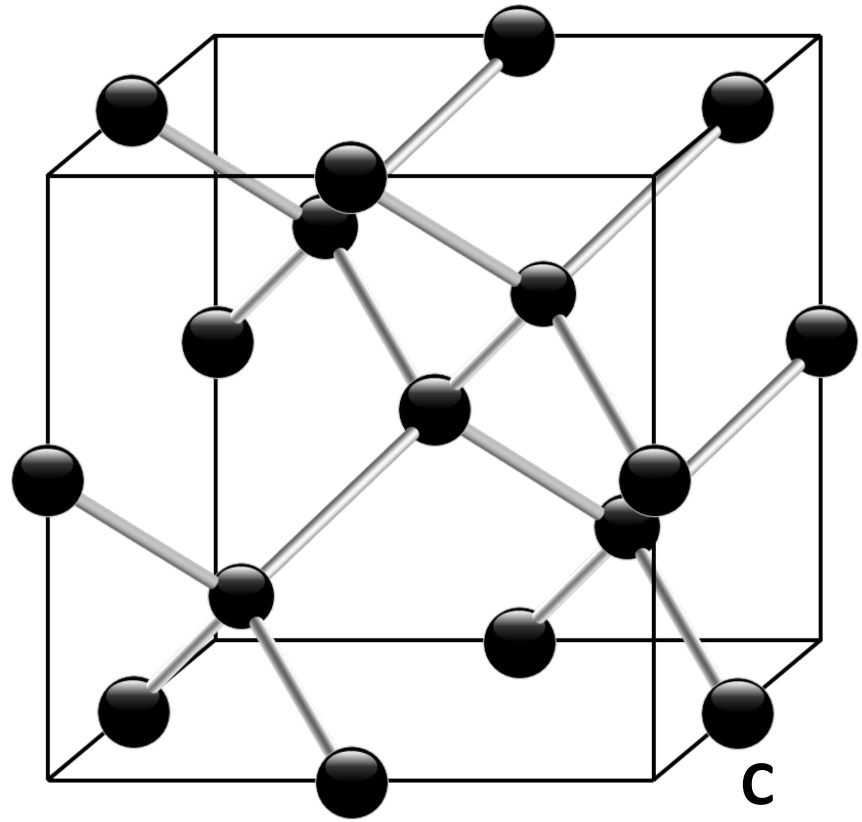
CMD Spintronics Design Course

(Online)

# Diamond envy

| III (13) | IV (14) | V (15) |
|---|---|---|
| B | **C** | N |

©GIA




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

# Diamond envy

| III (13) | IV (14) | V (15) |
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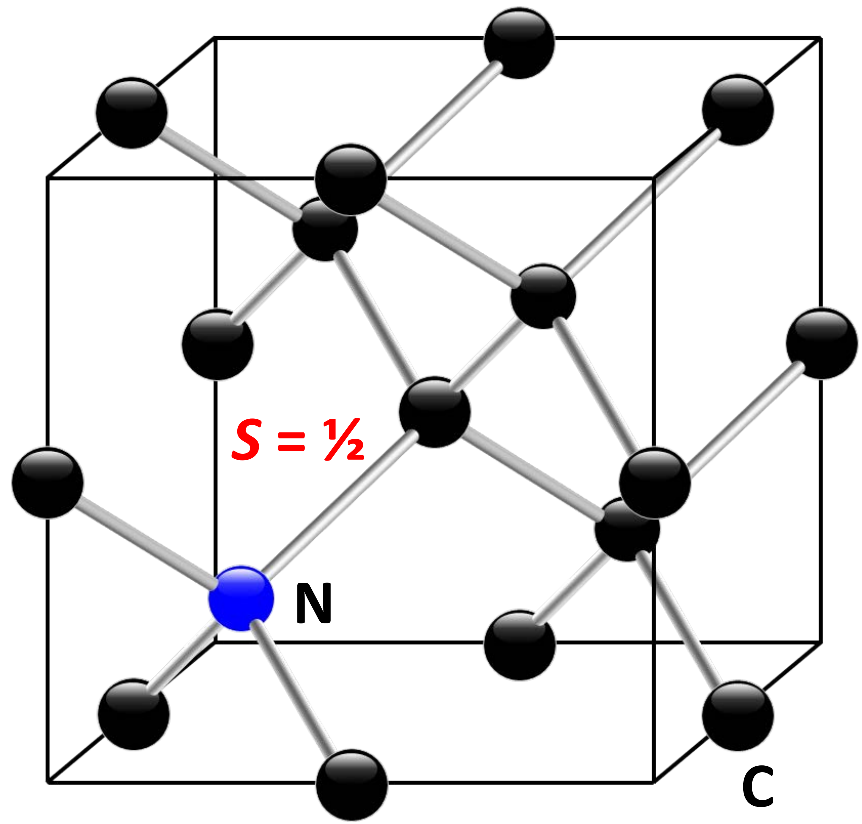


$\rho_N = 1.77 \times 10^{23}\ cm^{-3}$

# Diamond NV

| III (13) | IV (14) | V (15) |
| --- | --- | --- |
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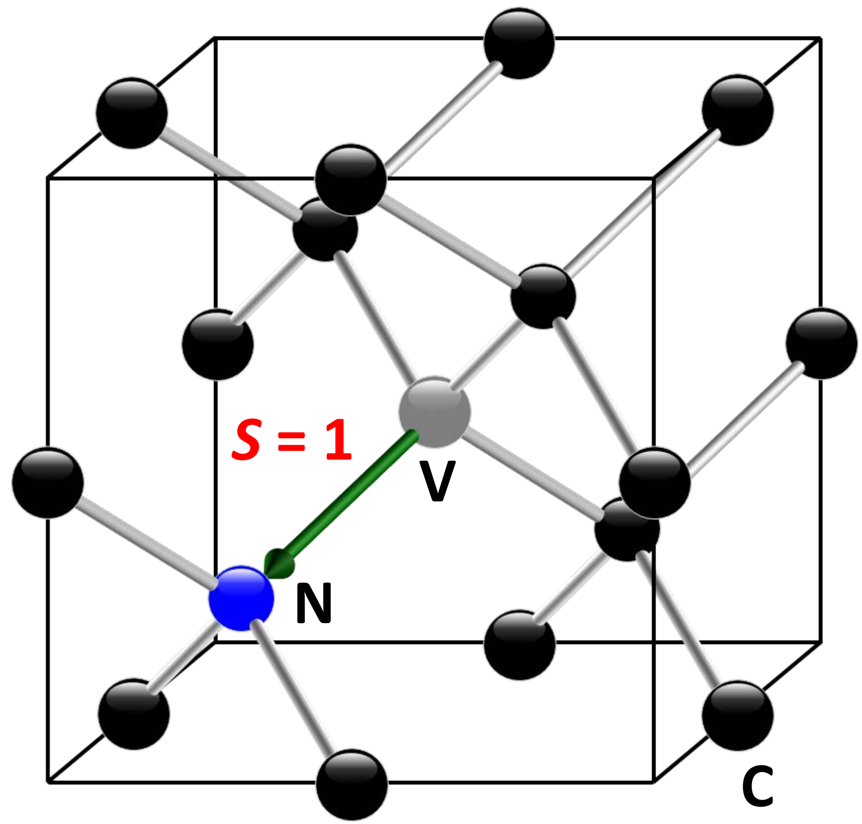
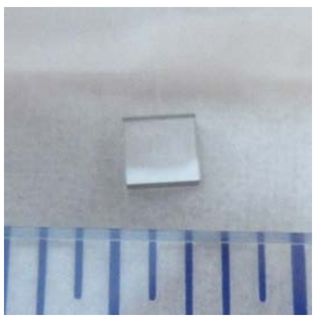



$\rho_N$ = 1.77 x $10^{23}$ $cm^{-3}$

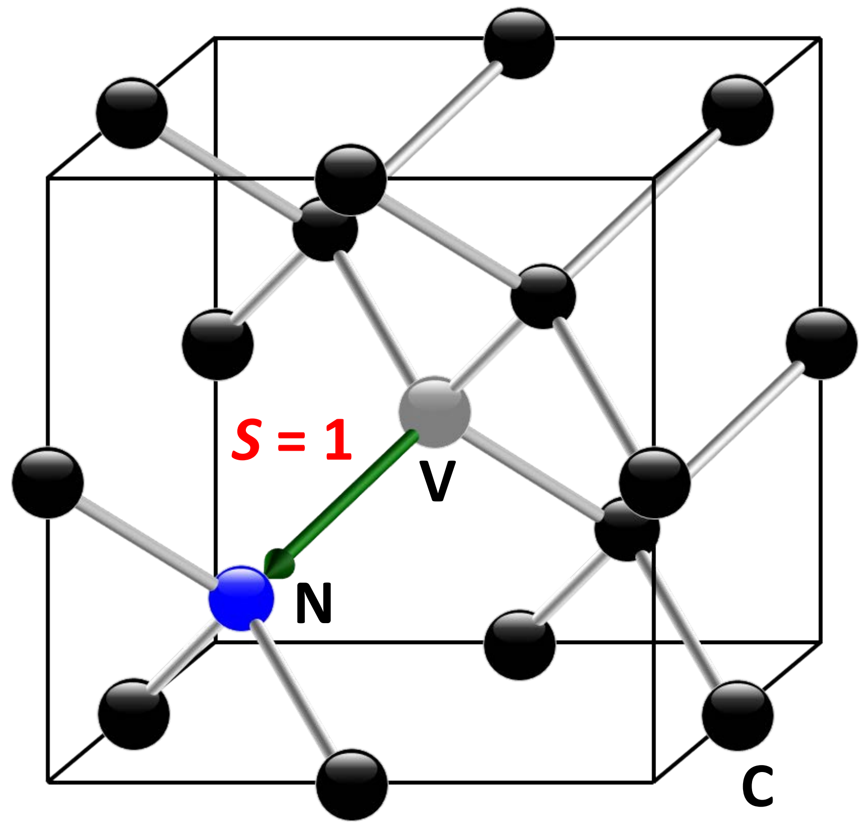
# Diamond NV

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



***Not like…***

©GIA

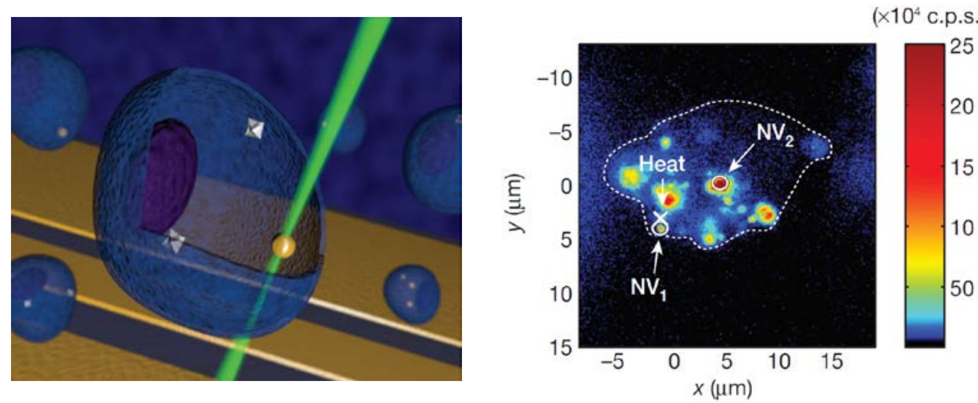



$\rho_N$ = 1.77 x $10^{23}$ $cm^{-3}$

# Quantum sensing with NV centers

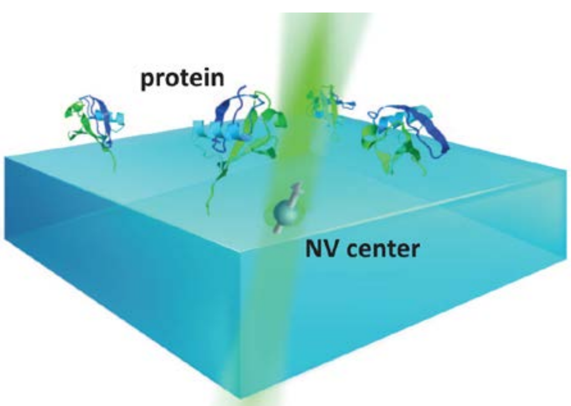
- *B*, *E*, *T*, *S*...
- DC & AC modes
- Wide temperature range
- Nondestructive
- High spatial resolution
- Various modalities

**Nanodiamond & biology**



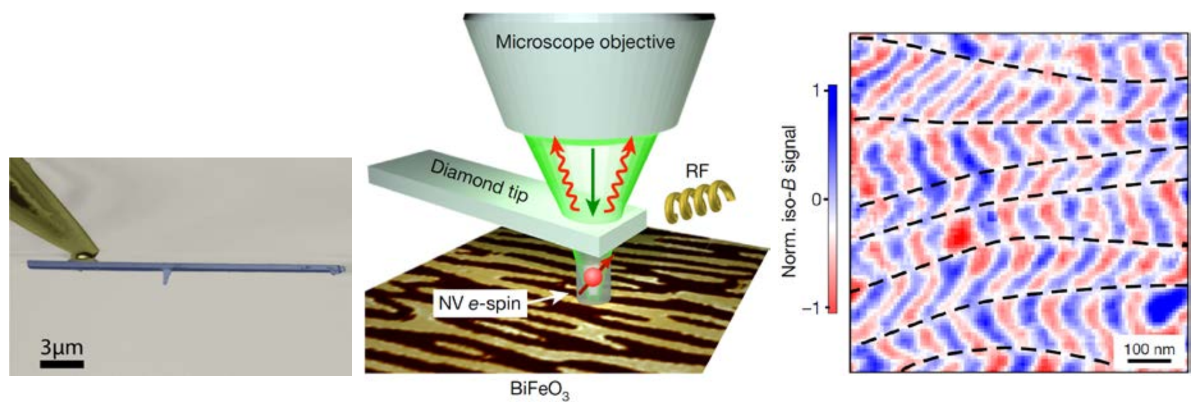

Nature **500**, 54 (2013)

**Near-surface NV center & NMR**




Science **351**, 836 (2016)

**Scanning probe & condensed matter**




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

# Outline

- **Basics of NV centers in diamond**
  - Structure
  - Optical & magnetic properties
- **Basics of magnetic resonance**
- **Quantum sensing**
  - AC magnetometry
  - Detection of proton spin ensemble
  - Detection and control of a single proton spin

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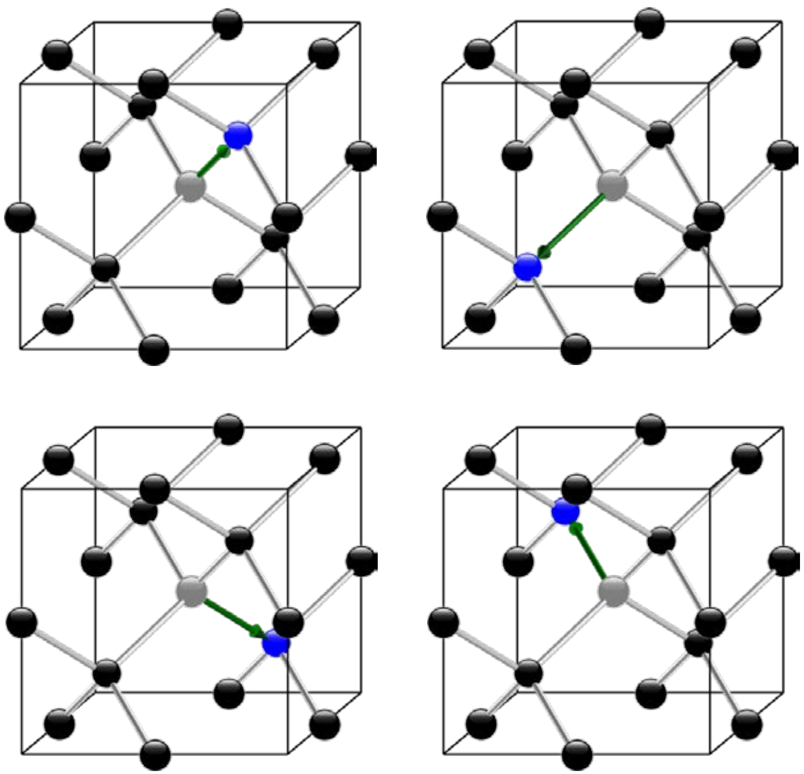
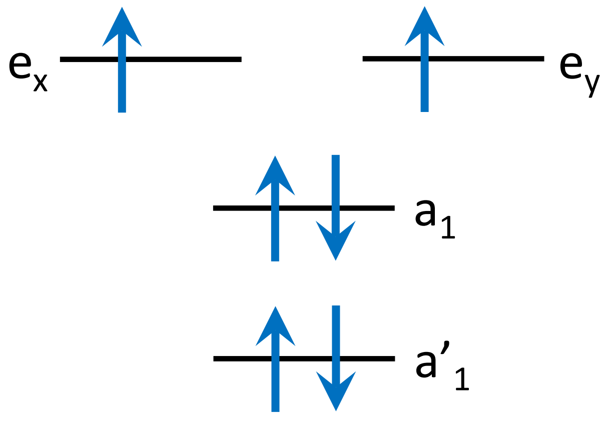
# Crystal & energy level structures

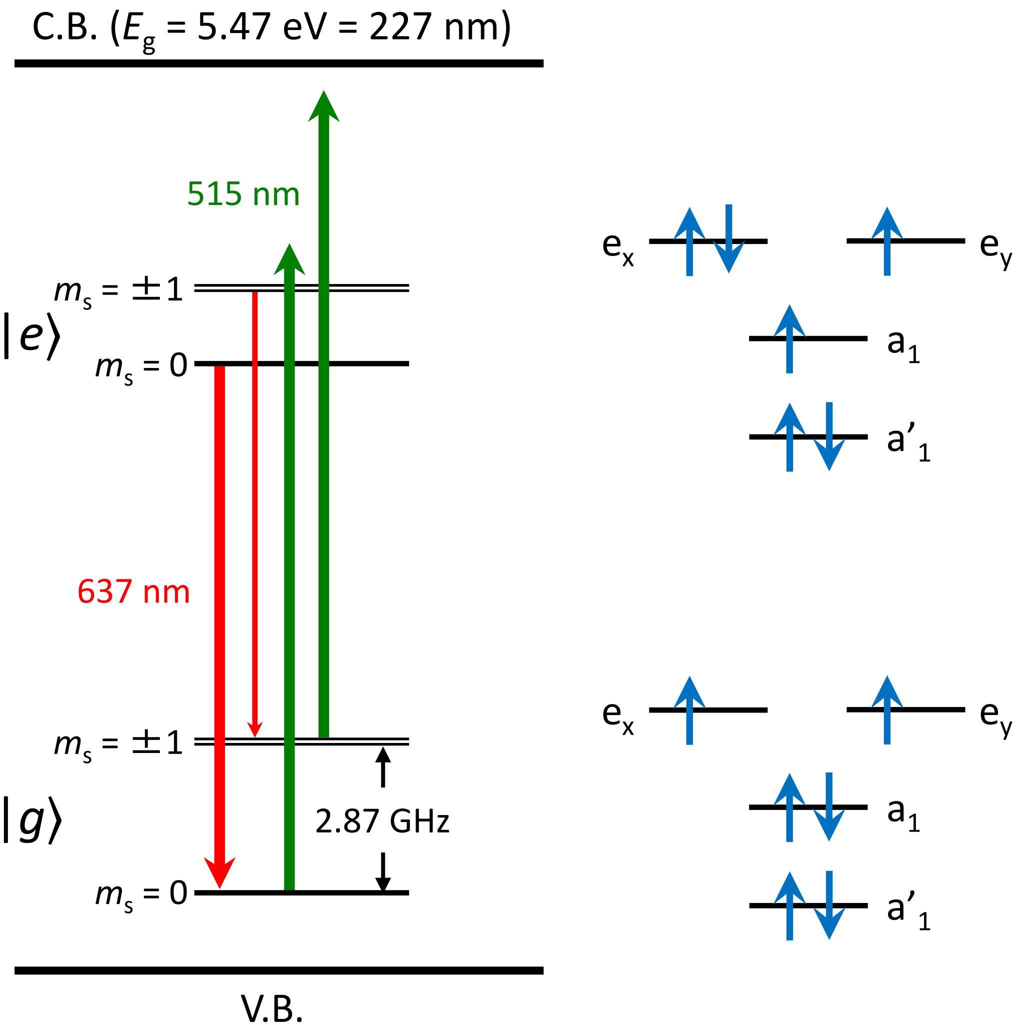
- Negatively-charged ($NV^-$)
- 4 $sp^3$ orbitals, 6 $e^-$ (5 from the defect, 1 captured)
- $C_{3v}$ (symmetry axis = quantization axis)



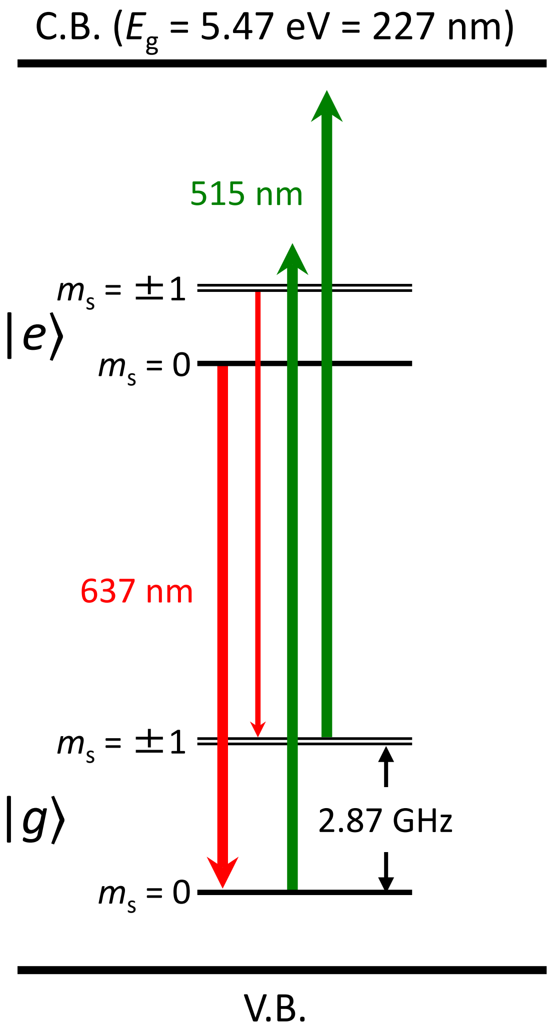
Effective spin-1 system
($e^2$-hole spin-triplet)

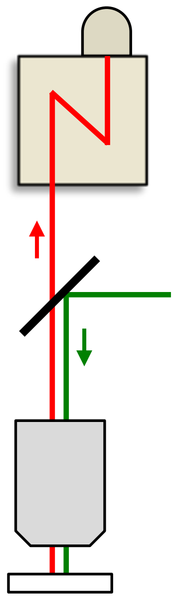


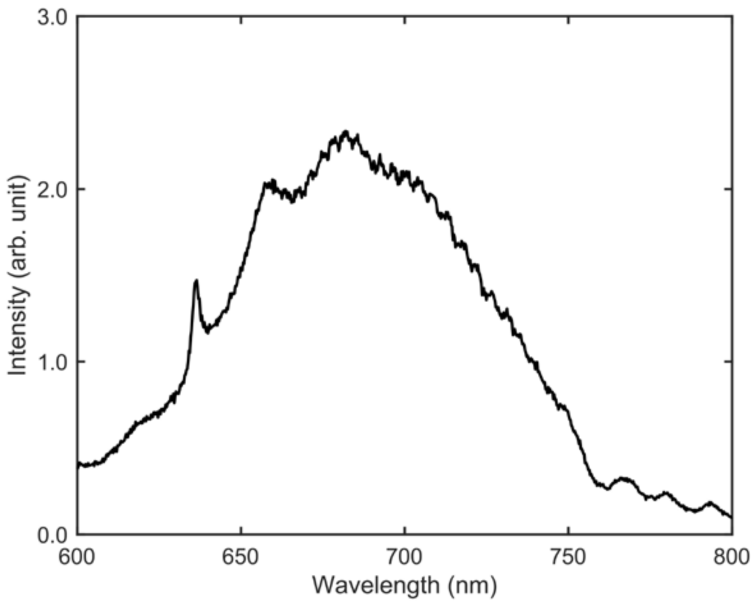
# Energy levels



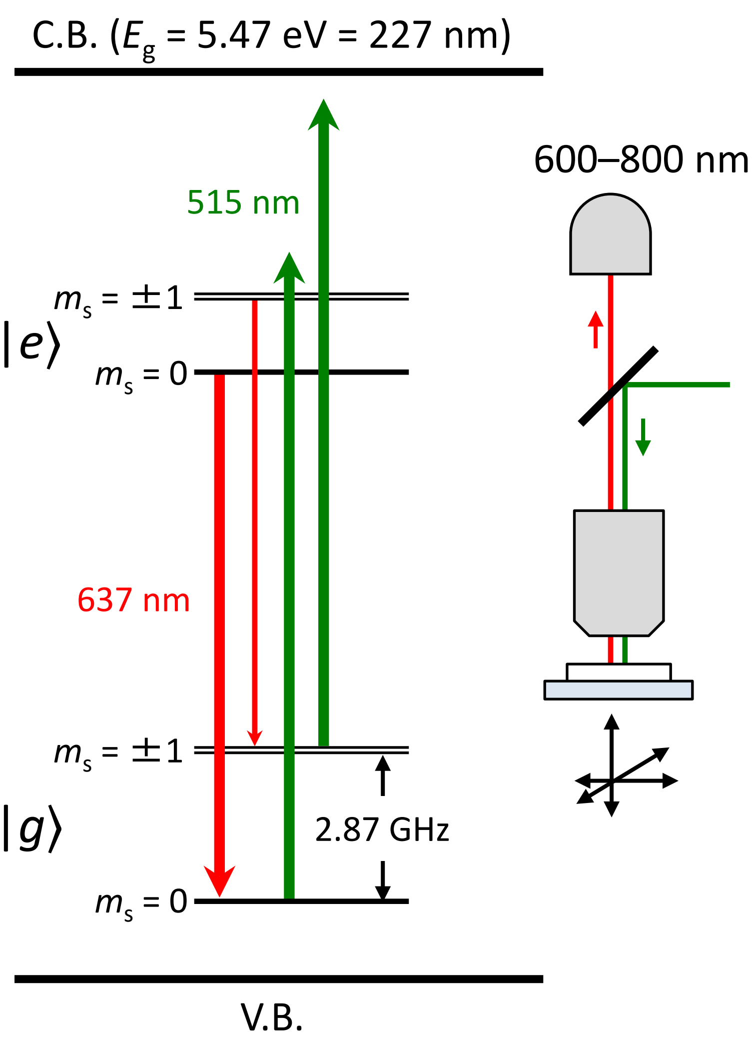
# PL spectroscopy & imaging

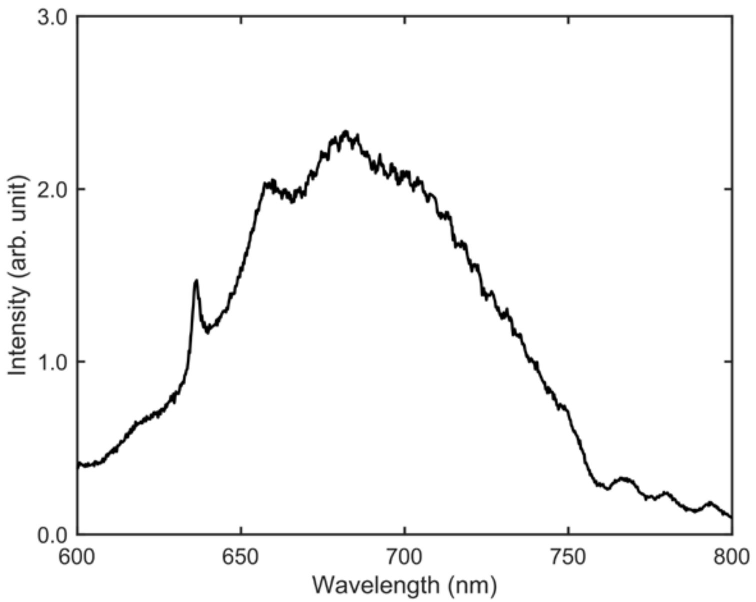


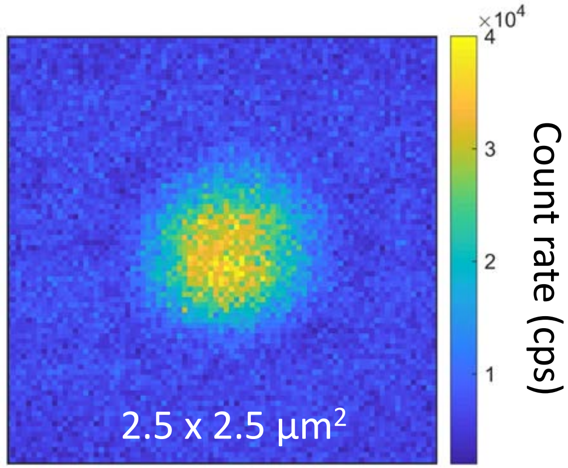





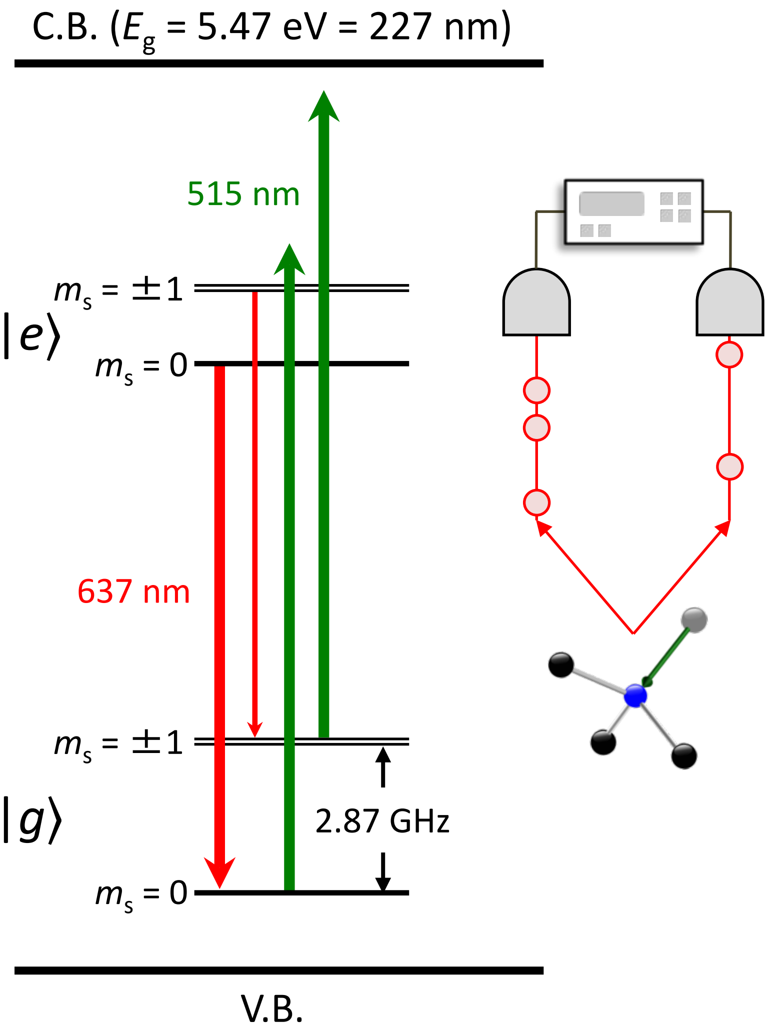
# PL spectroscopy & imaging



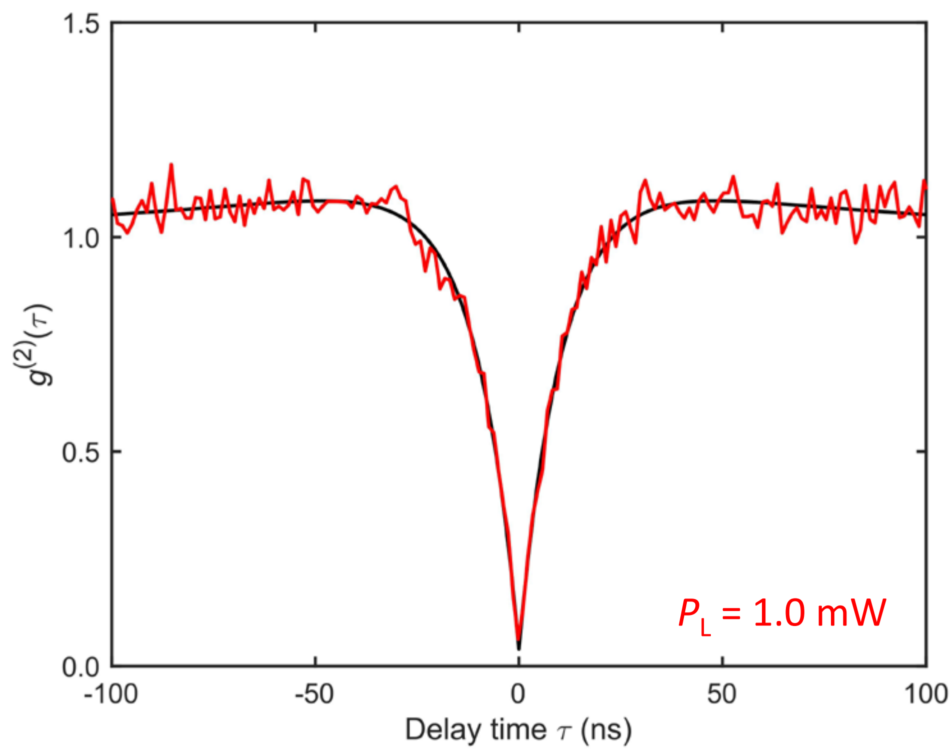



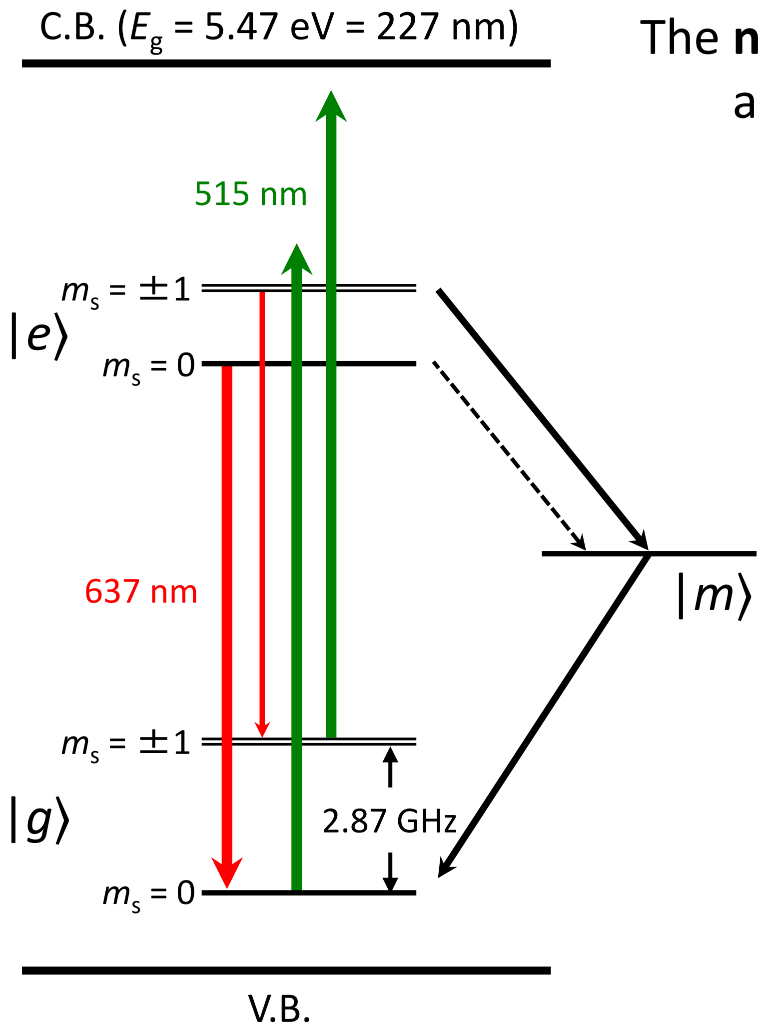
# Photon statistics



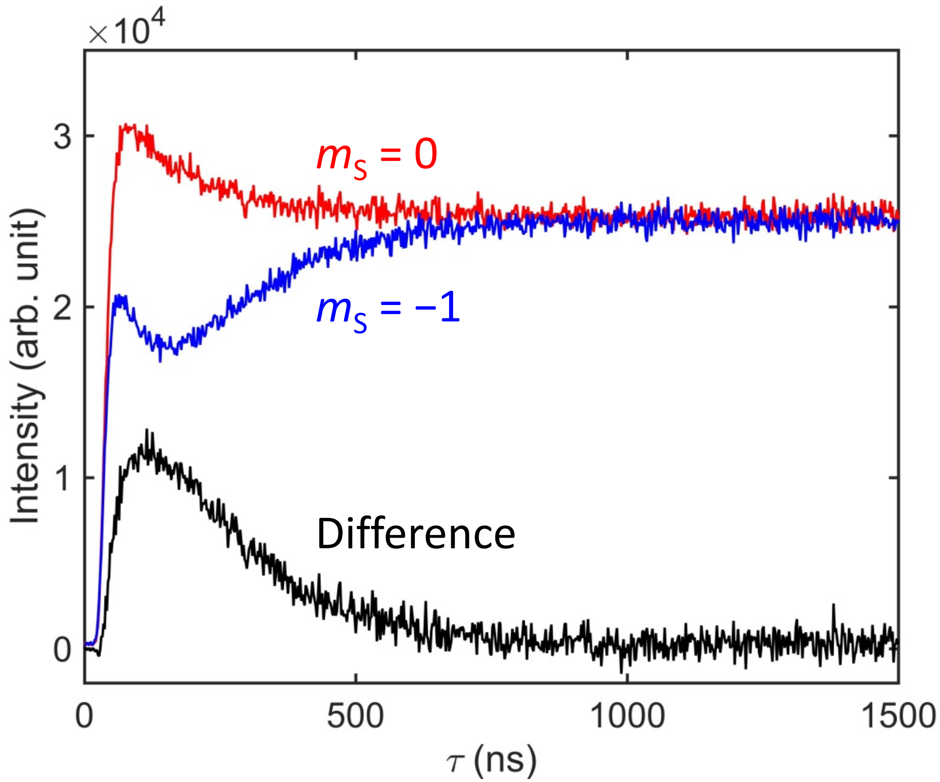

One photon at a time



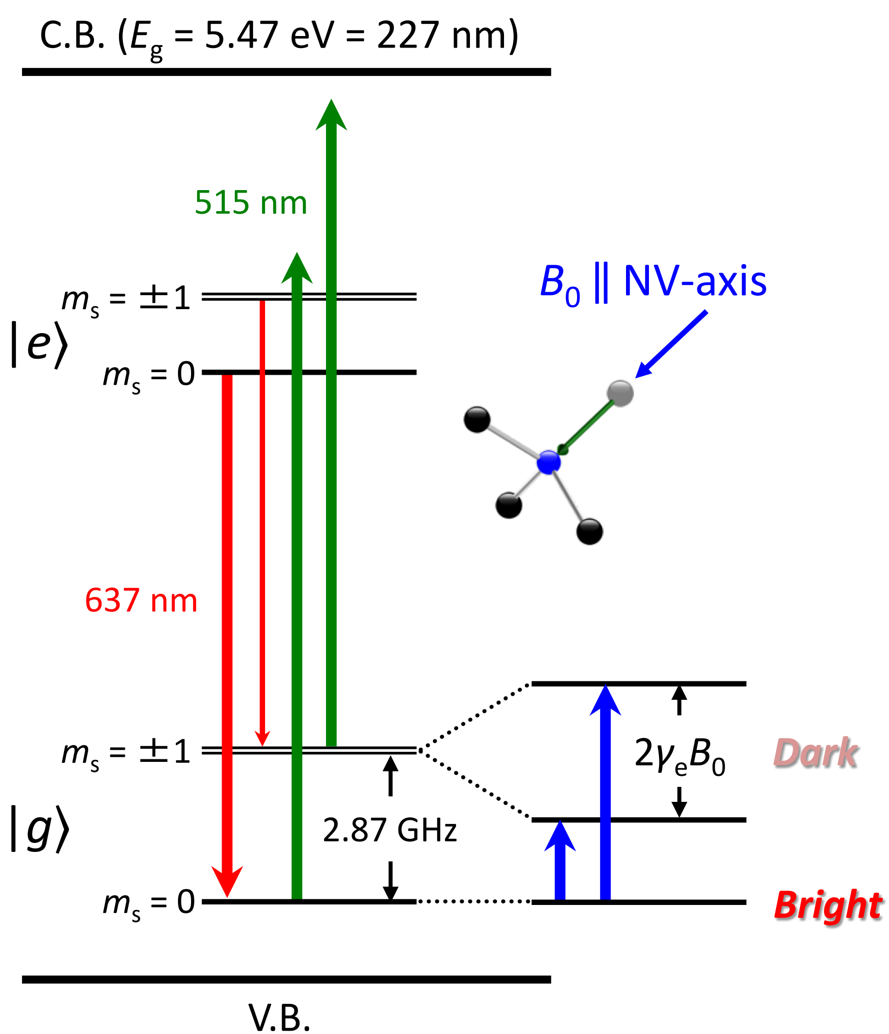
# Time-resolved fluorescence




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



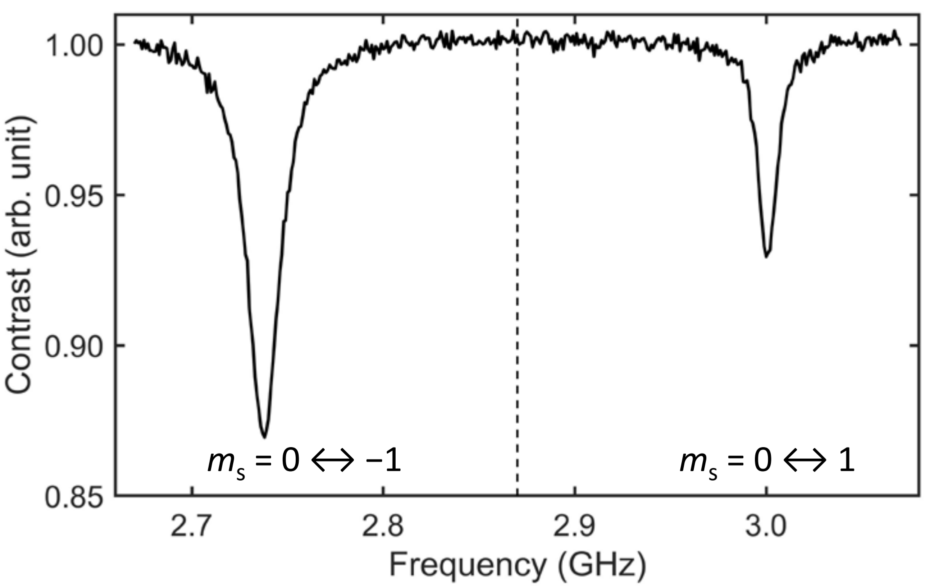
# Optically detected magnetic resonance



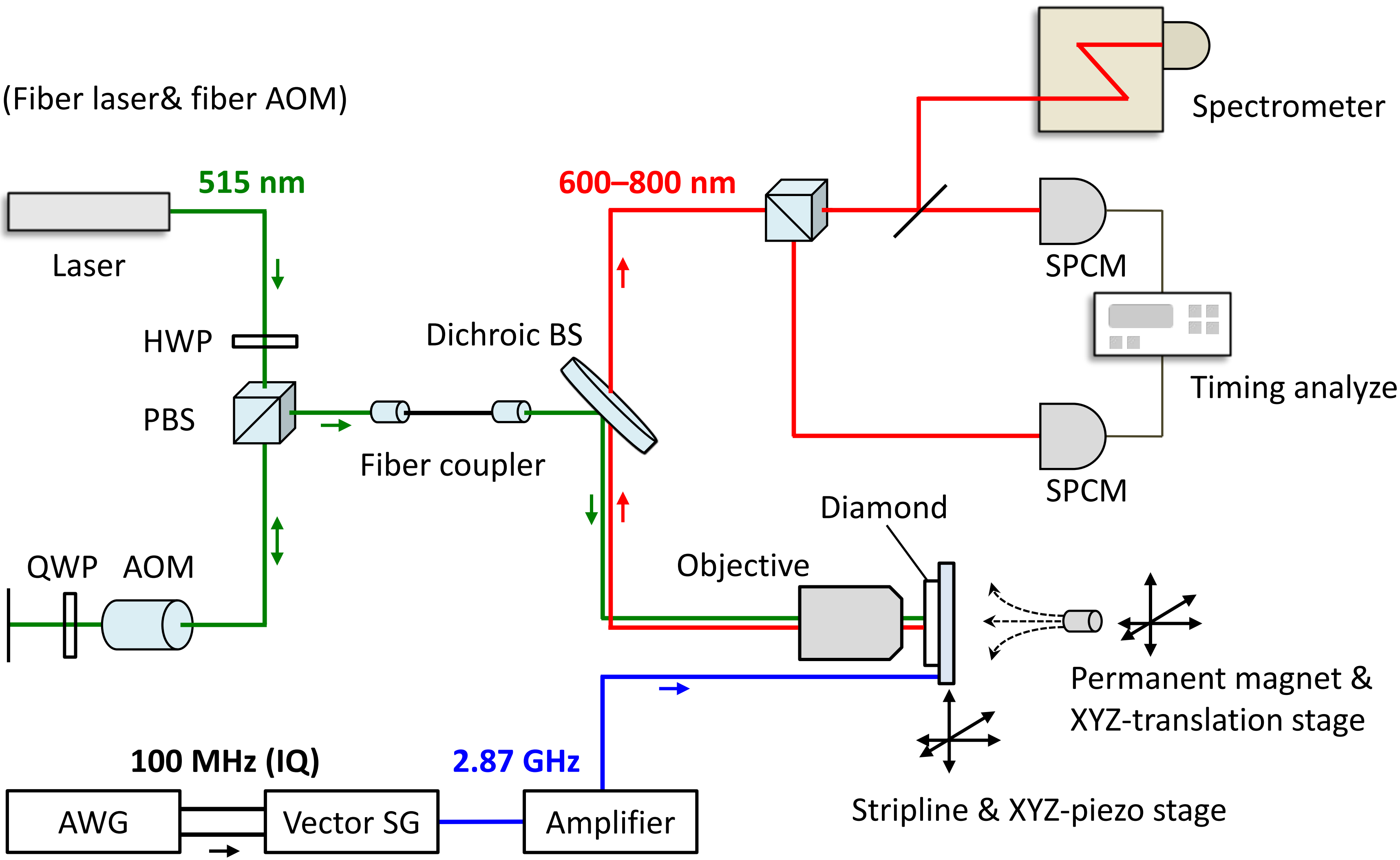

$$H = DS_z^2 + \gamma_e B_0 S_z$$

$D$ = 2.87 GHz, $\gamma_e$ = 28 MHz/mT

$B_0$ = 4.7 mT, $f_\pm$ = 2.87±0.132 GHz

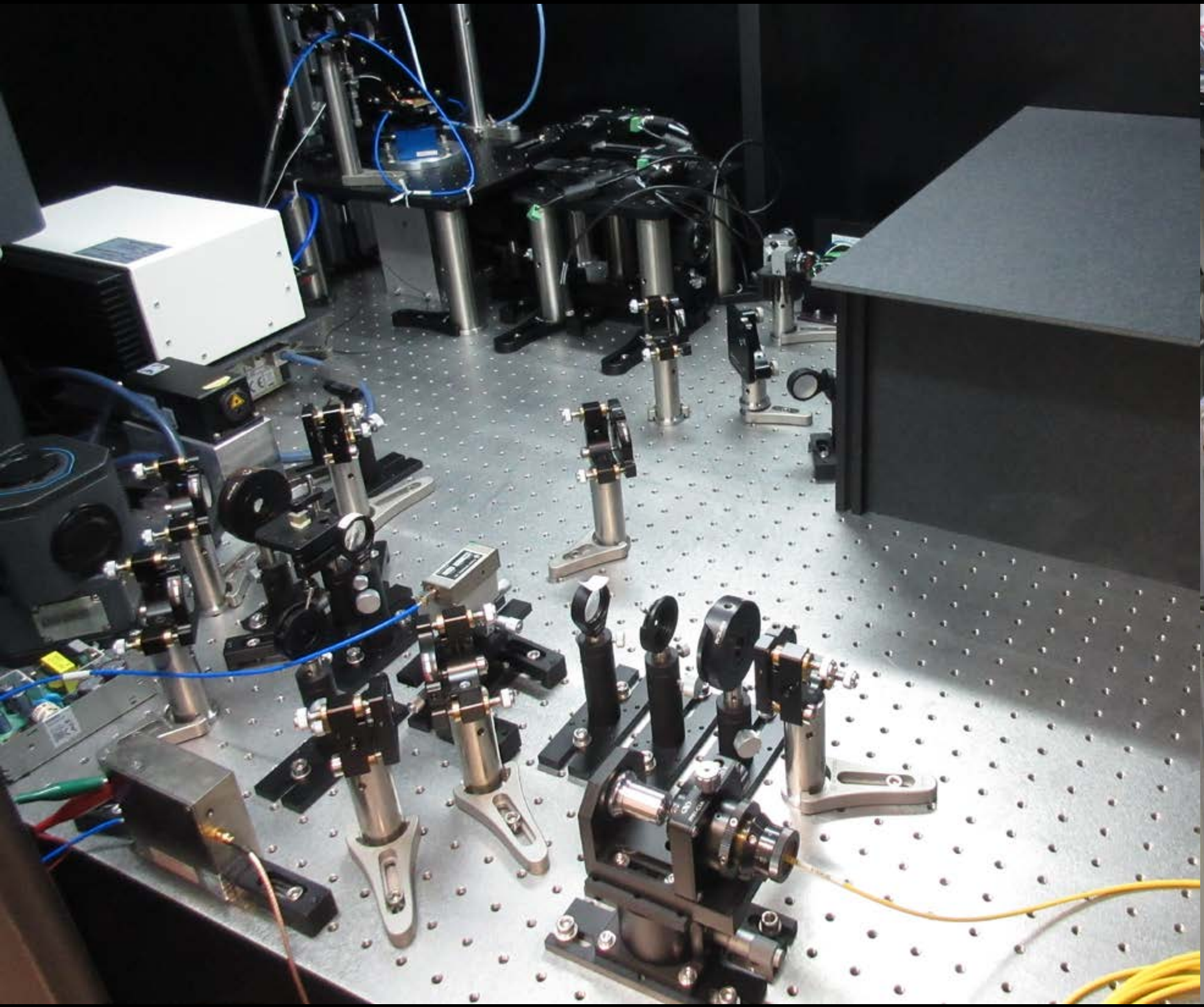


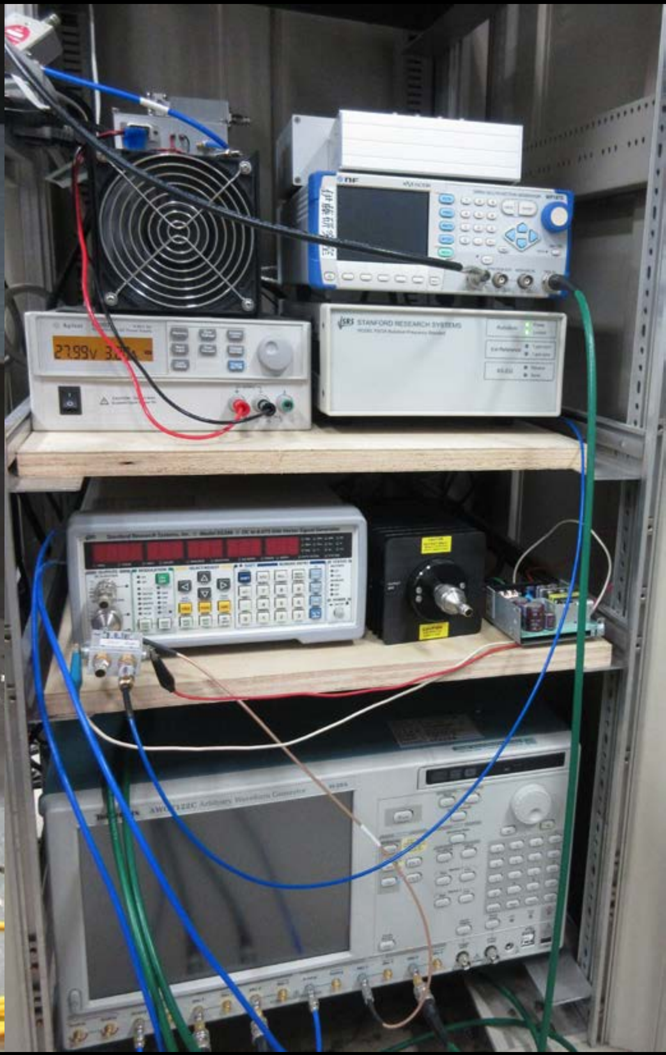
# Experimental setup



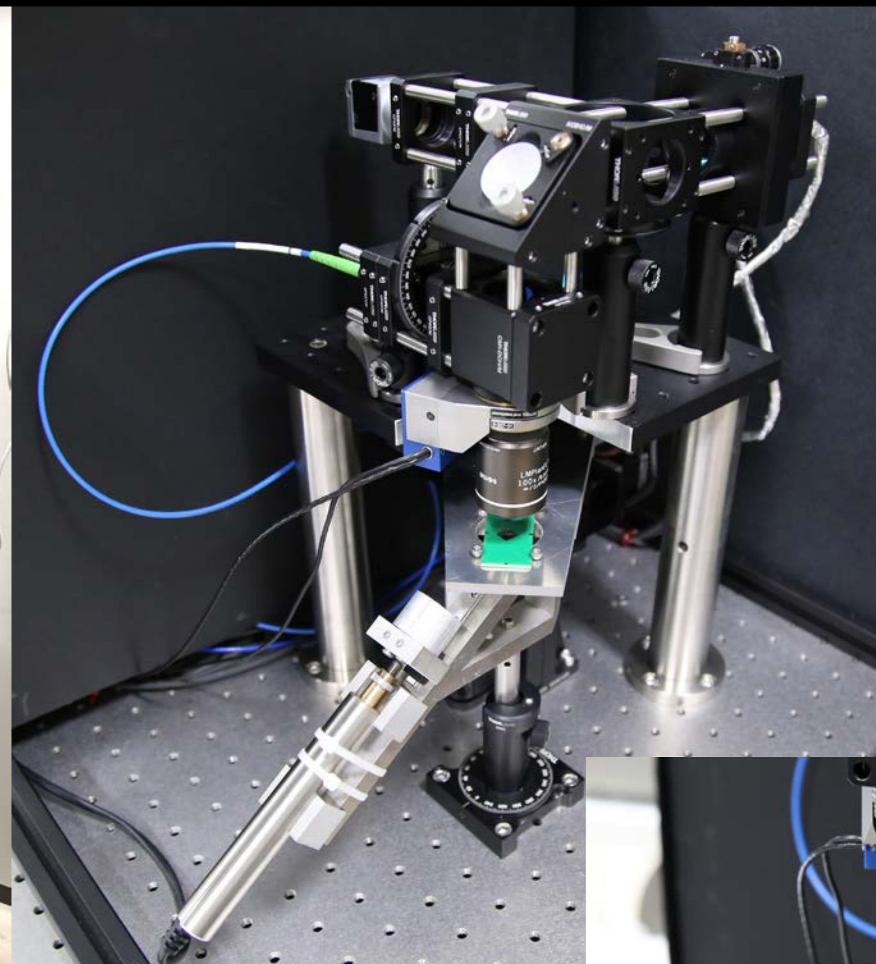

(XY-galvo + Z-piezo & 1-axis magnet)

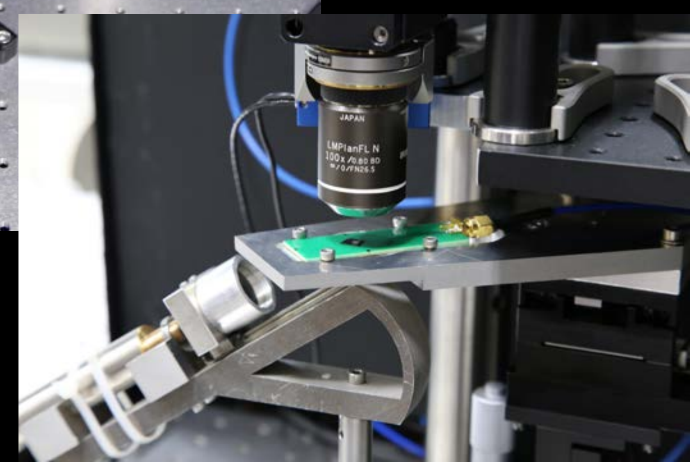
# Experimental setup





# Experimental setup





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

# Outline

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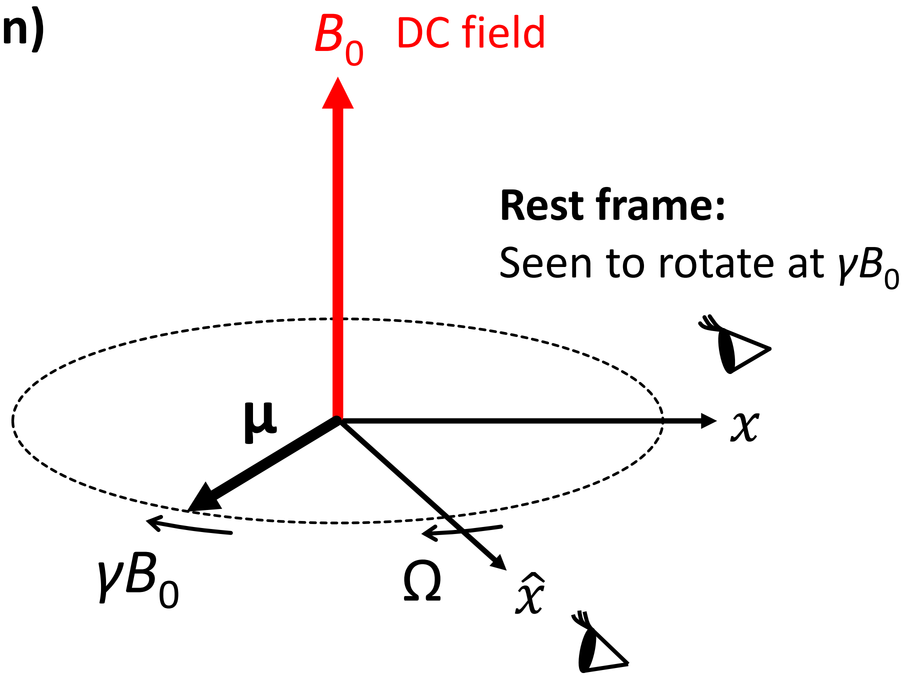
# Magnetic resonance

**Torque equation (Larmor precession)**

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

Gyromagnetic ratio

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

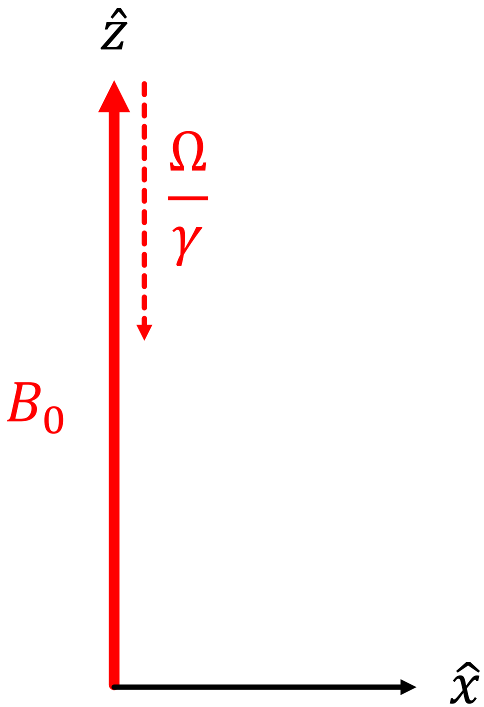


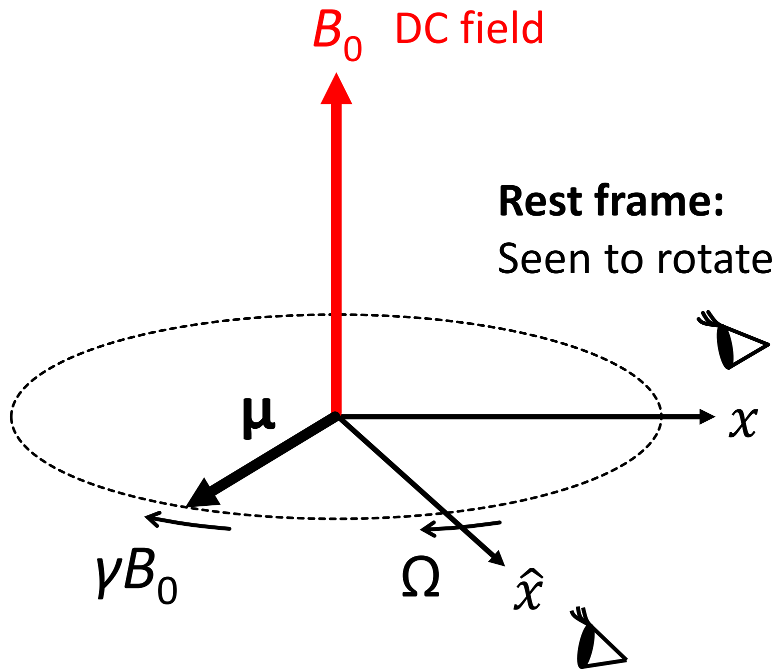

**Frame rotating at angular velocity Ω:**
Rotate slower…why?

Joseph Larmor
(1857–1942)

(from Wikipedia)

# Magnetic resonance



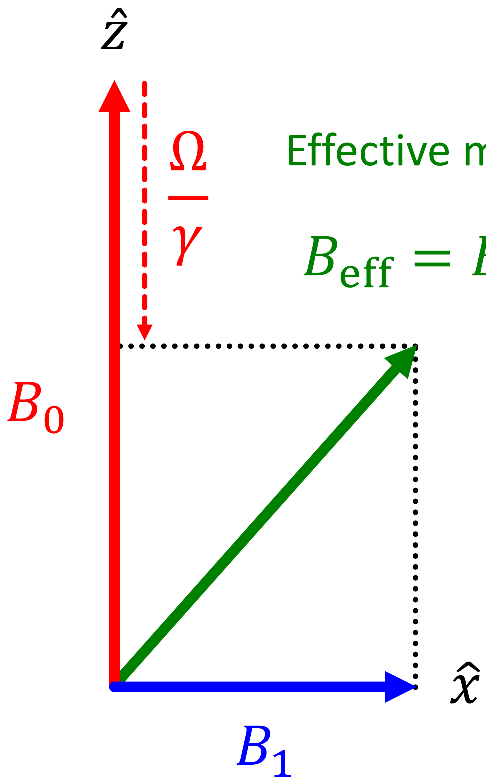

**Rest frame:**
Seen to rotate at $\gamma B_0$

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

⇓

DC field along the *z* direction becomes weaker

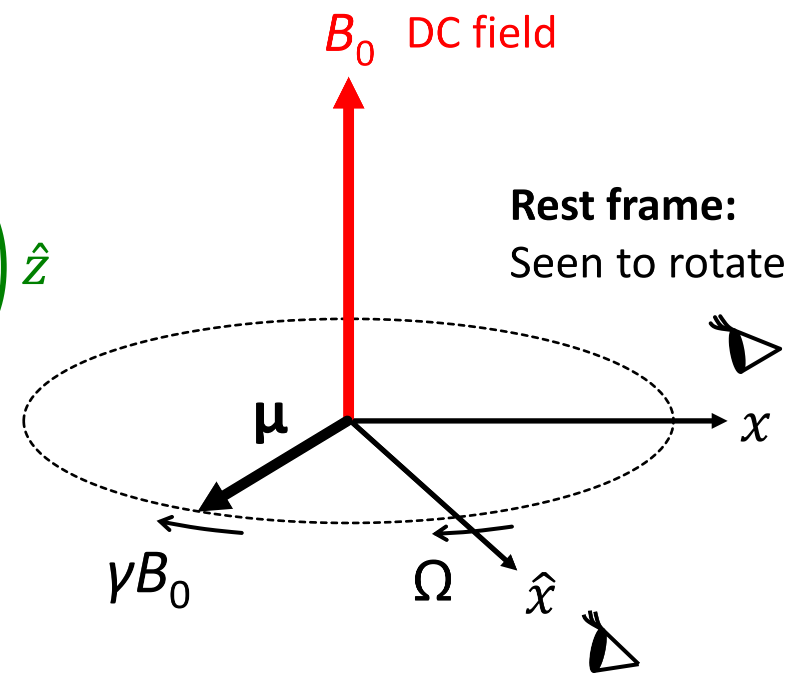
# Magnetic resonance




Effective magnetic field

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

AC field rotating in the *xy* plane at Ω




**Rest frame:**
Seen to rotate at $\gamma B_0$

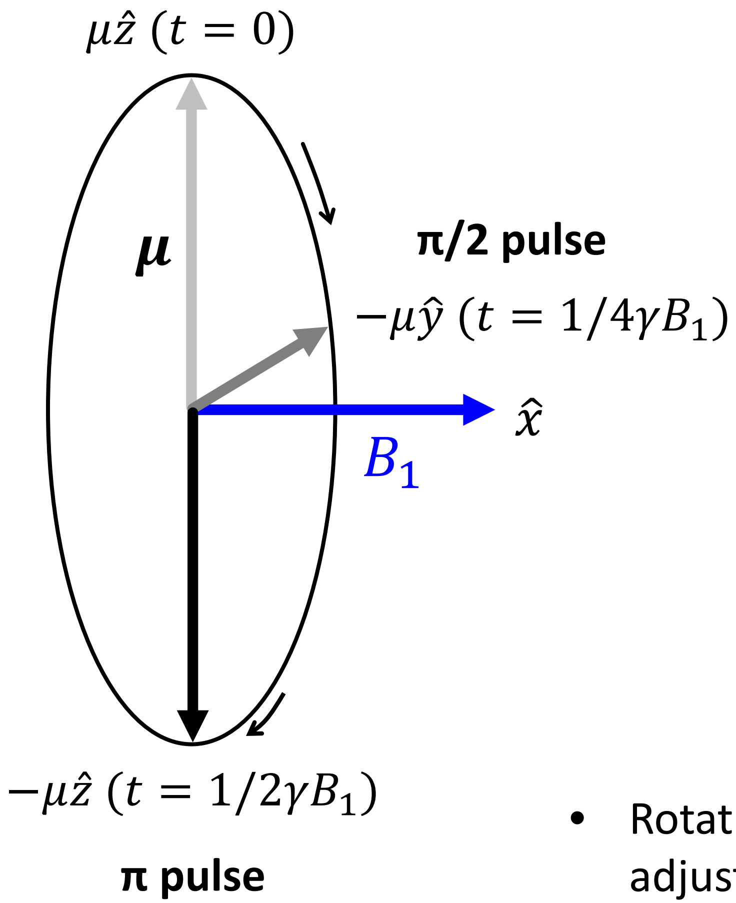
**Frame rotating at angular velocity Ω:**
Rotate slower…why?

⇓

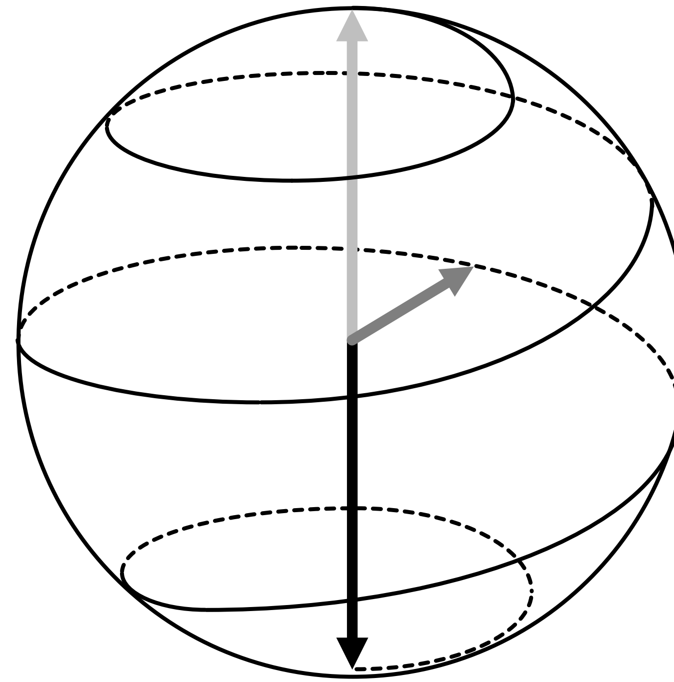
DC field along the *z* direction becomes weaker

# 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

# Description as a quantum bit

**Qubit, spin-½ (NV is spin-1!)**

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

**Superposition state**

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

⇩

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

Global phase

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

⇩

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

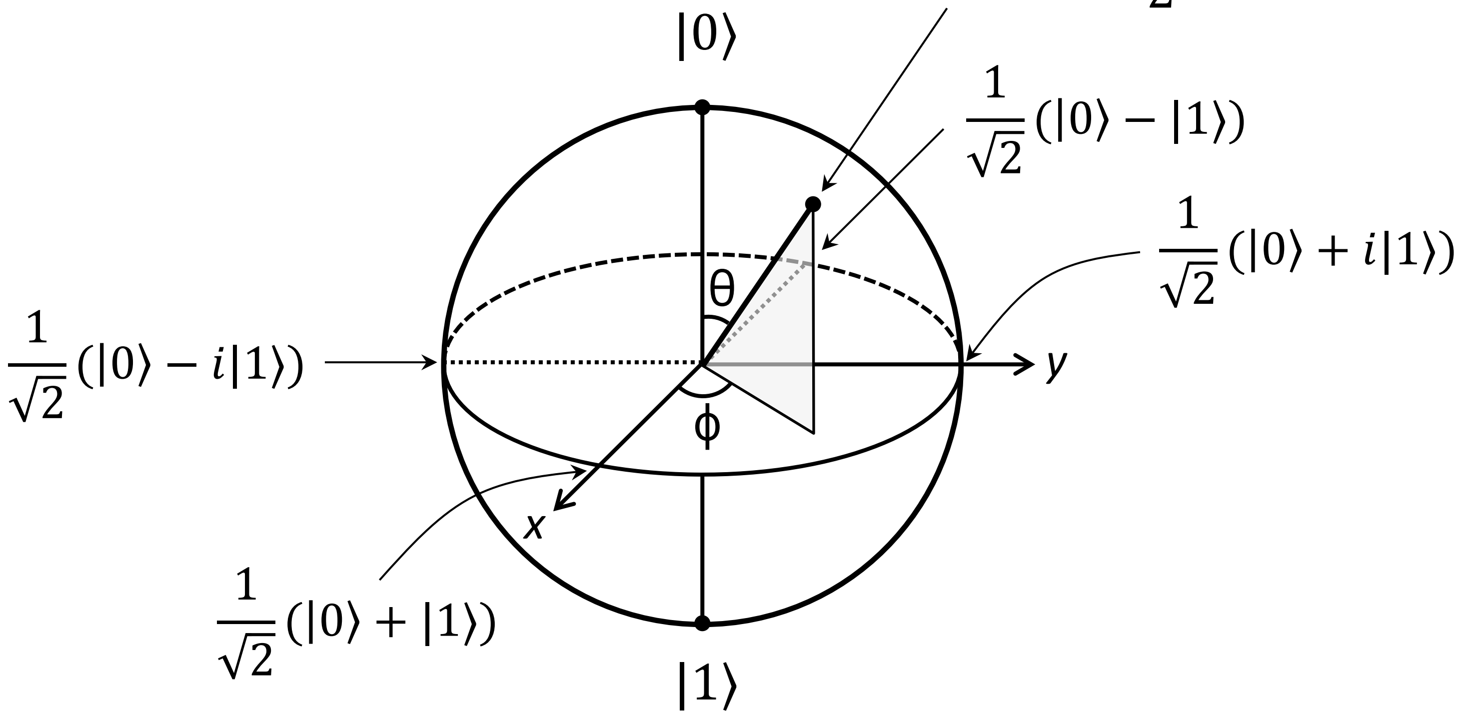
$$0 \le \theta \le \pi$$
$$0 \le \phi < 2\pi$$

# Bloch sphere

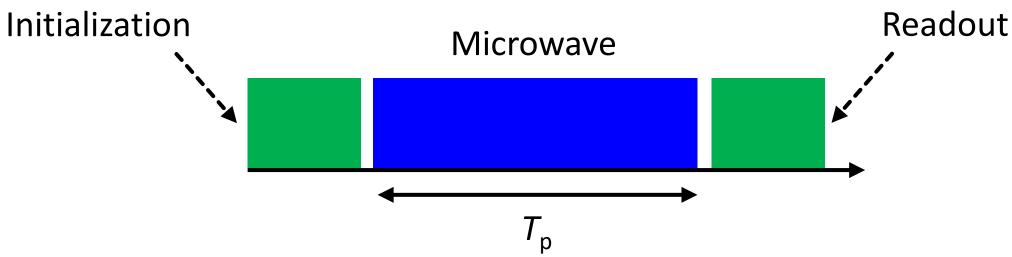
**Qubit, spin-½ (NV is spin-1!)**

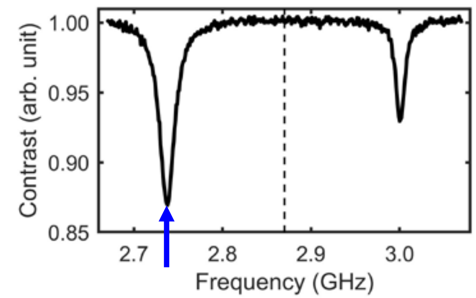
$$\begin{cases} |"0"\rangle \equiv |m_s = 0\rangle \\ |"1"\rangle \equiv |m_s = -1\rangle \end{cases}$$

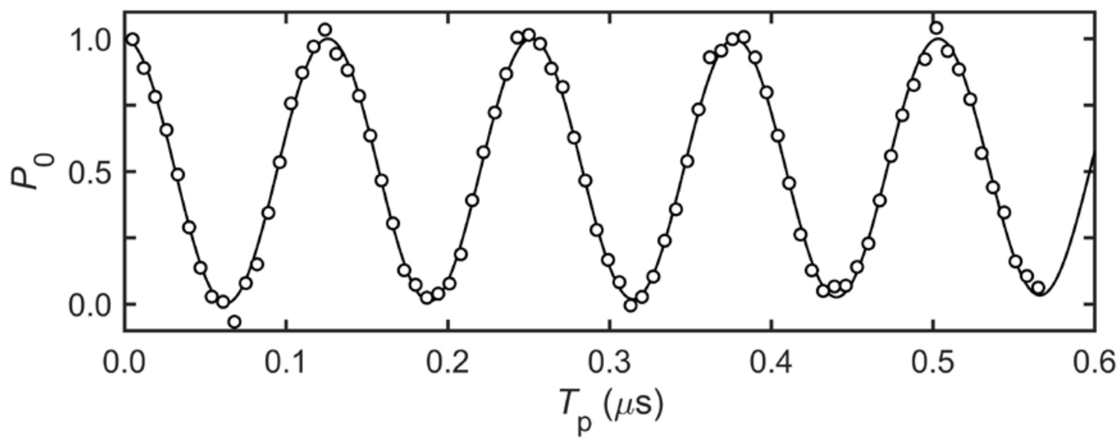
$$|\psi\rangle = \cos\frac{\theta}{2}|0\rangle + e^{i\phi}\sin\frac{\theta}{2}|1\rangle$$

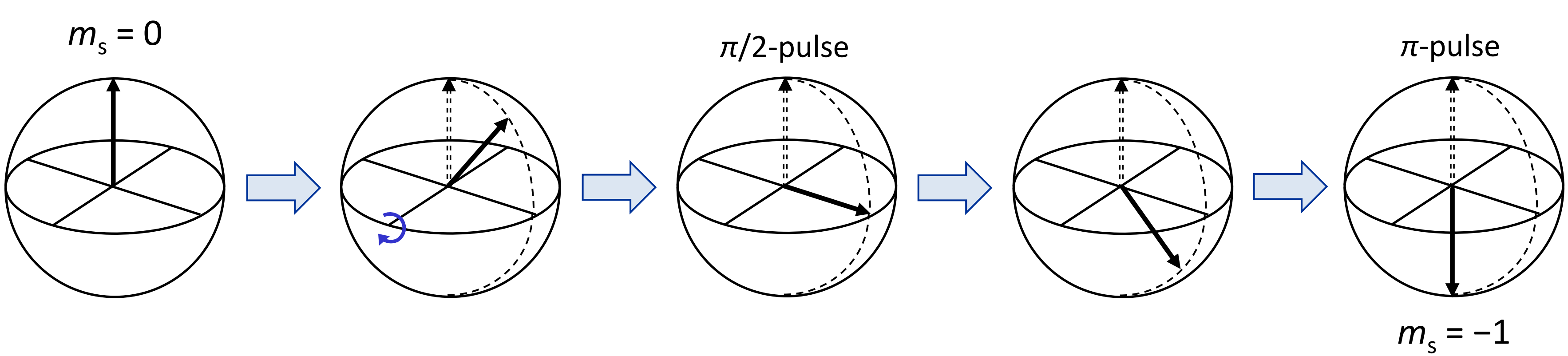


# Rabi oscillation

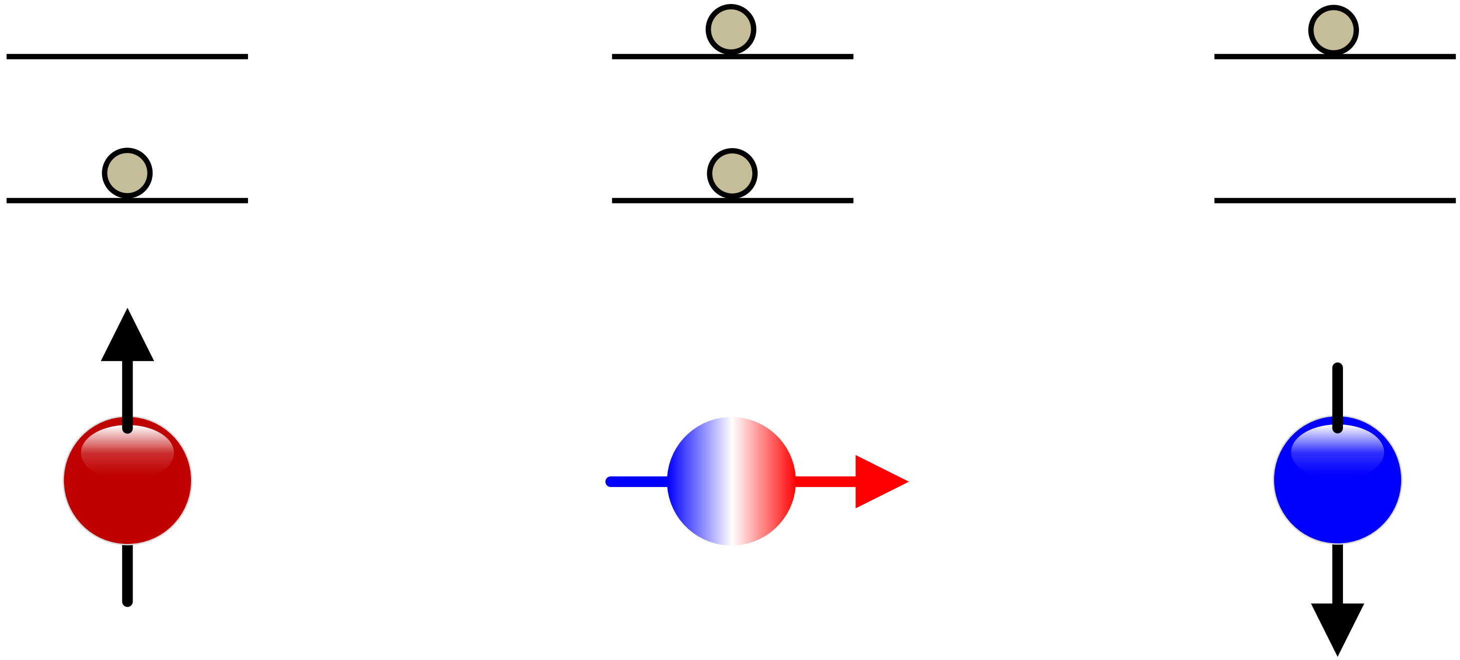


# Quantum coherence

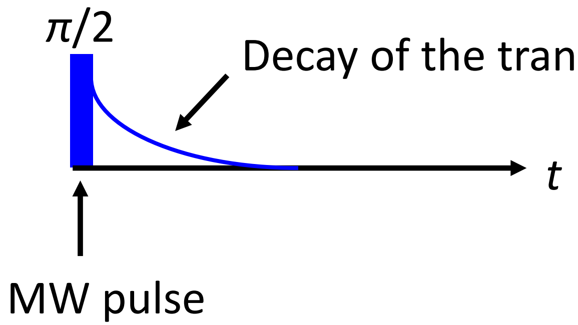


$$|0\rangle \equiv |m_s = 0\rangle \qquad |\Psi\rangle = \alpha|0\rangle + \beta|1\rangle \qquad |1\rangle \equiv |m_s = -1\rangle$$

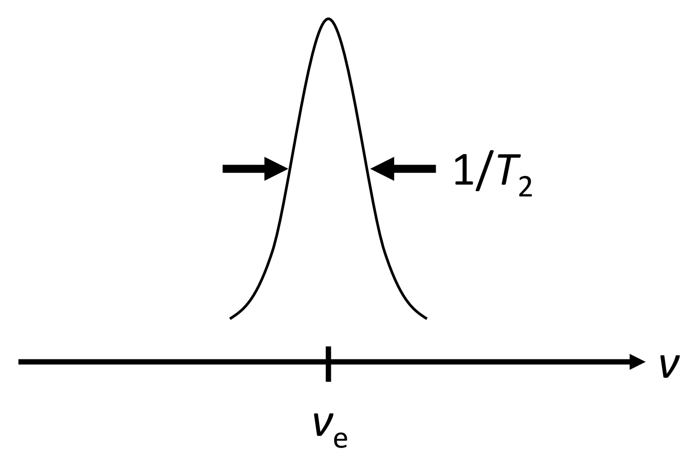
**$T_2$: measure of how long a superposition state is preserved**

# Measurement of $T_2$

**Time domain** → Decay time constant $T_2$

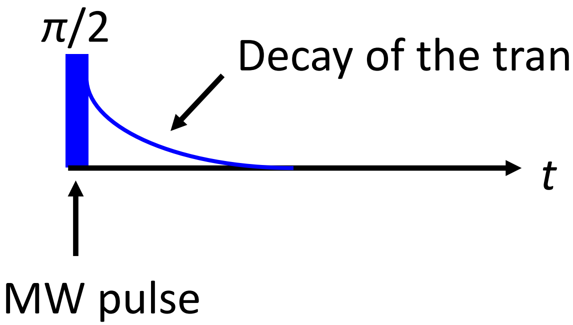



**Frequency domain** → Lorentz width

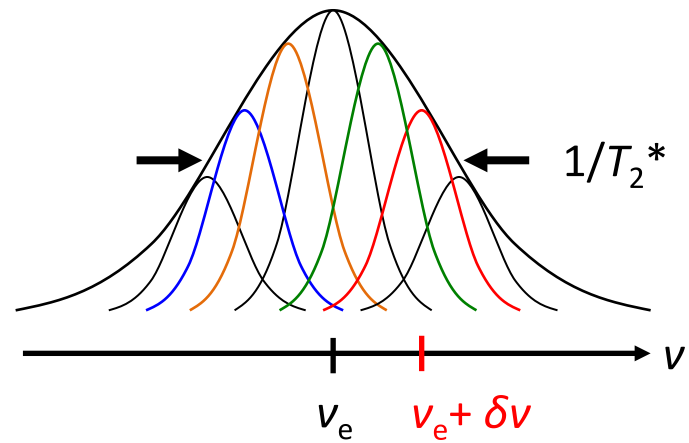


# Measurement of $T_2$

**Time domain** → Decay time constant $T_2$

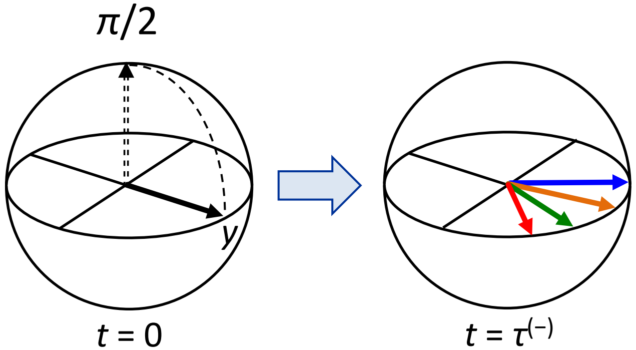


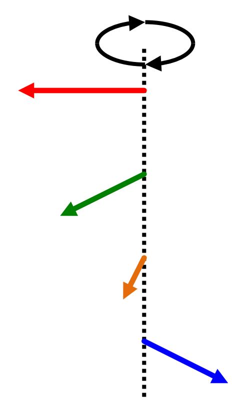

**Frequency domain** → Lorentz width



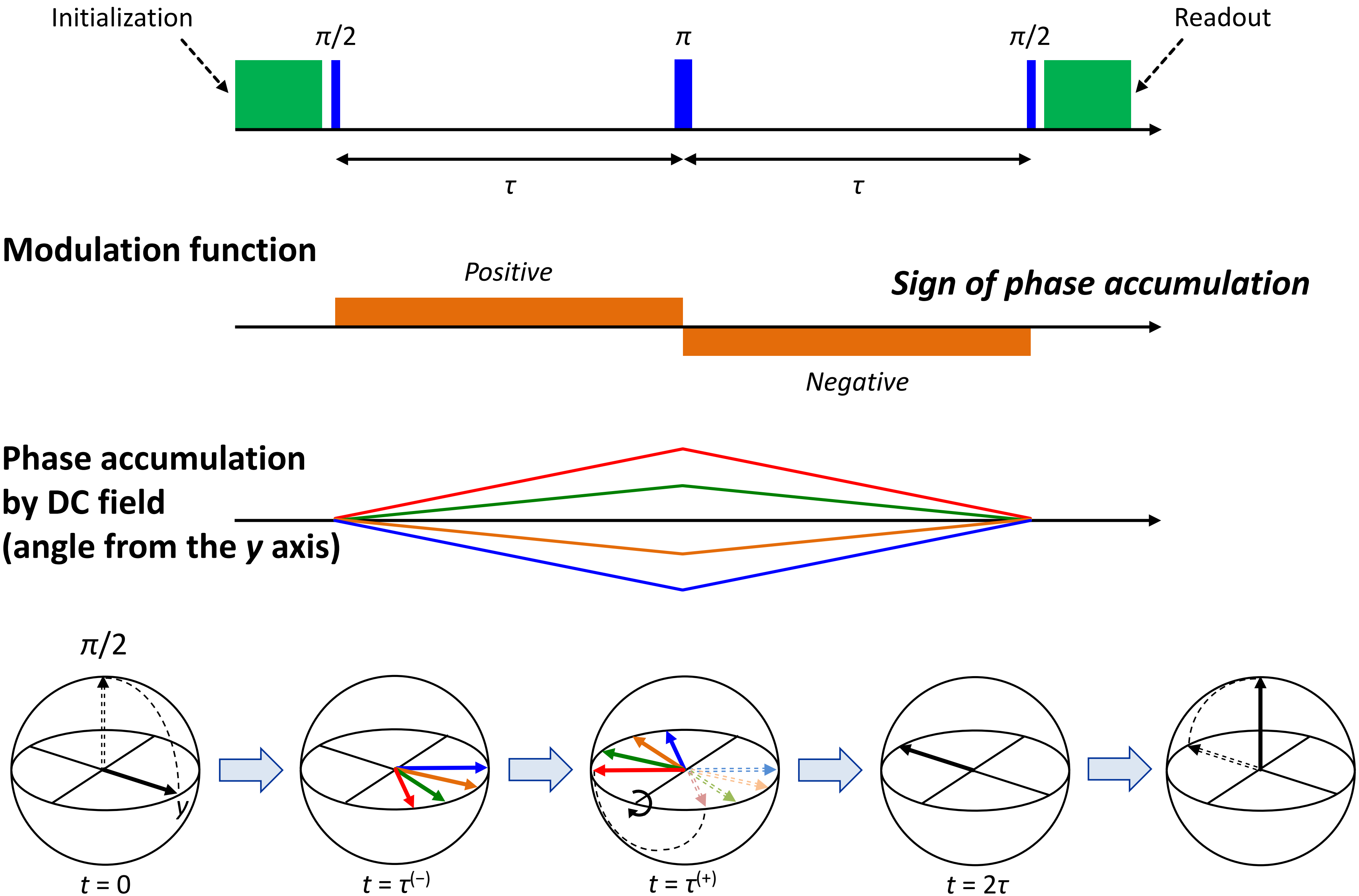

Inhomogeneous line broadening

Seen to precess at $\delta\nu$ in the frame rotating at $\nu_e$



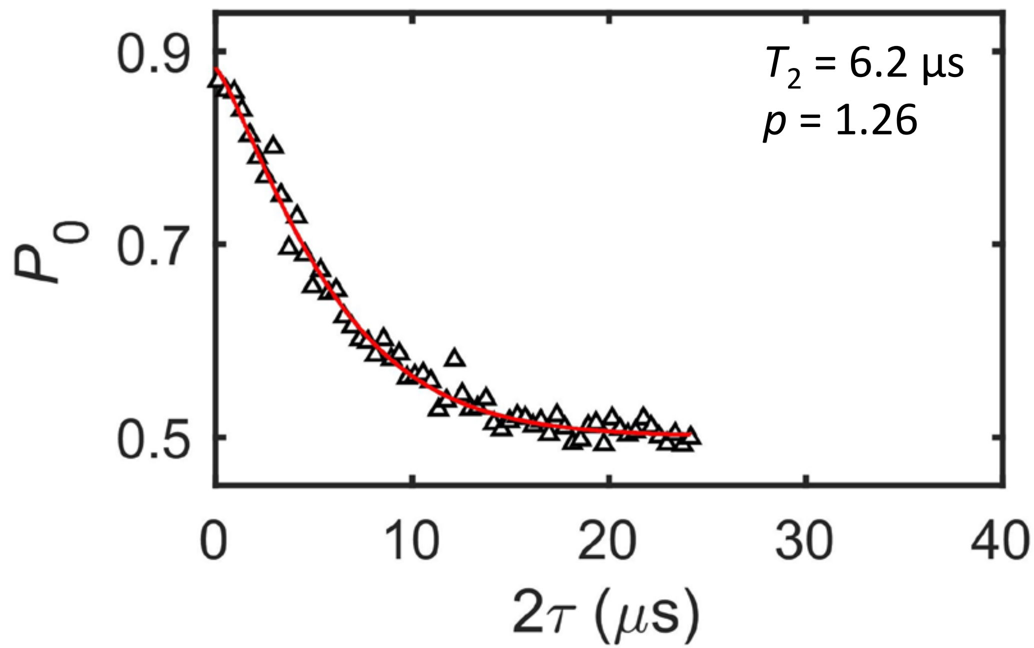



# Spin echo



Initialization
$\pi/2$
$\pi$
$\pi/2$
Readout
$\tau$
$\tau$
Modulation function
Positive
Sign of phase accumulation
Negative
Phase accumulation
by DC field
(angle from the y axis)
$\pi/2$
y
$t = 0$
$t = \tau^{(-)}$
$t = \tau^{(+)}$
$t = 2\tau$

# 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 Adv. **10**, 025206 (2020) Misonou *et al.*

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- **Basics of magnetic resonance**

- **Quantum sensing**
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  - Detection of proton spin ensemble
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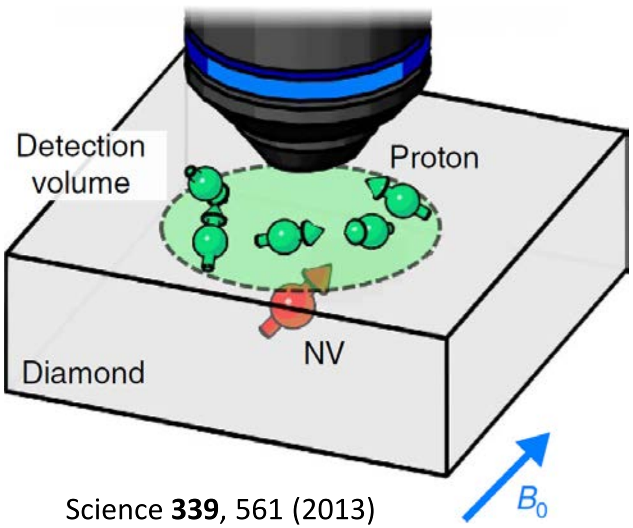
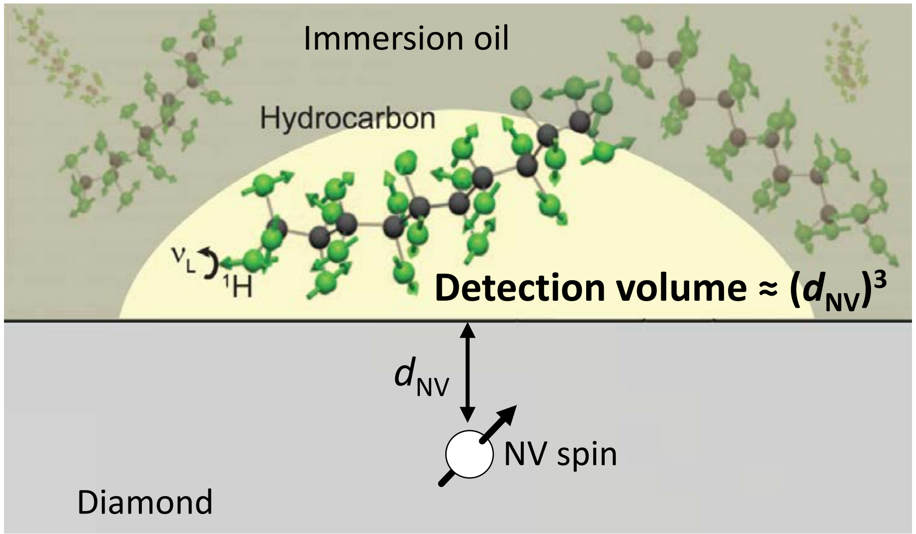
# Nuclear spin sensing




Science **339**, 561 (2013)



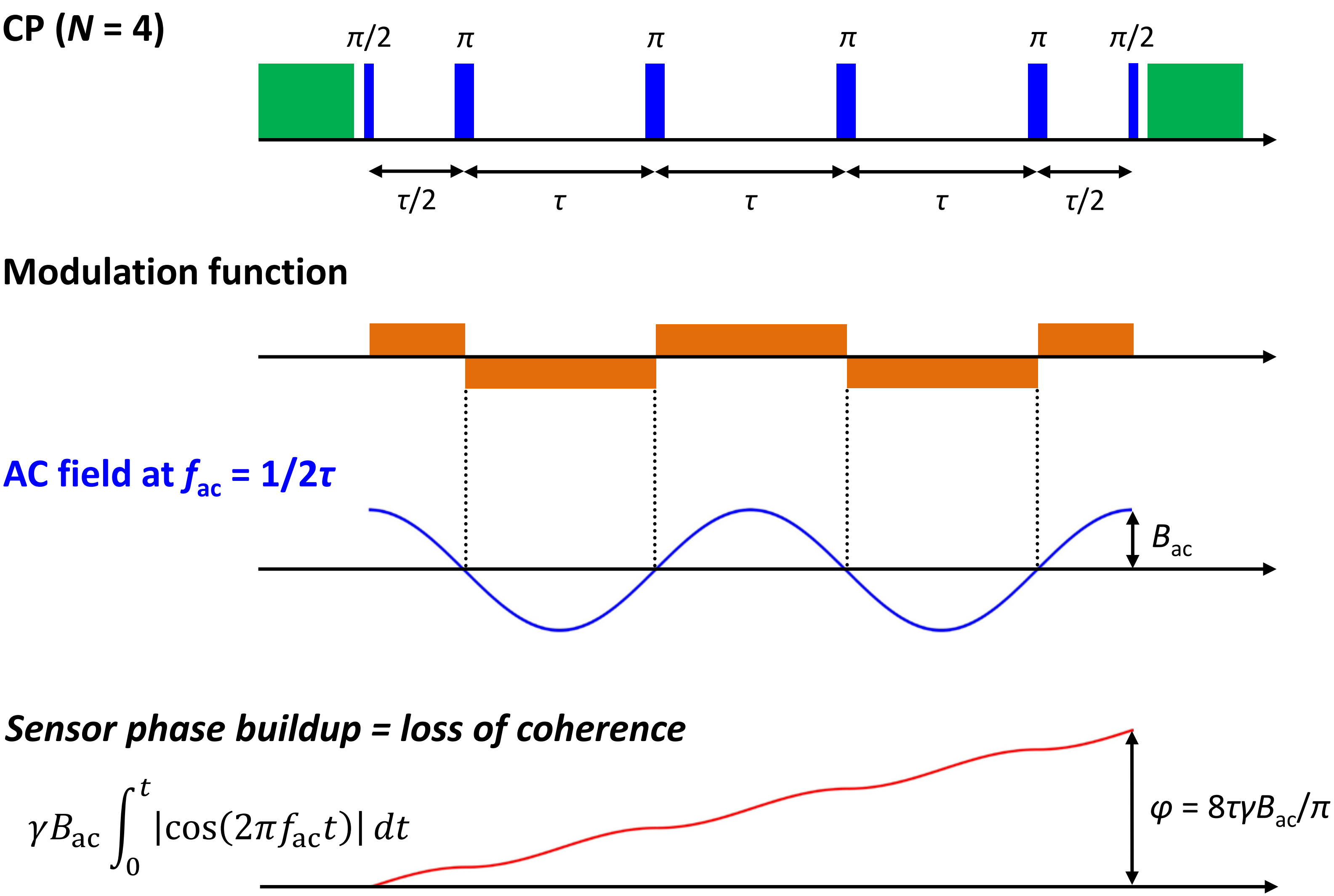

Nature Commun. **6**, 8527 (2015)

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

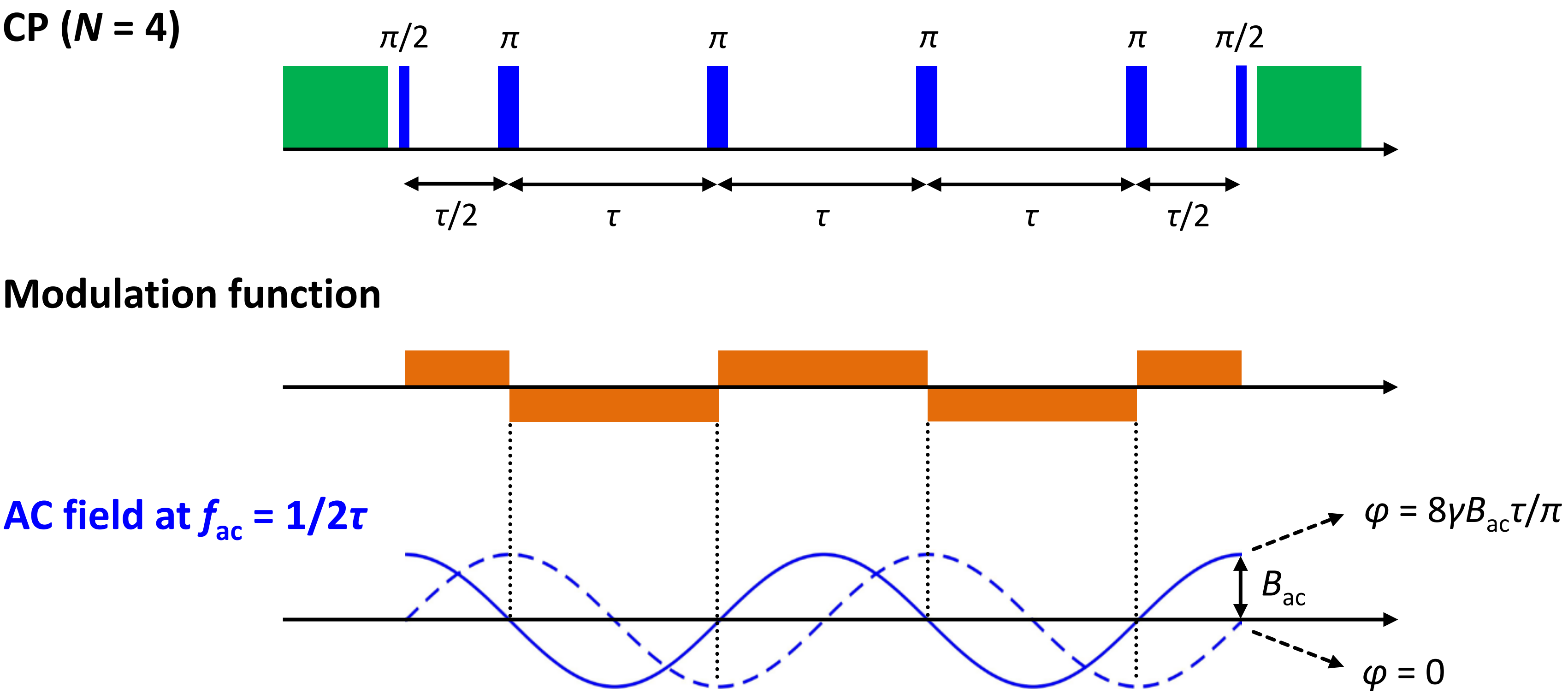
⇨ **Weak AC magnetic field** on the NV spin

⇨ Detect using **quantum coherence**

# AC magnetometry

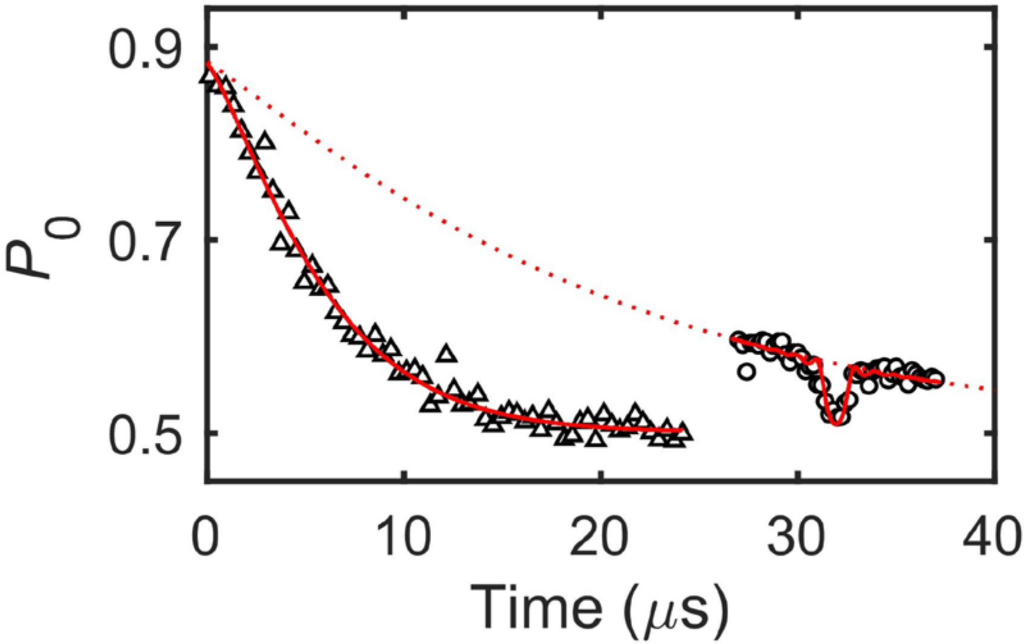


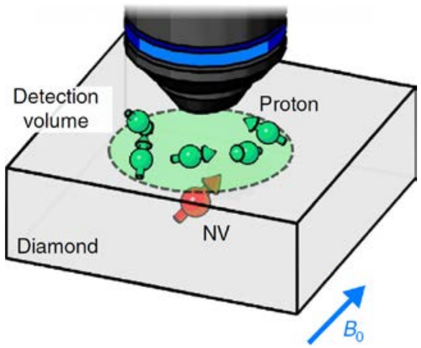
# AC magnetometry




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

# Nuclear spin sensing



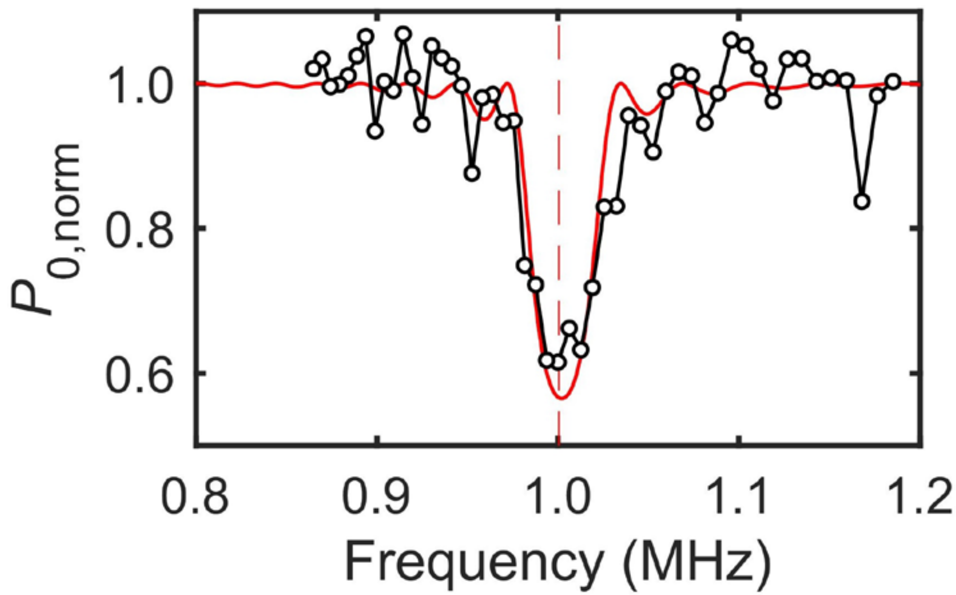




- $T_2$ = 6.2 μs @$B_0$ = 23.5 mT
- $N$ = 64 (XY16)
- $2\tau$ = 2 x 32 μs/64 = 1 μs

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

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

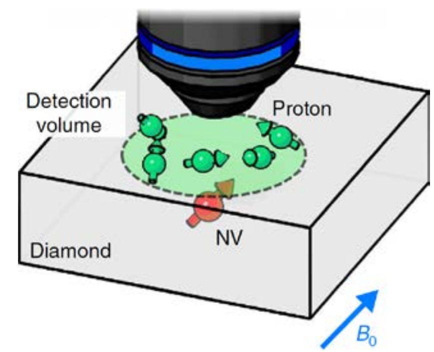
# Nuclear spin sensing




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

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

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



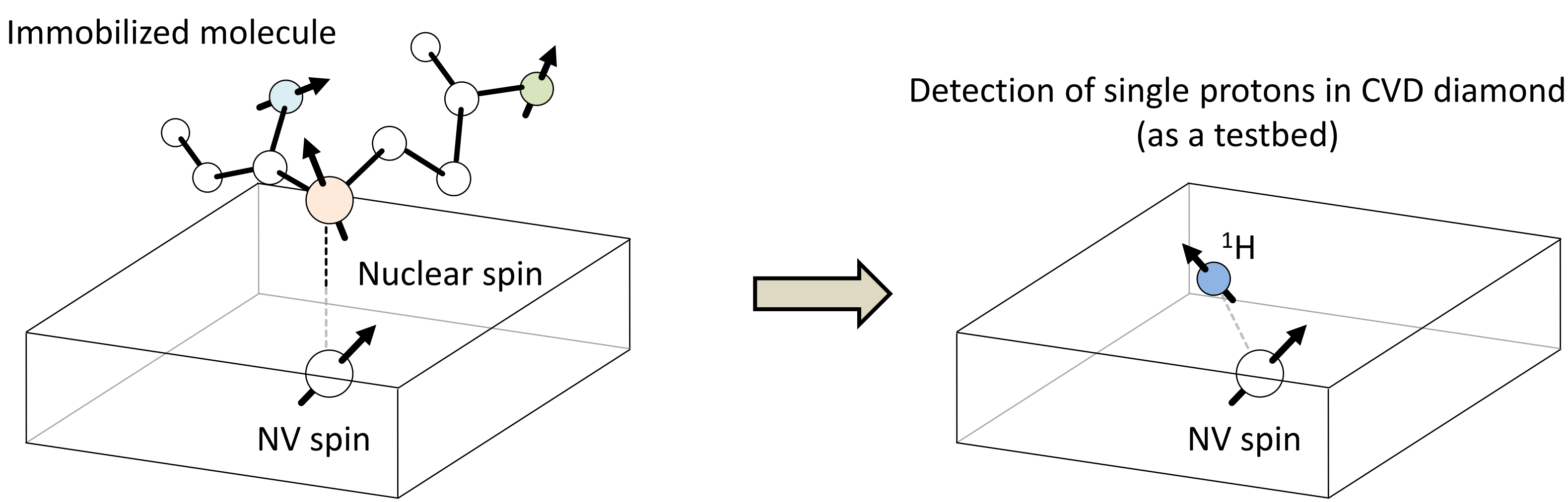

- Proton density $\rho$ = 6 x $10^{28}$ $m^{-3}$ (known)
- $d_{\mathrm{NV}}$ = 6.26 nm
- $B_{\mathrm{rms}}$ ≈ 560 nT
- Detection volume $(d_{\mathrm{NV}})^3$ ≈ 0.25 zL (zepto = $10^{-21}$)
- # of proton $\rho(d_{\mathrm{NV}})^3$ ≈ 1500
- Thermal pol. ($10^{-7}$) vs. statistical pol. $(1500)^{0.5}$ ≈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

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

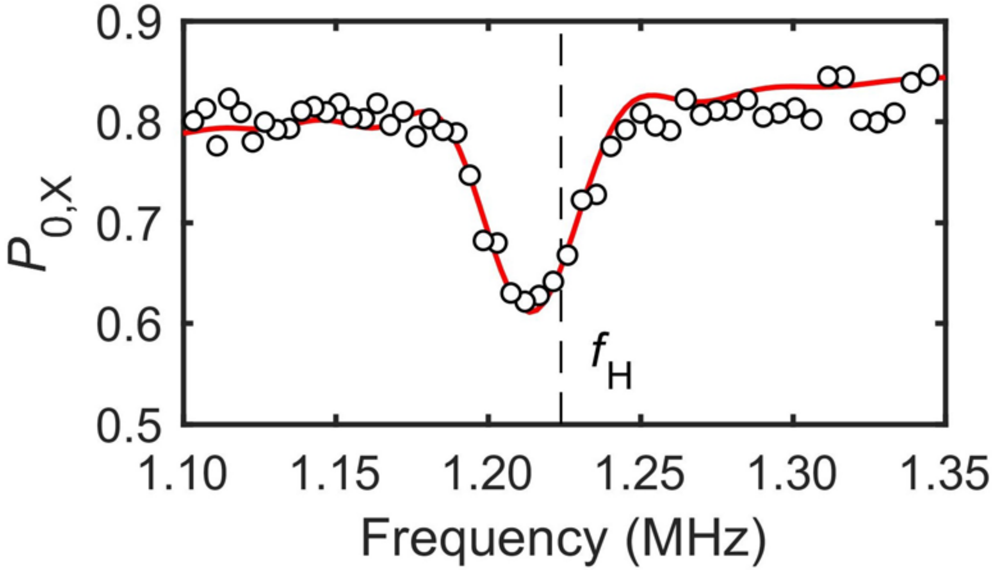
# Toward single-molecular imaging

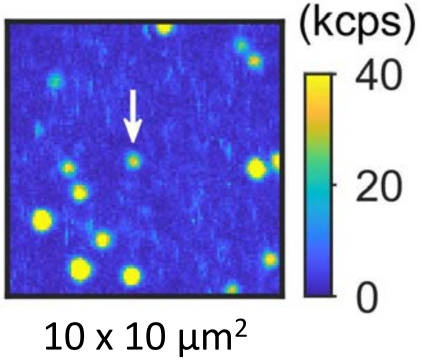
- **Strategy**
  → Detect **individual nuclear spins** in a single molecule
  → Determine their **nuclear species (& chemical shifts)** and **positions**

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



# Nuclear spin sensing

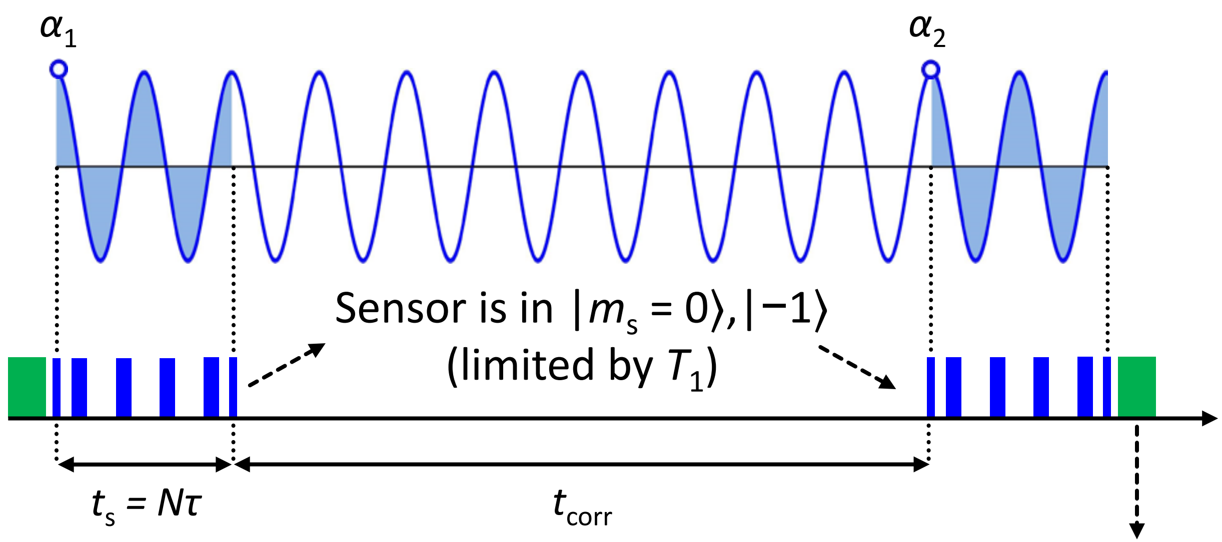



- Single NV in a N-doped CVD film ([$^{12}$C] = 99.999%)
- $N$ = 64 (XY16)
- $f_H = \gamma_H B_0$ = 42.577 kHz/mT x 28.7 mT = 1.2239 MHz

Appl. Phys. Lett. **117**, 114002 (2020) Sasaki *et al.*

# Correlation spectroscopy




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

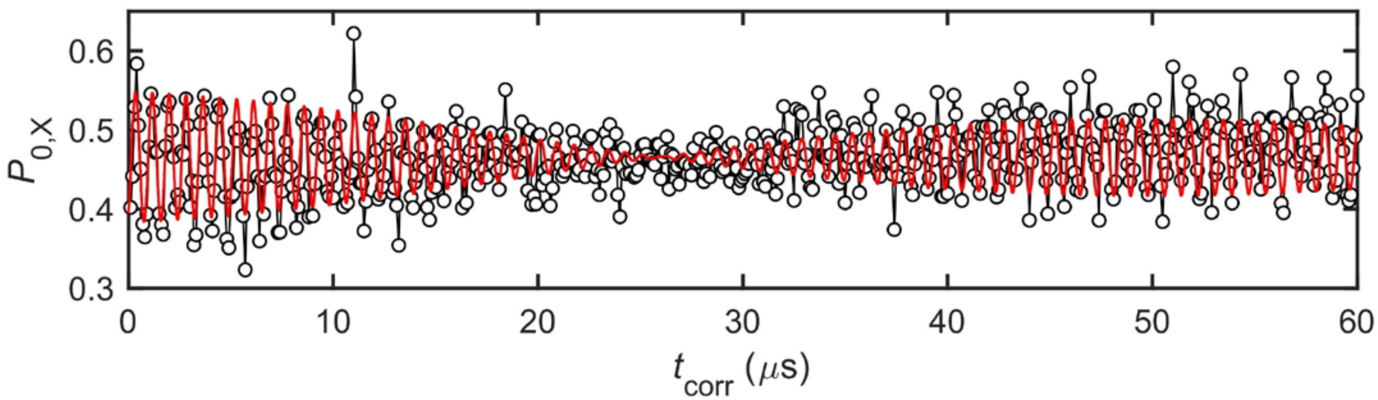
→ Sweep $t_{corr}$

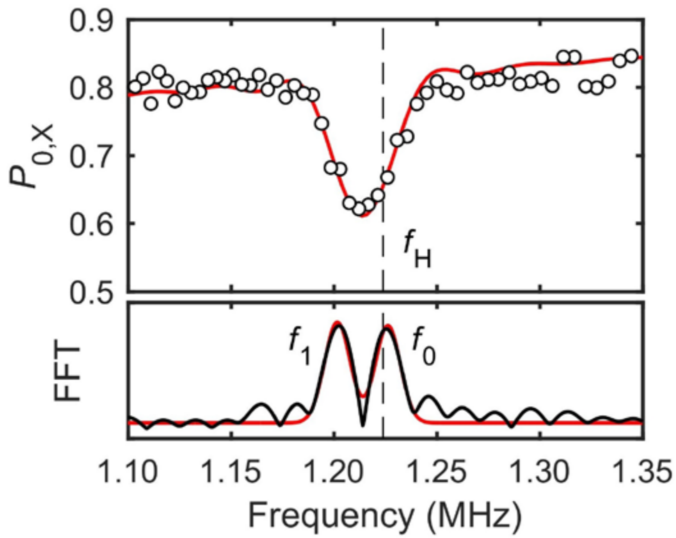
**The transition probability for random phases (α)**

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

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 of a nucleus

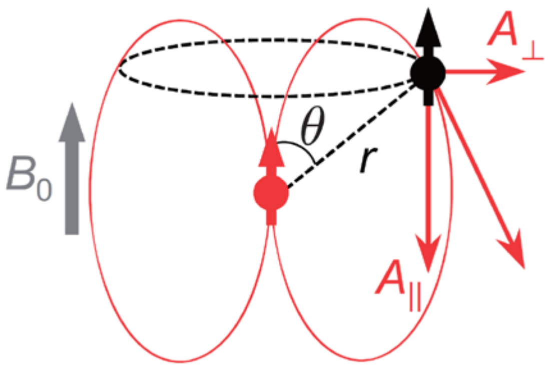



- $f_0$ = 1.2234 MHz
- $f_1$ = 1.2046 MHz

Appl. Phys. Lett. **117**, 114002 (2020) Sasaki *et al.*

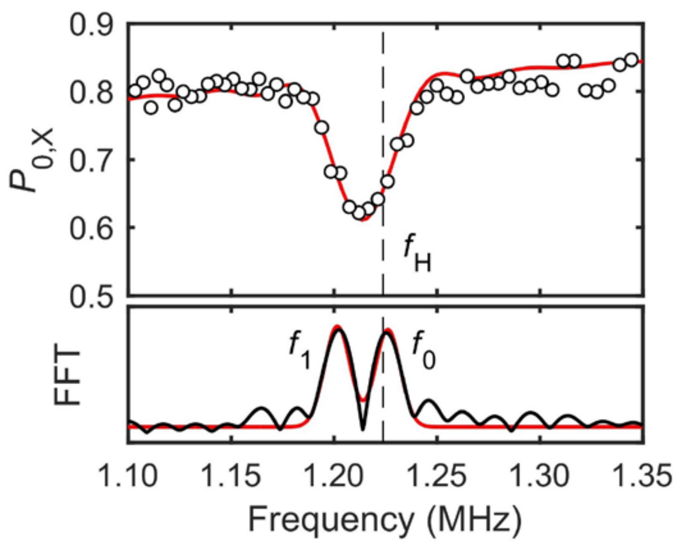
# Correlation spectroscopy of a nucleus




**Hamiltonian of NV–[1]H coupled system**

$$H = f_{\mathrm{H}} I_z + |m_s = -1\rangle\langle -1|(A_\parallel I_z + A_\perp I_x)$$

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

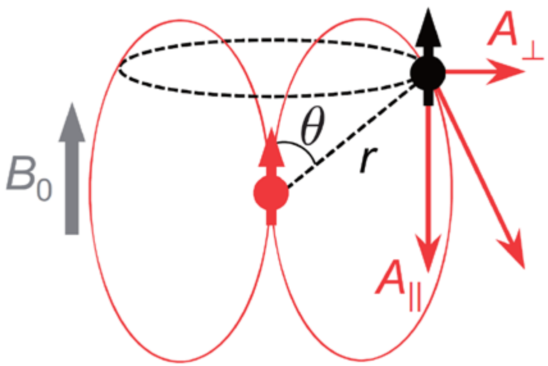



- $f_0$ = 1.2234 MHz = $f_H$ ($m_s$ = 0)
- $f_1$ = 1.2046 MHz = $f_H + A'_\parallel$ ($m_s$ = −1)

$A'_\parallel$ = −18.8 kHz
$(f_0 + f_1)/2$ = 1.2140 MHz → dip

Appl. Phys. Lett. **117**, 114002 (2020) Sasaki *et al.*

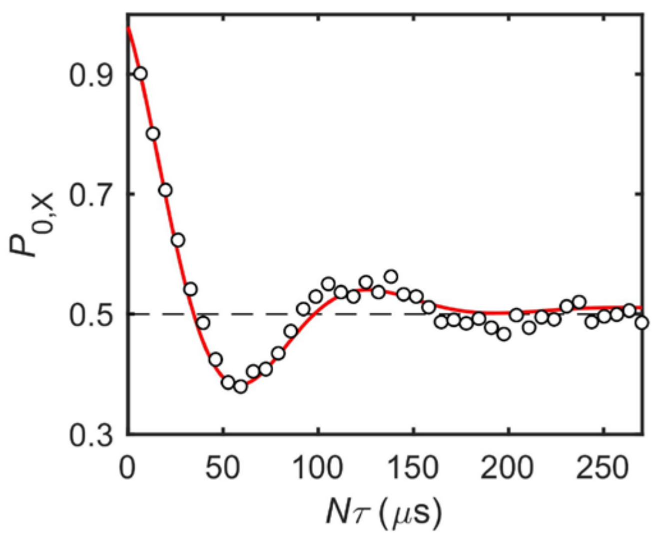
# Coherent control of a nuclear spin




**Hamiltonian of NV–[1]H coupled system**

$$H = f_{\mathrm{H}} I_z + |m_s = -1\rangle\langle -1|(A_\parallel I_z + A_\perp I_x)$$

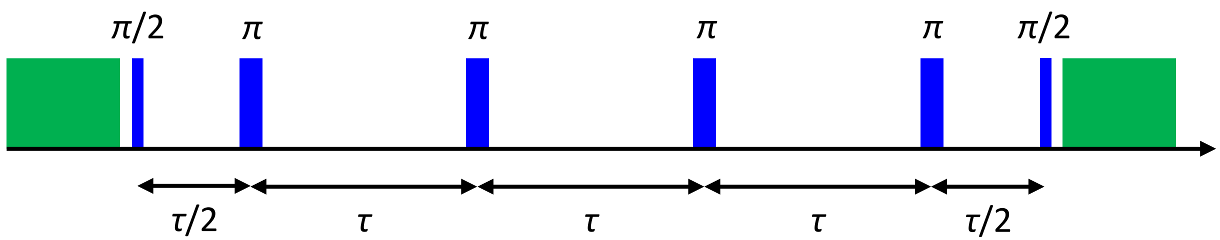
**→ The single [1]H *n*-spin rotates about the $A_\perp$ axis**



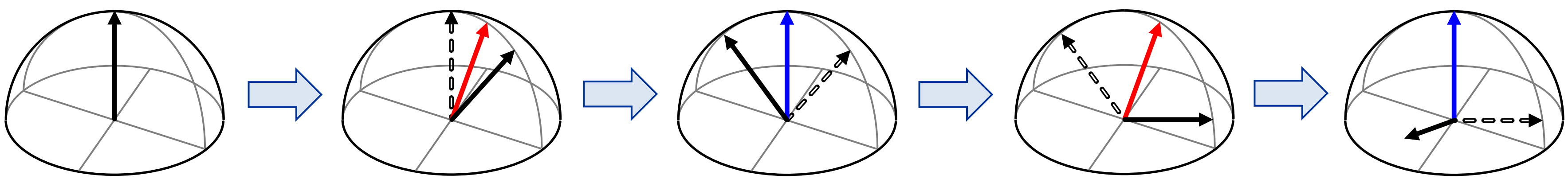

- $N$ → 656 ($\tau$ = 412.5 ns, fixed)
- $f_{osc}$ = 7.414 kHz = $A'_\perp/2$

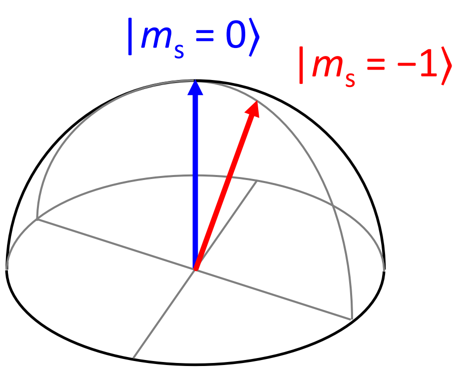
Appl. Phys. Lett. **117**, 114002 (2020) Sasaki *et al.*

# Conditional rotation of a nuclear spin



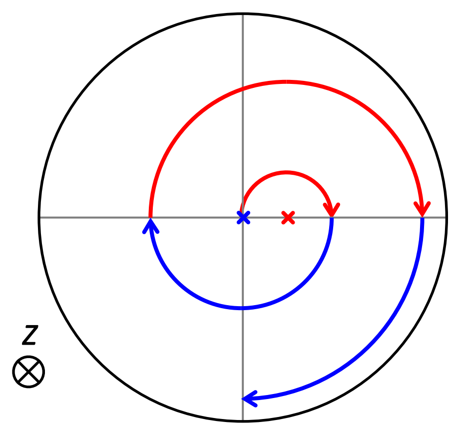

**Evolution of *n*-spin vector**



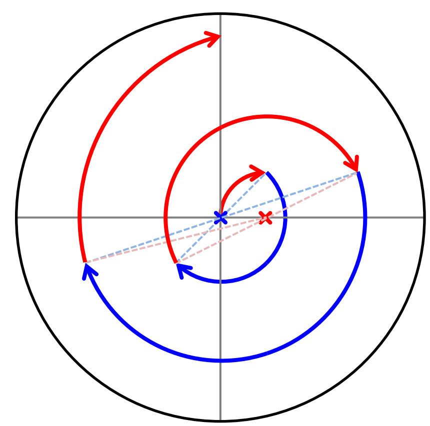



q-axis of *n*-spin

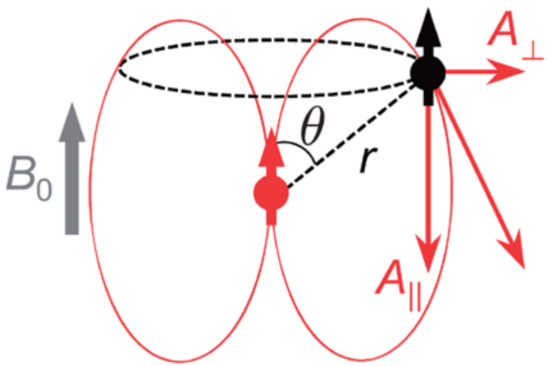
***Start from*** $|m_s = 0\rangle$




***Start from*** $|m_s = -1\rangle$



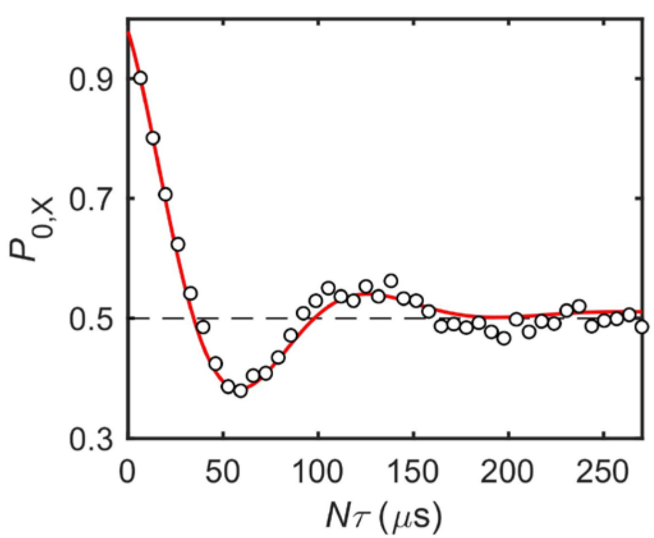
# Coherent control of a nuclear spin




**Transition probability of the NV spin**

$$P_{0,\mathrm{X}} = 1 - \frac{1}{2}(1 - \underbrace{\boldsymbol{n}_0 \cdot \boldsymbol{n}_{-1}}_{-1}) \sin^2 \frac{N\phi_{\mathrm{cp}}}{2}$$

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

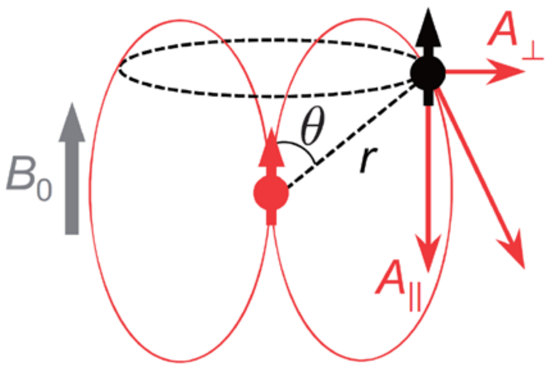



- $N \rightarrow 656$ ($\tau$ = 412.5 ns, fixed)
- $f_{osc}$ = 7.414 kHz = $A'_\perp/2$

$P_X < 0.5 \rightarrow$ Single proton!

Appl. Phys. Lett. **117**, 114002 (2020) Sasaki *et al.*

# Determination of hyperfine constants




**Magnetic dipole interaction**

$$A_\parallel = h\gamma_e\gamma_H \frac{3\cos^2\theta - 1}{r^3}$$

$$A_\perp = h\gamma_e\gamma_H \frac{3\cos\theta\sin\theta}{r^3}$$

$A_\parallel$ = −19.0 kHz
$A_\perp$ = 22.9 kHz

⟺

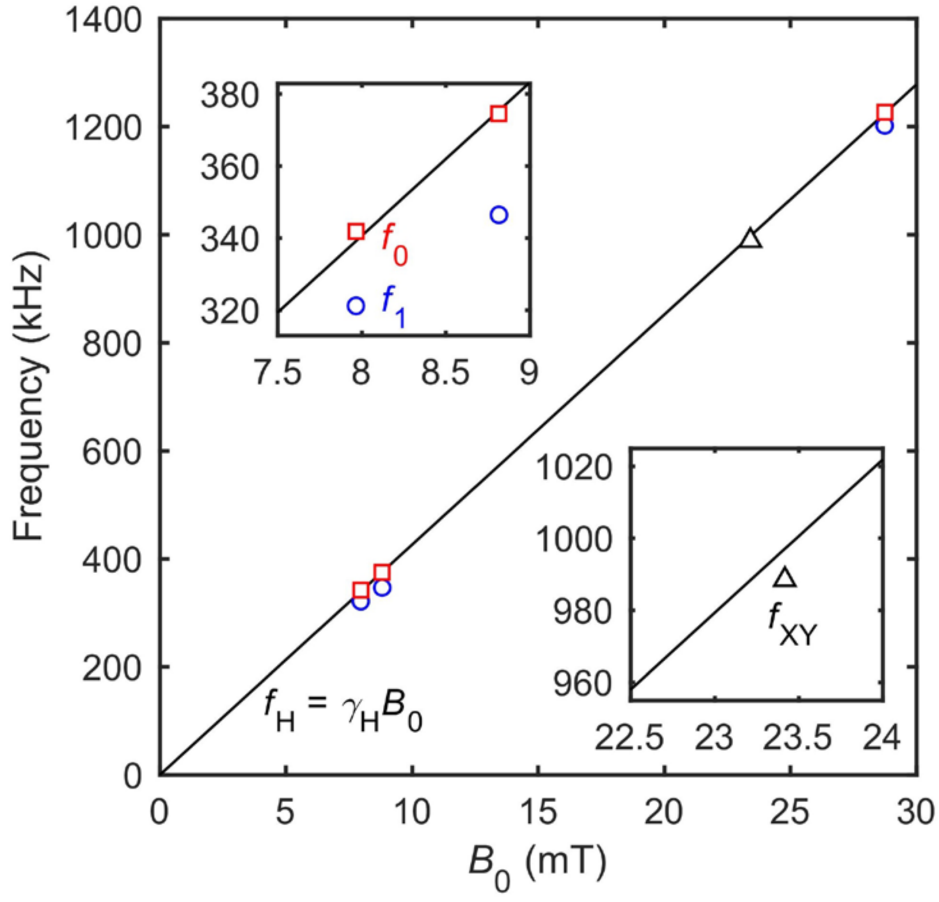
$r$ = 1.44 nm
$\theta$ = 72.3°

The position of the nucleus can be determined
→ Molecular structure analysis

(Azimuthal angle $\phi$) Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

Appl. Phys. Lett. **117**, 114002 (2020) Sasaki *et al.*

# Magnetic field dependence



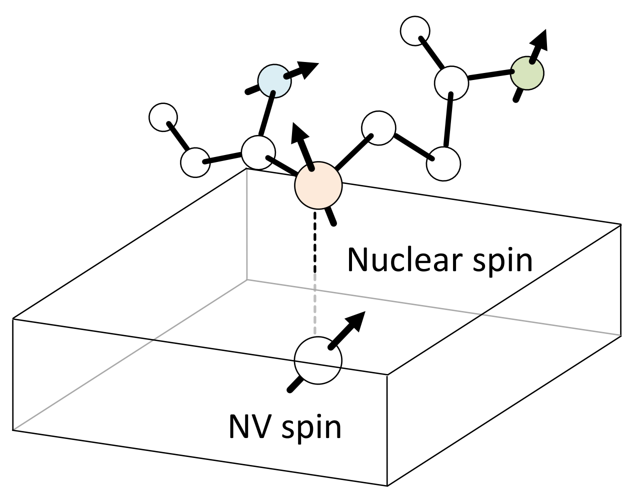

($\gamma_H/\gamma_C$ = 3.97 → Spurious harmonics?) Phys. Rev. X **5**, 021009 (2015) Loretz *et al.*

Appl. Phys. Lett. **117**, 114002 (2020) Sasaki *et al.*

# Toward single-molecular imaging

- **Spatial resolution**
  → Accurate measurement of *e*–*n* int. const's ($A_{\parallel}$, $A_{\perp}$) ≈ ($r$, $\theta$)
  → Information on the azimuthal angle $\phi$

- **Spectral resolution**
  → Nuclear species
  → *J*-couplings & chemical shifts (ppm!)
  → Limited by sensor/memory lifetimes ($T_{2e/n}$, $T_{1e/n}$)



# Toward single-molecular imaging

- **Spatial resolution**
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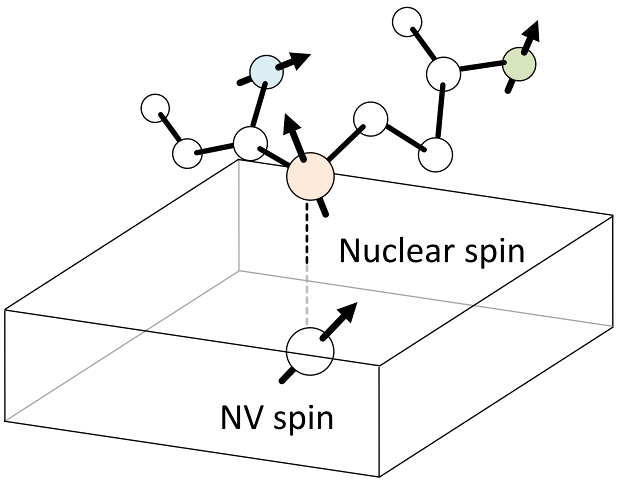
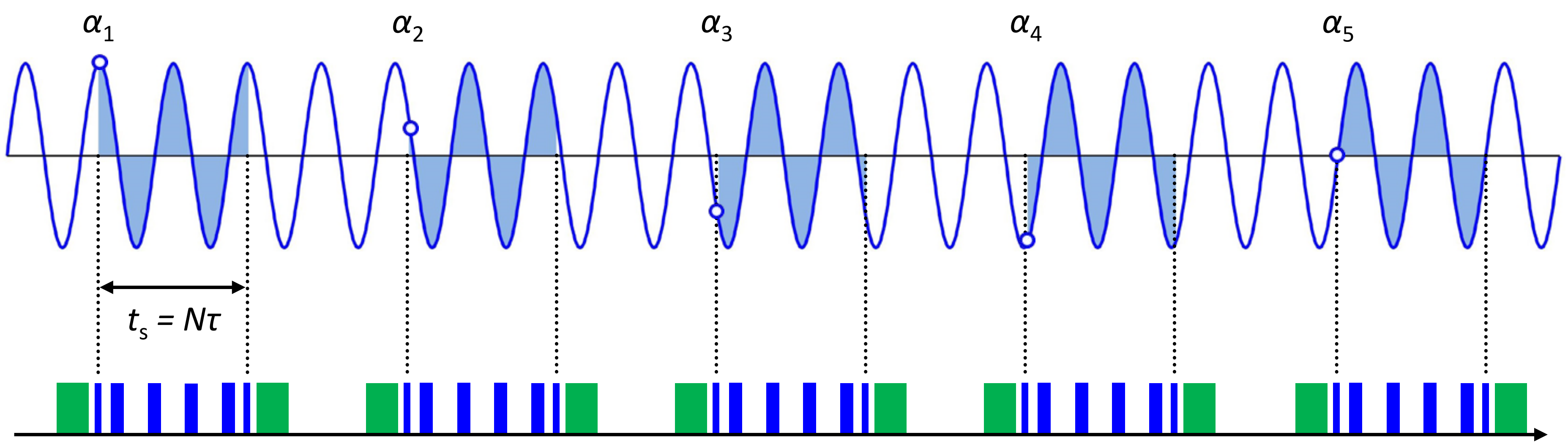
  → Limited by sensor/memory lifetimes ($T_{2e/n}$, $T_{1e/n}$)

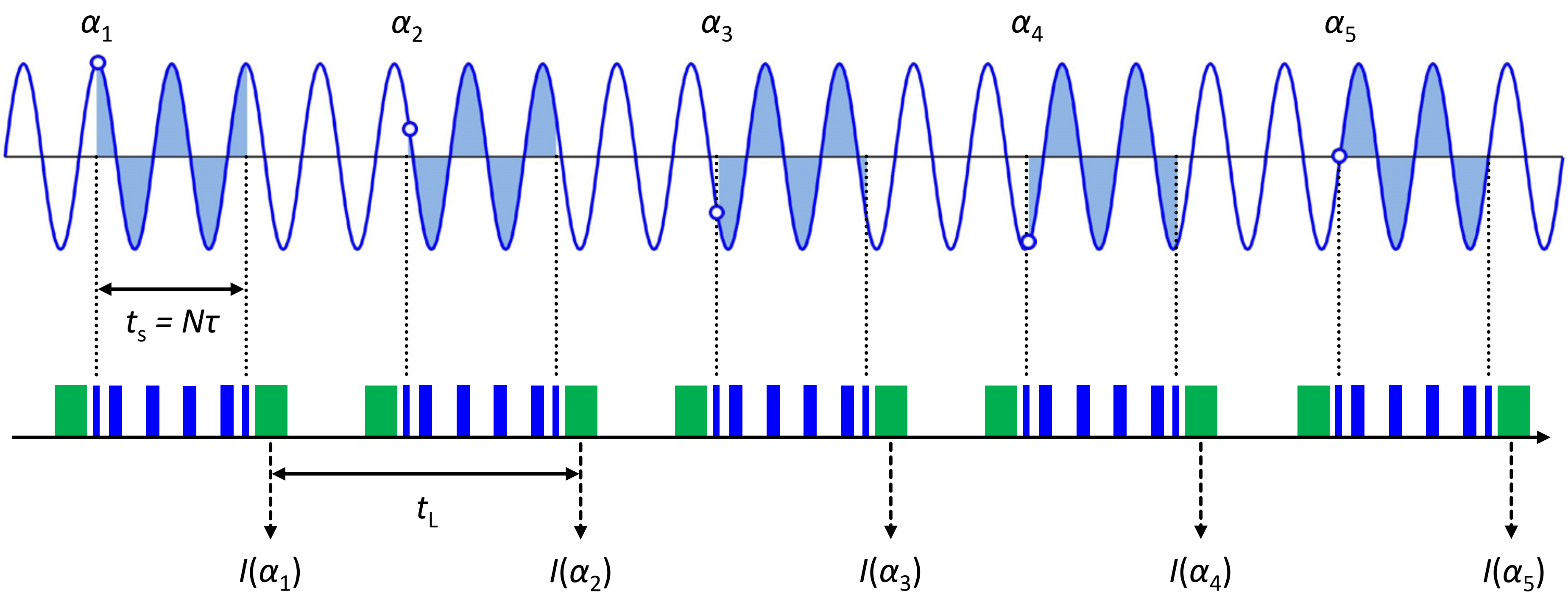


# AC magnetometry revisited




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

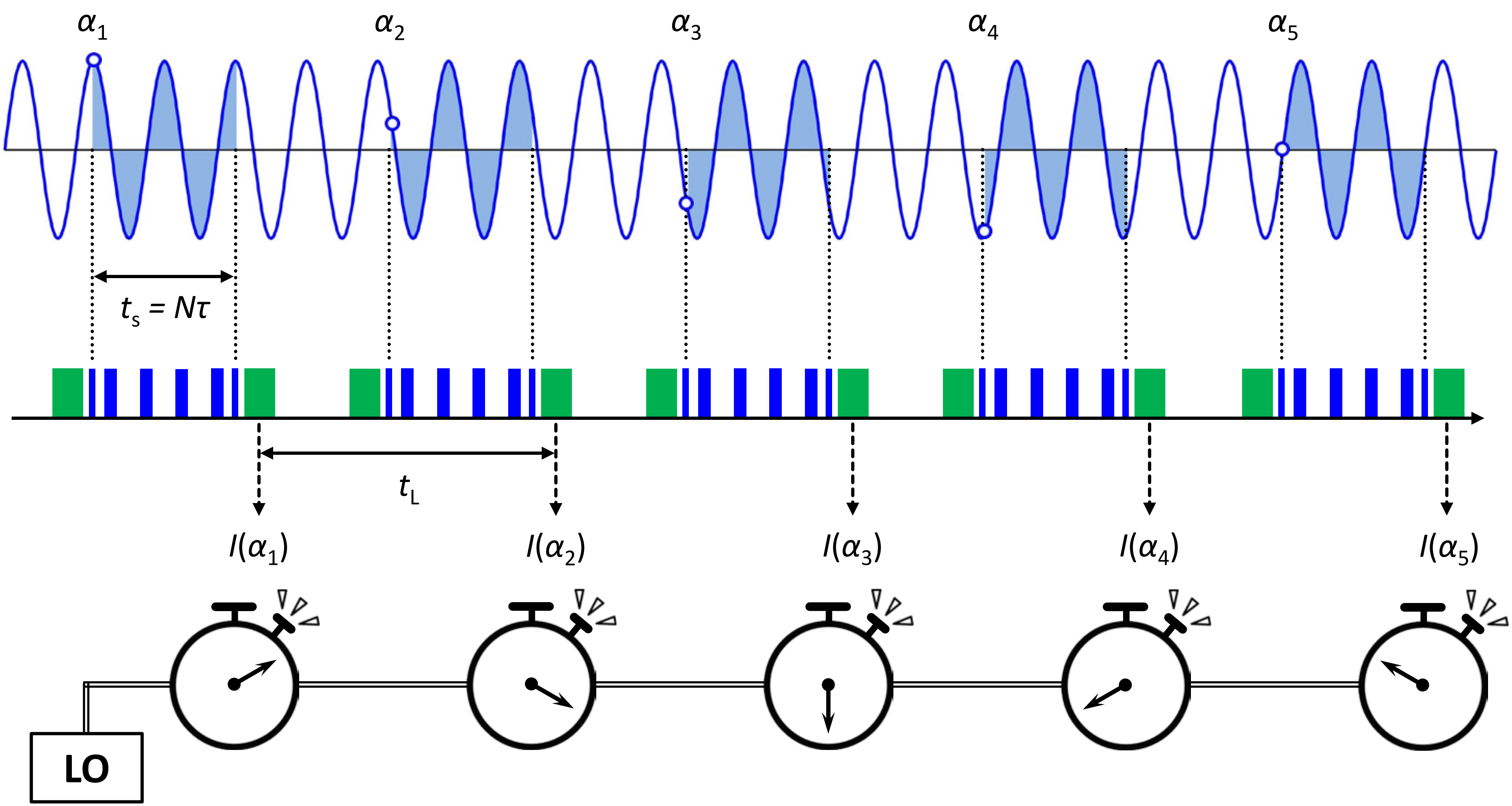
# Ultrahigh resolution sensing




- $\varphi$ 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 $\alpha$'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

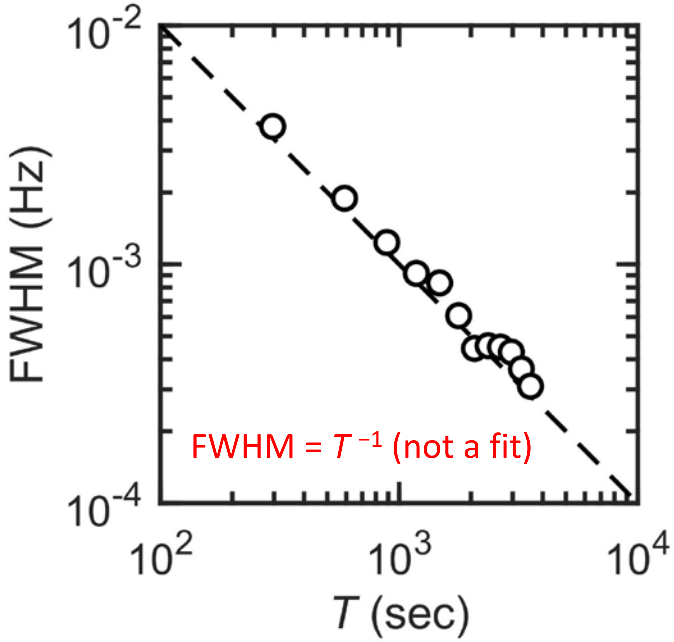


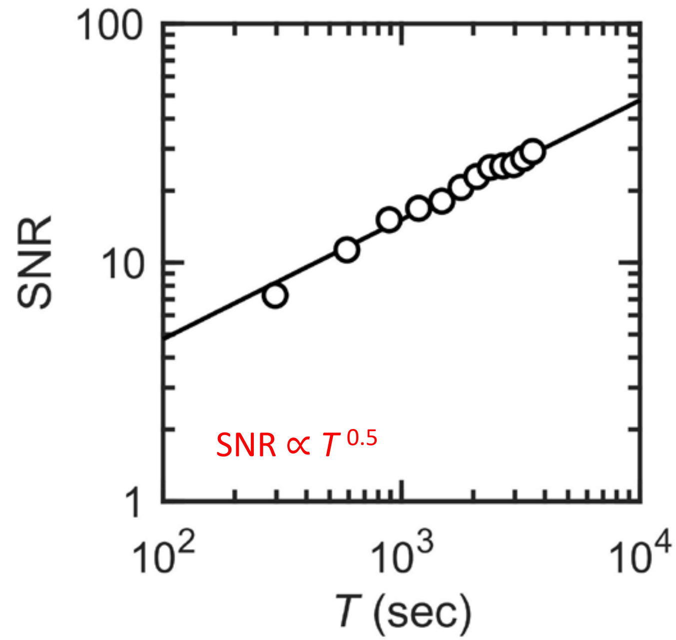

**Undersampled, sensor-lifetime-unlimited signal**

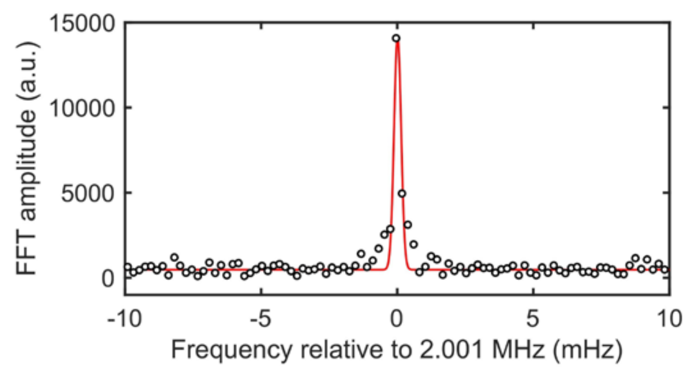
Science **356**, 832 (2017) Schmitt *et al.*; Science **356**, 837 (2017) Boss *et al.*; Nature **555**, 351 (2018) Glenn *et al.*

# Ultrahigh resolution sensing

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



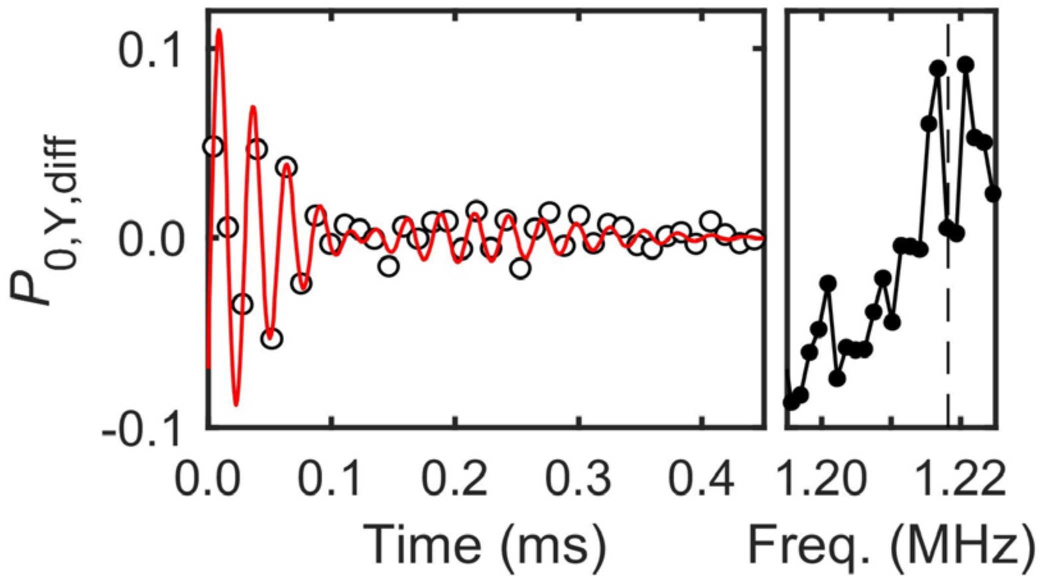



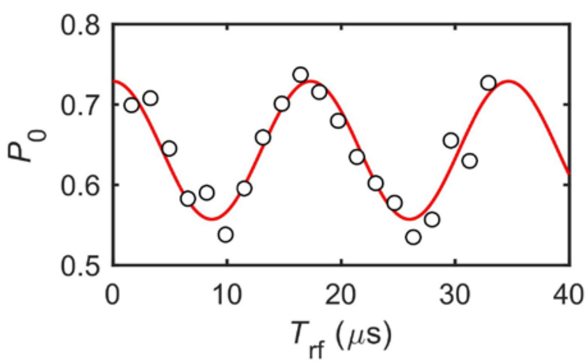

- $T$ = 3600 sec
- FWHM = 0.304 mHz

J. Appl. Phys. **123**, 161101 (2018) Abe *et al.*

# Free induction decay




**Nuclear Rabi oscillation**




- $T_{rf,\ \pi/2}$ = 4.115 μs
- [PulsePol]–$T_{rf,\ \pi/2}$–[X/2–(XY16)–Y/2–$L_{RO}$]$^{50}$
- $f_{sample} = 1/t_L$ = 84.46 kHz
- $f_p = (f_0+f_1)(t_s/t_L)/2+f_0(t_s-t_L)/t_L$ = 1.2182 MHz
  → Split (analogous to chemical shifts)

Appl. Phys. Lett. **117**, 114002 (2020) Sasaki *et al.*

# Summary

- **Tools for single-molecule imaging/structural analysis are being developed**
  → Ultrahigh resolution sensing[1,2,3], resolving chemical shifts[3,4] & suppression of back action from *n*-spins[5,6]
  → Determination of the position of individual *n*-spins[7,8,9]
  → Detection and control of single proton spins[10,11]


[1] Science **356**, 832 (2017) Schmitt *et al.* (Ulm)
[2] Science **356**, 837 (2017) Boss *et al.* (ETH)
[3] Nature **555**, 351 (2018) Glenn *et al.* (Harvard)
[4] Science **357**, 67 (2017) Aslam *et al.* (Stuttgart)
[5] Nature Commun. **10**, 594 (2019) Pfender *et al.* (Stuttgart)
[6] Nature **571**, 230 (2019) Cujia *et al.* (ETH)
[7] Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.* (Keio)
[8] Phys. Rev. Lett. **121**, 170801 (2018) Zopes *et al.* (ETH)
[9] Nature **576**, 411 (2019) Abobeih *et al.* (Delft)
[10] Phys. Rev. Lett. **113**, 197601 (2014) Sushkov *et al.* (Harvard)
[11] Appl. Phys. Lett. **117**, 114002 (2020) Sasaki *et al.* (Keio)