# Detection of Nuclear Spins Using Nitrogen-Vacancy Centers in Diamond

**Eisuke Abe**

*Spintronics Research Center, Keio University*

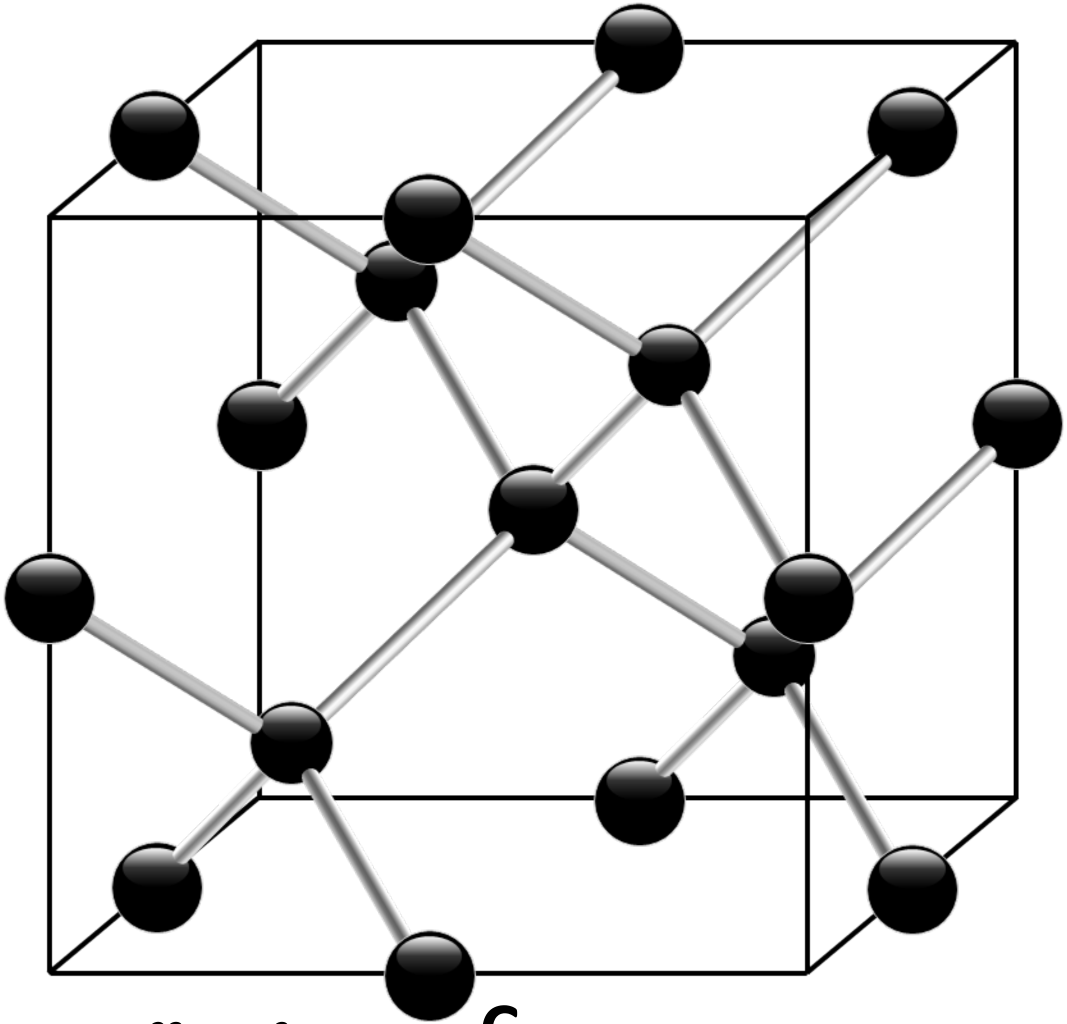
2018.12.07

Materials Science Seminar@JAIST

# Diamond envy

©Lucara Diamond

1109 carats, $70M



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

**C**

# Diamond NV

©Lucara Diamond

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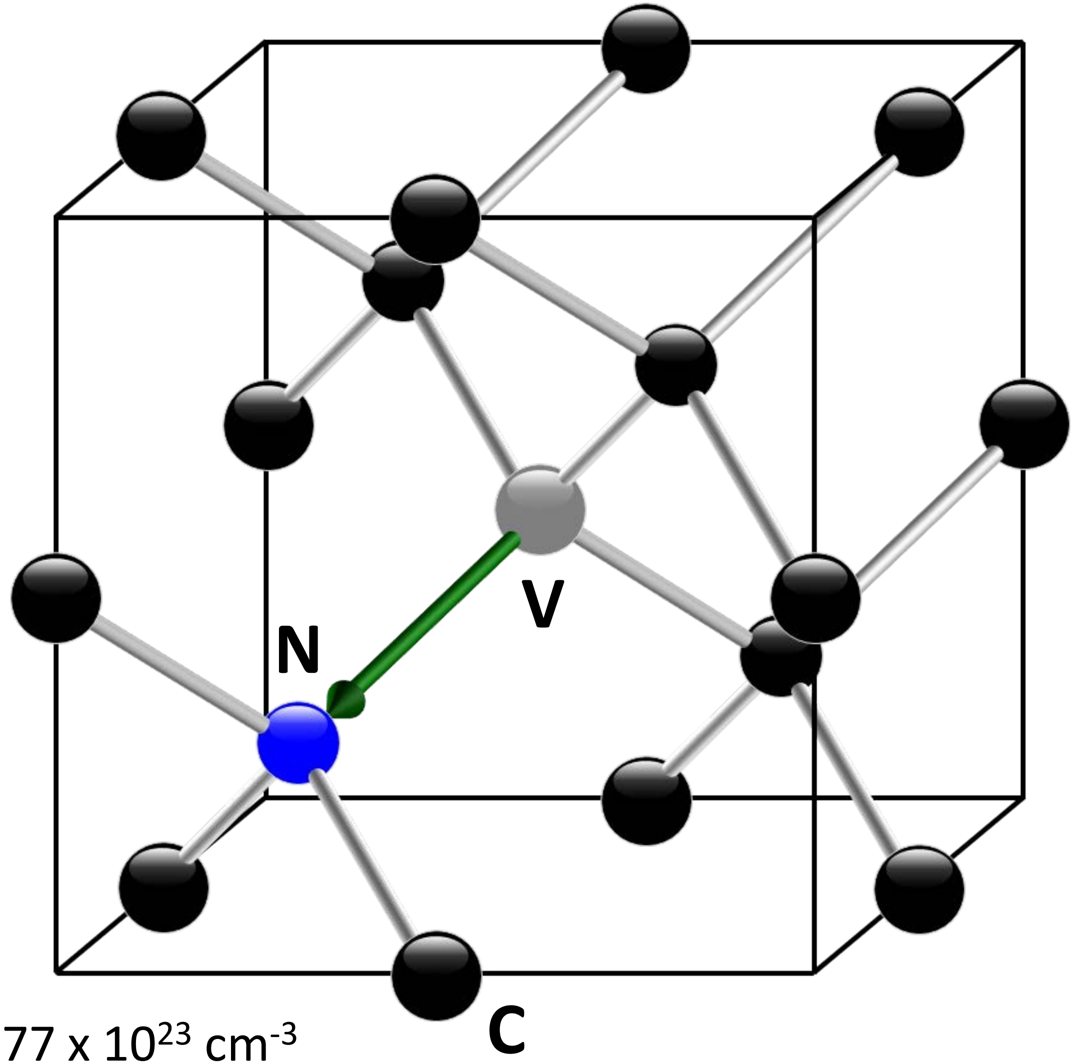
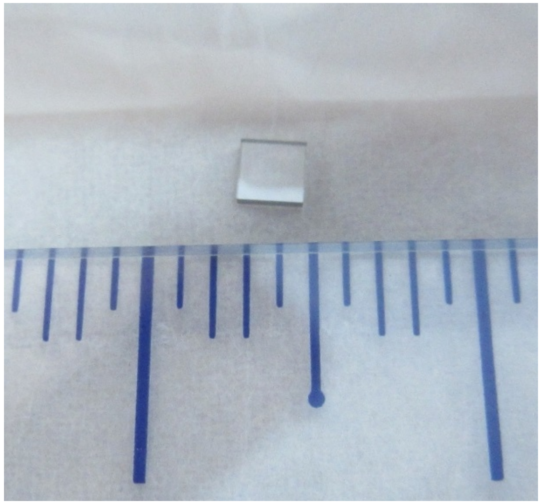
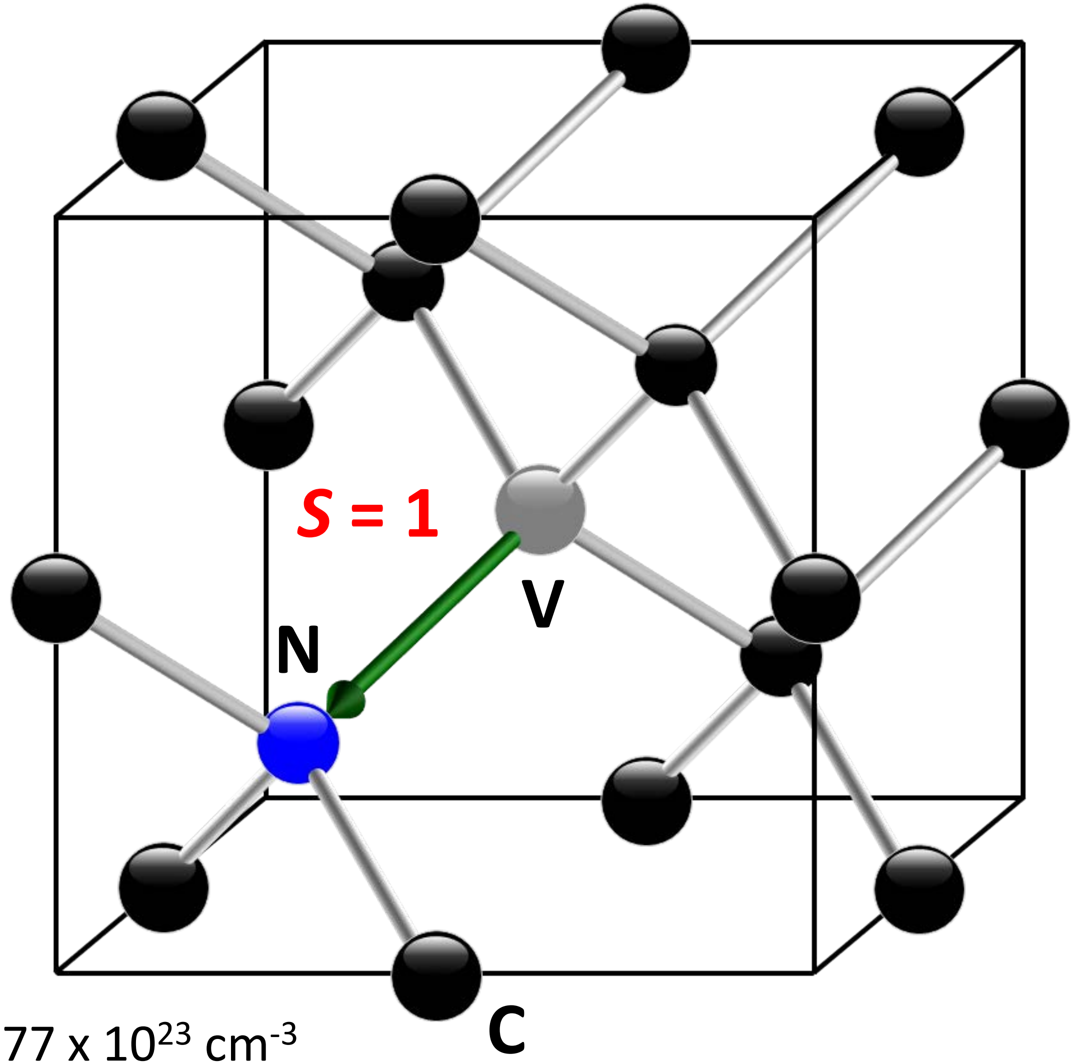


$\rho_N = 1.77 \times 10^{23}\ \mathrm{cm}^{-3}$

# Diamond NV



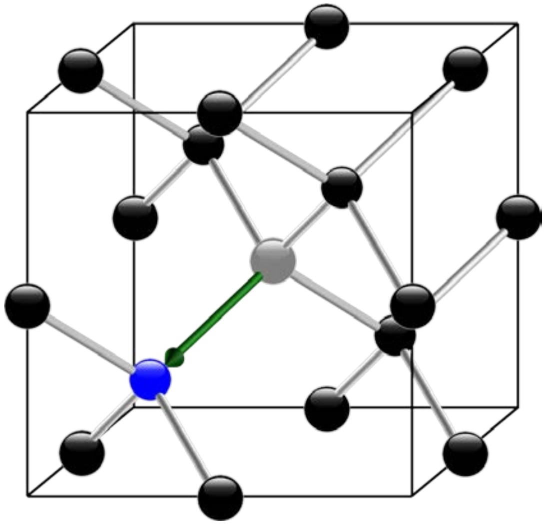
$2^2$ x 0.5 $mm^3$, \$700 (E6)
[N] < 5 ppb, [NV] < 0.03 ppb



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

# Why a single NV spin?

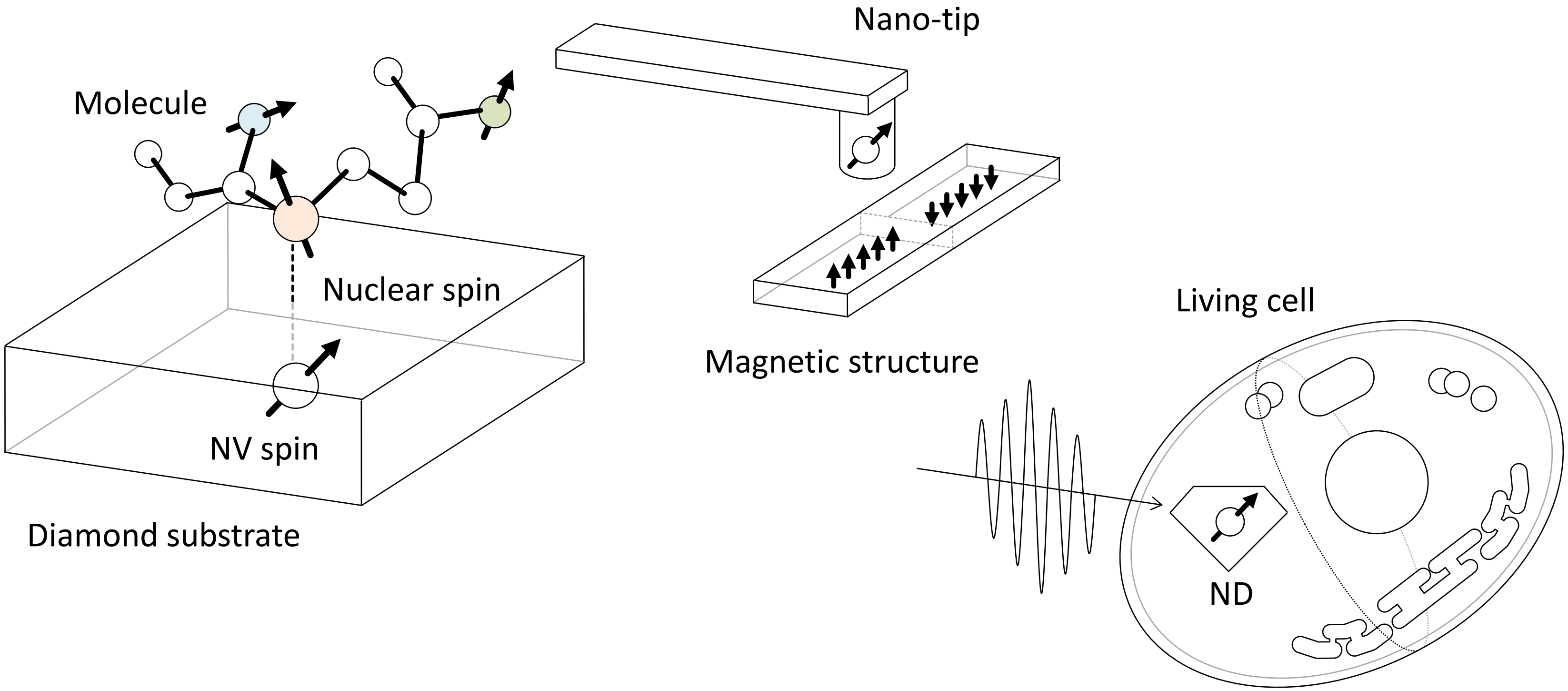
- Optically active (init. & readout)
- Microwave spin control
- High coherence (LT–RT–500 K)



⇨ **Quantum sensing & Quantum network**

[**Biology**] Annu. Rev. Phys. Chem. **65**, 83 (2014) Schirhagl *et al.*
[**Magnetometry**] Rep. Prog. Phys. **77**, 056503 (2014) Rondin *et al.*
[**Magnetic resonance**] J. Mag. Res. **269**, 225 (2016) Wrachtrup *et al.*
[**Quantum technologies**] Nature Photon. **12**, 516 (2018) Awschalom *et al.*
[**Quantum internet**] Science **362**, eaam9288 (2018) Wehner *et al.*

# Quantum sensing

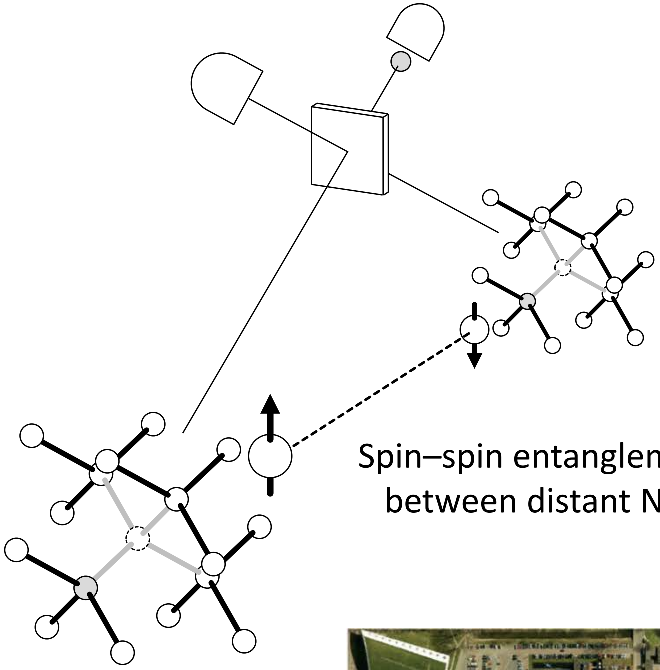


- Room T. operation
- High spatial resolution
- Nondestructive
- Various modalities

⇒

- Nano MRI
- Probe for CM systems
- Biology

# Quantum network



Spin–spin entanglement
between distant NVs

LETTER

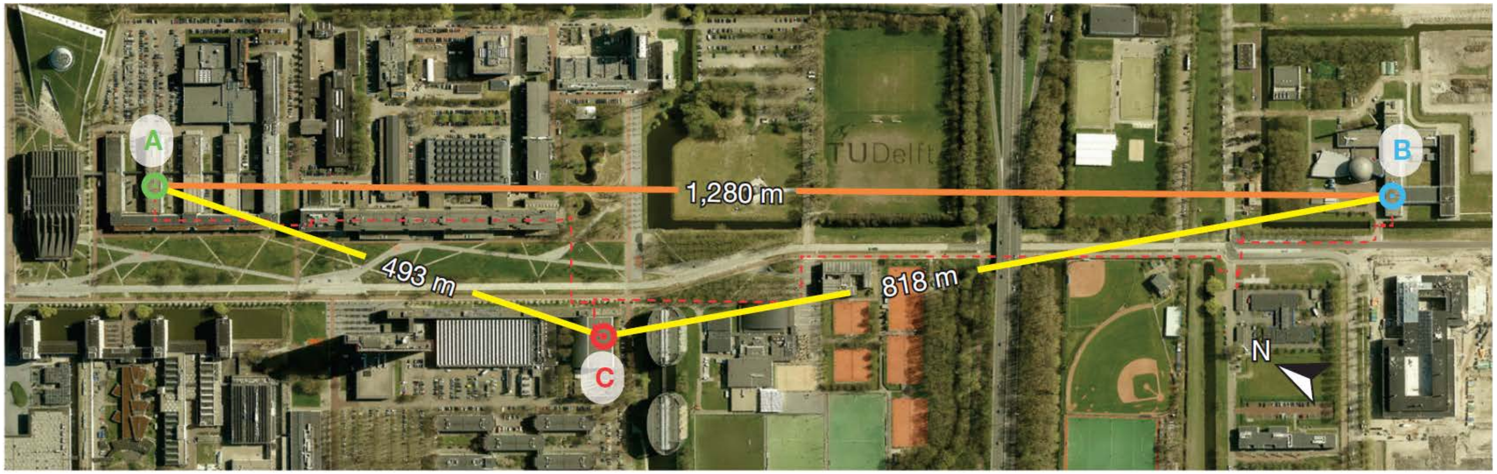
doi:10.1038/nature15759

## Loophole-free Bell inequality violation using electron spins separated by 1.3 kilometres

B. Hensen[1,2], H. Bernien[1,2]†, A. E. Dréau[1,2], A. Reiserer[1,2], N. Kalb[1,2], M. S. Blok[1,2], J. Ruitenberg[1,2], R. F. L. Vermeulen[1,2],
R. N. Schouten[1,2], C. Abellán[3], W. Amaya[3], V. Pruneri[3,4], M. W. Mitchell[3,4], M. Markham[5], D. J. Twitchen[5], D. Elkouss[1],
S. Wehner[1], T. H. Taminiau[1,2] & R. Hanson[1,2]

Nature **526**, 682 (2015) Hensen *et al.*

**Times Cited**: 1036 (Google Scholar)



# Outline

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

- **Quantum sensing**
    - Basics
    - Correlation spectroscopy and detection of nuclear spins
    - Ultrahigh resolution sensing
    - Determination of the position of a single nuclear spin

# Outline

- **Basics of NV centers in diamond**
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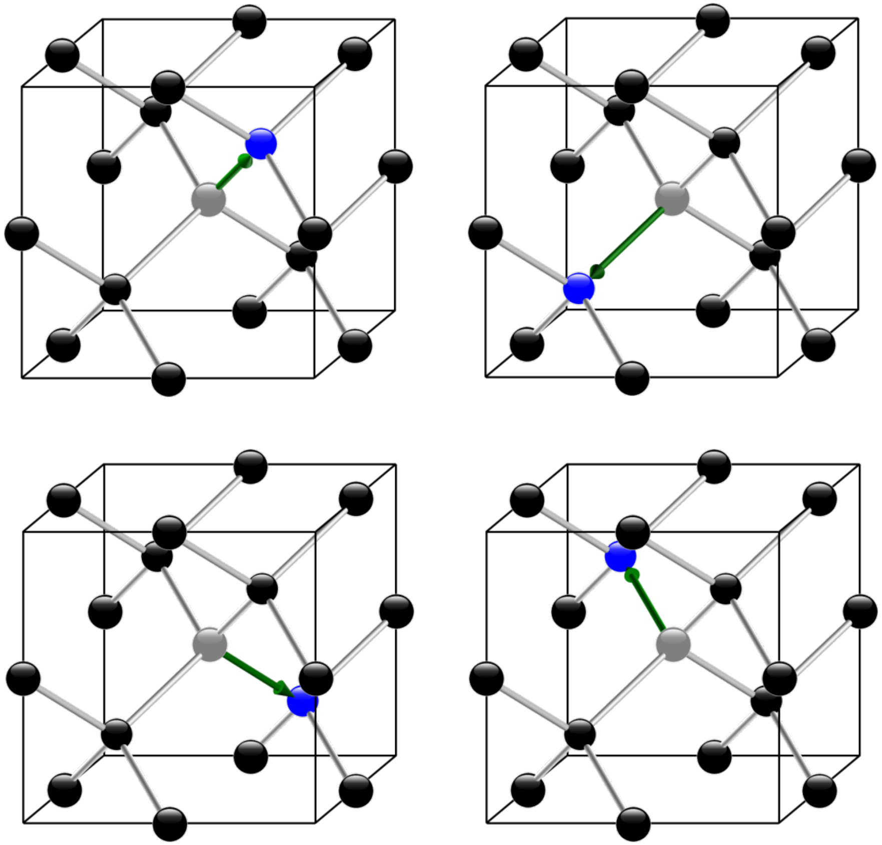
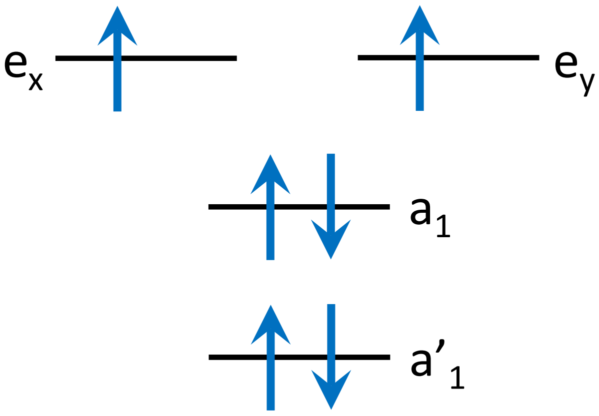
# Crystal & energy level structures

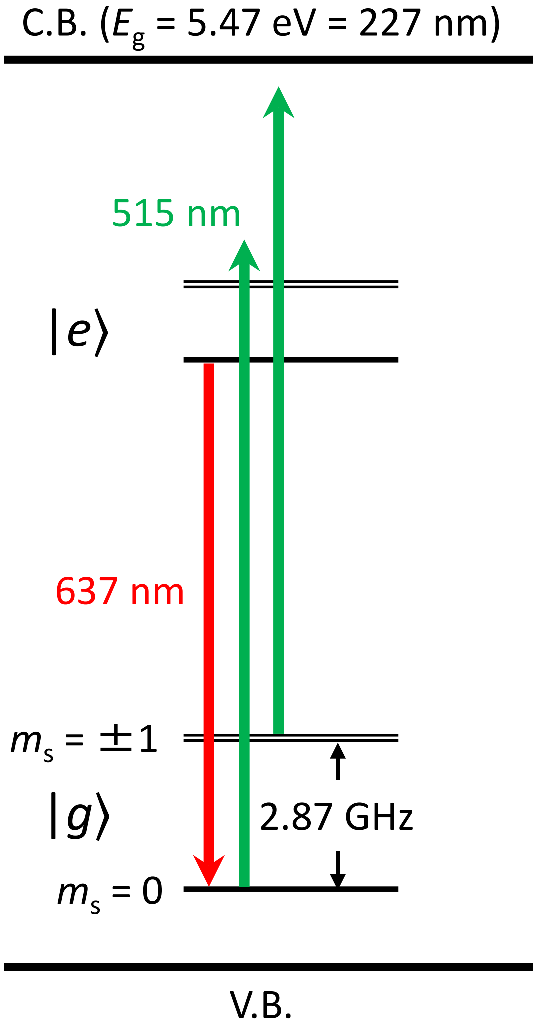
- Negatively-charged ($NV^-$)
- 4 $sp^3$ orbitals, 6 $e^-$ (5 from the defect, 1 captured)
- $C_{3v}$ (symmetry axis = quantization axis)



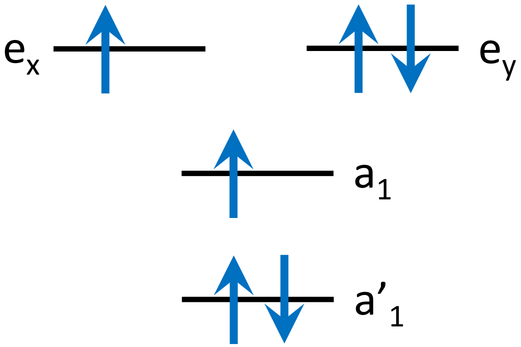
Effective spin-1 system
($e^2$-hole spin-triplet)



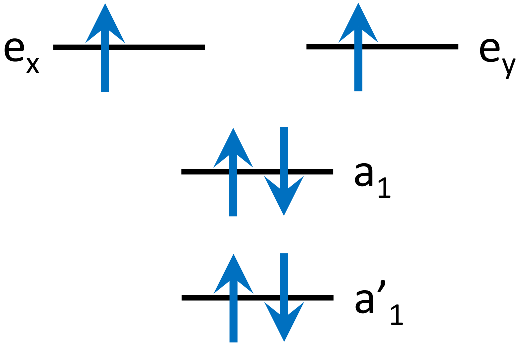
# Optical transitions



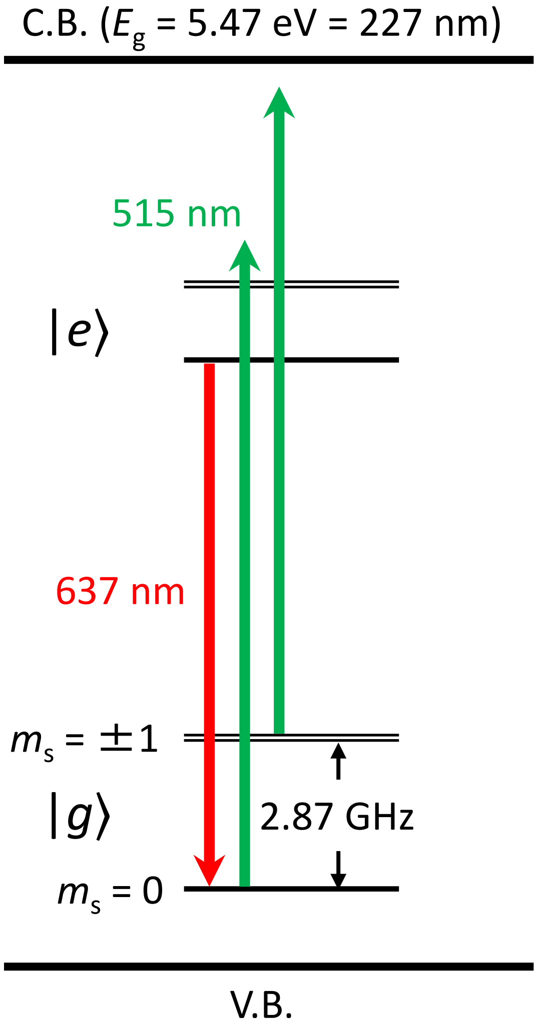
(ae-hole)

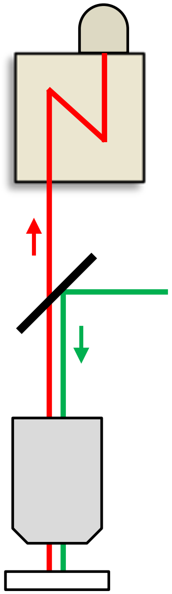


($e^2$-hole)

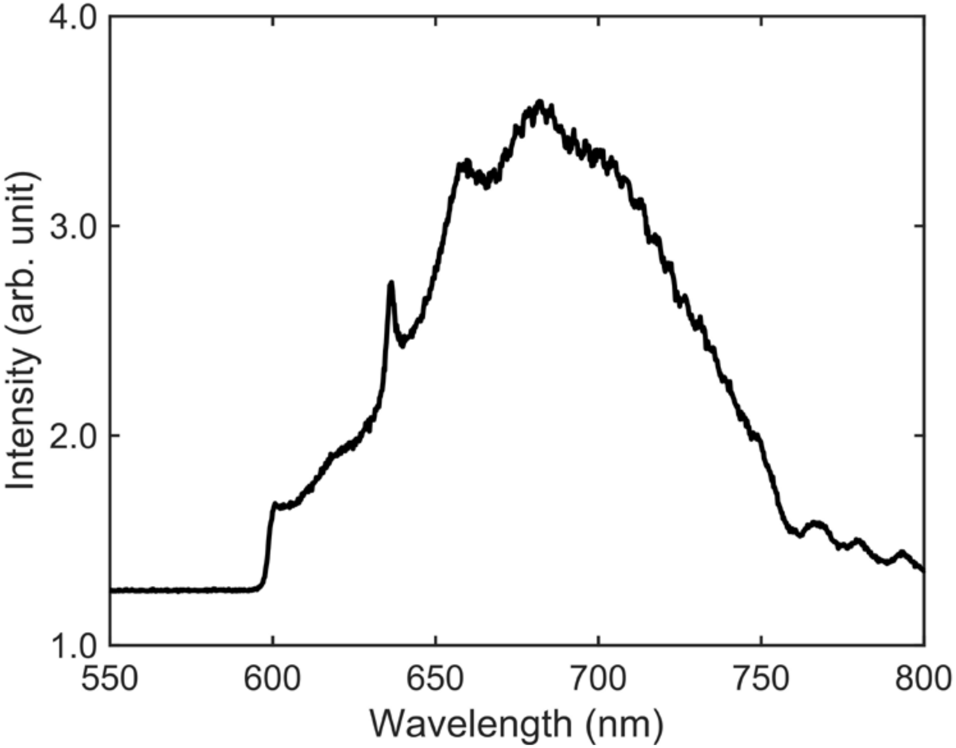


# PL spectroscopy

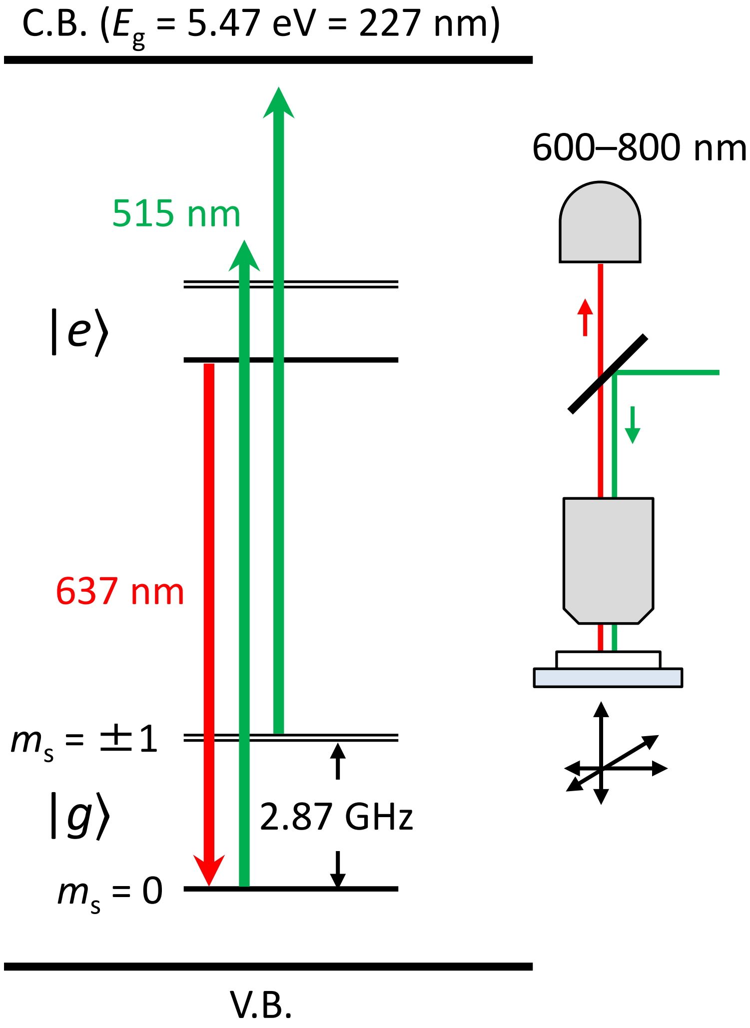




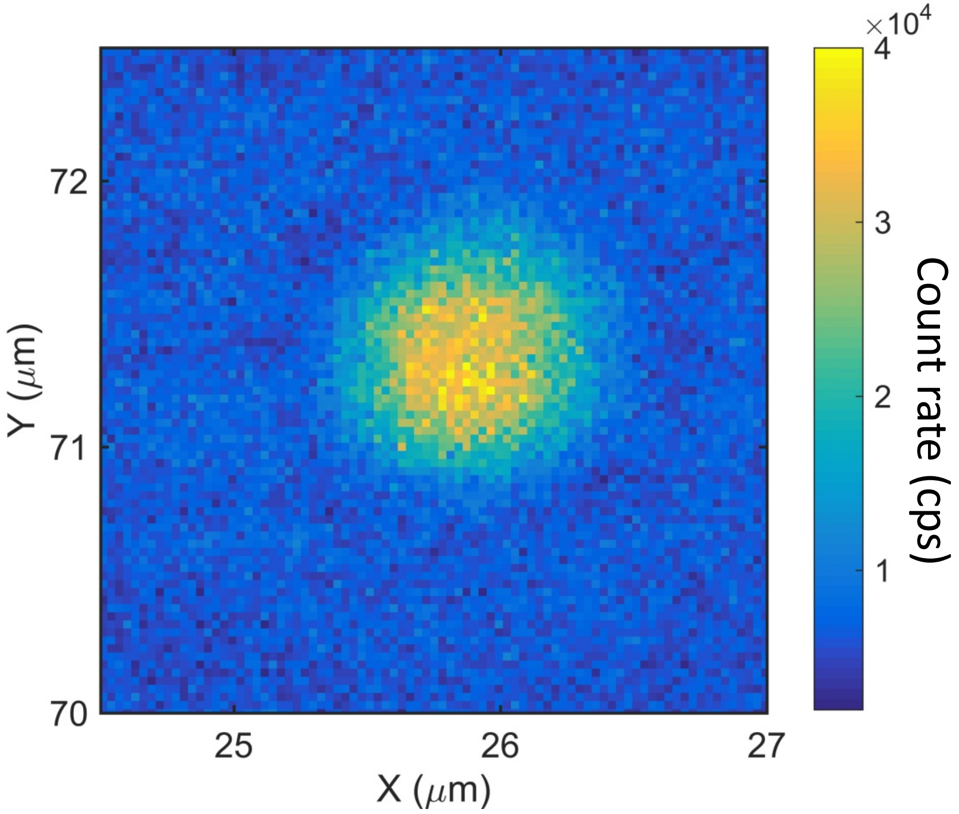
ZPL and PSB



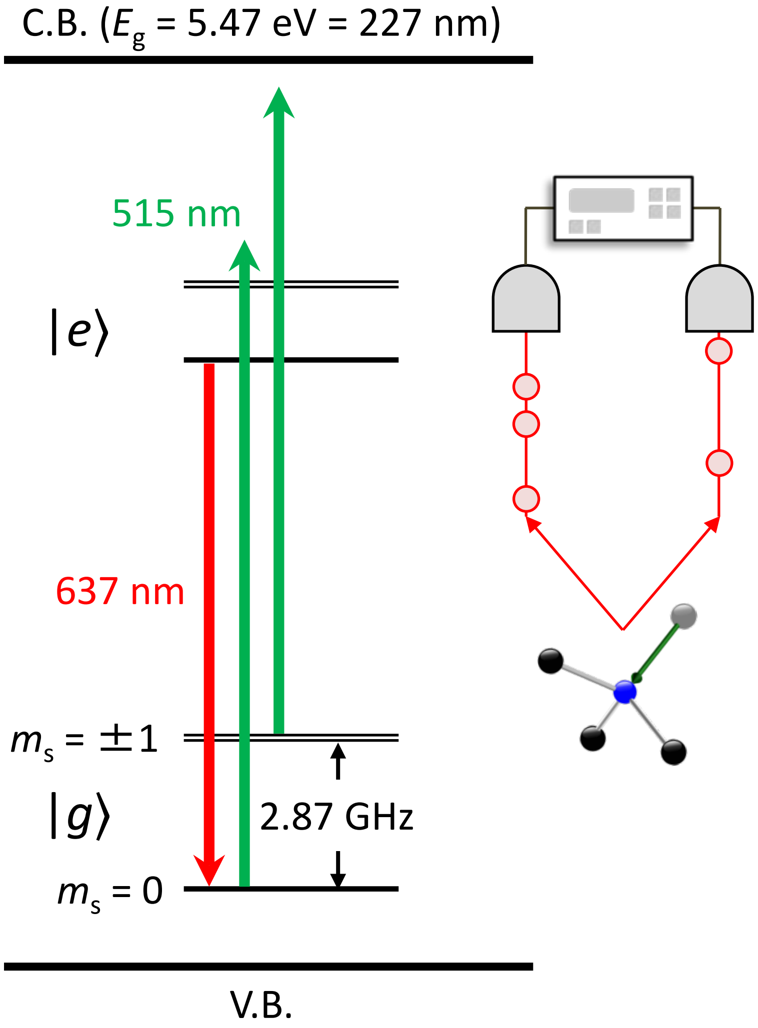
# PL imaging



Bright spot... single NV?



# Photon statistics



C.B. ($E_g$ = 5.47 eV = 227 nm)

515 nm

$|e\rangle$

637 nm

$m_s = \pm 1$

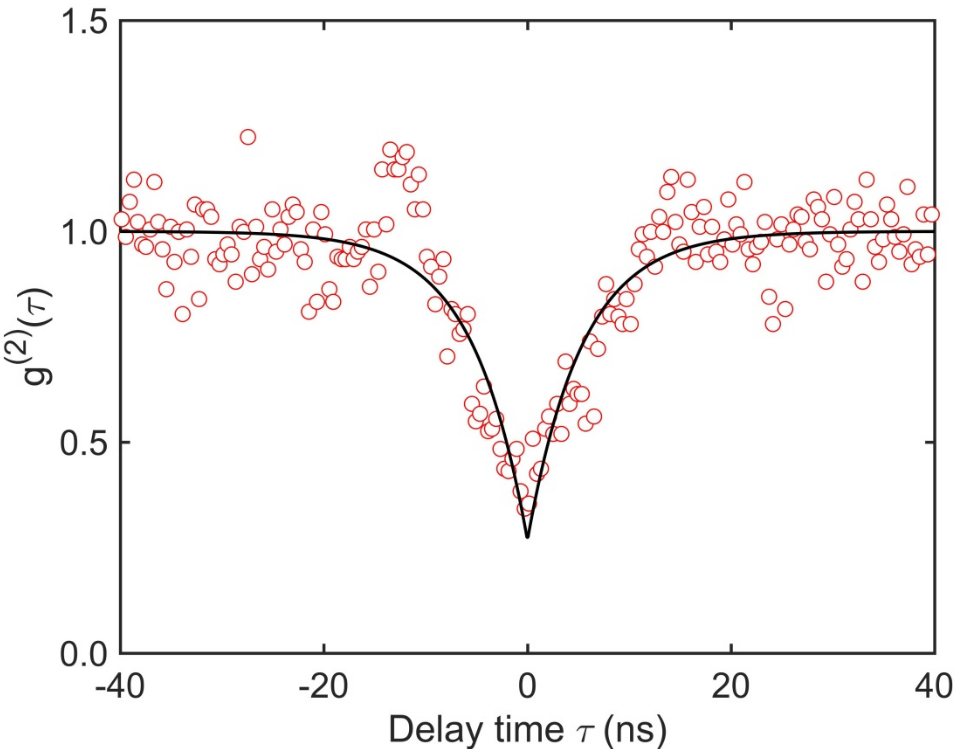
$|g\rangle$

2.87 GHz

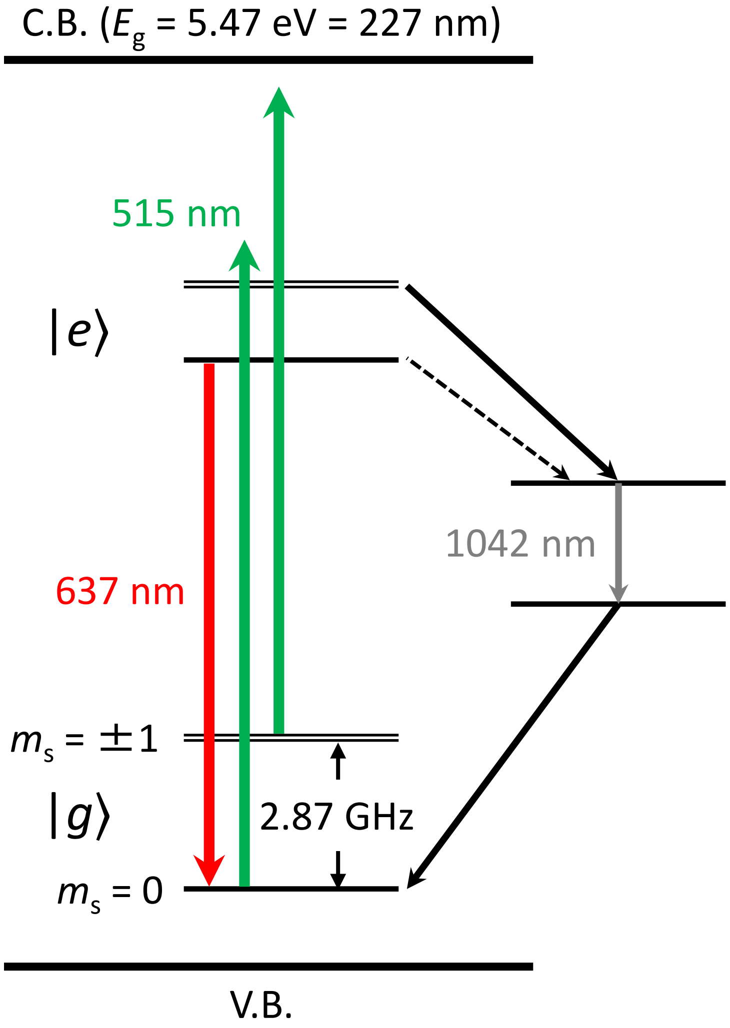
$m_s = 0$

V.B.

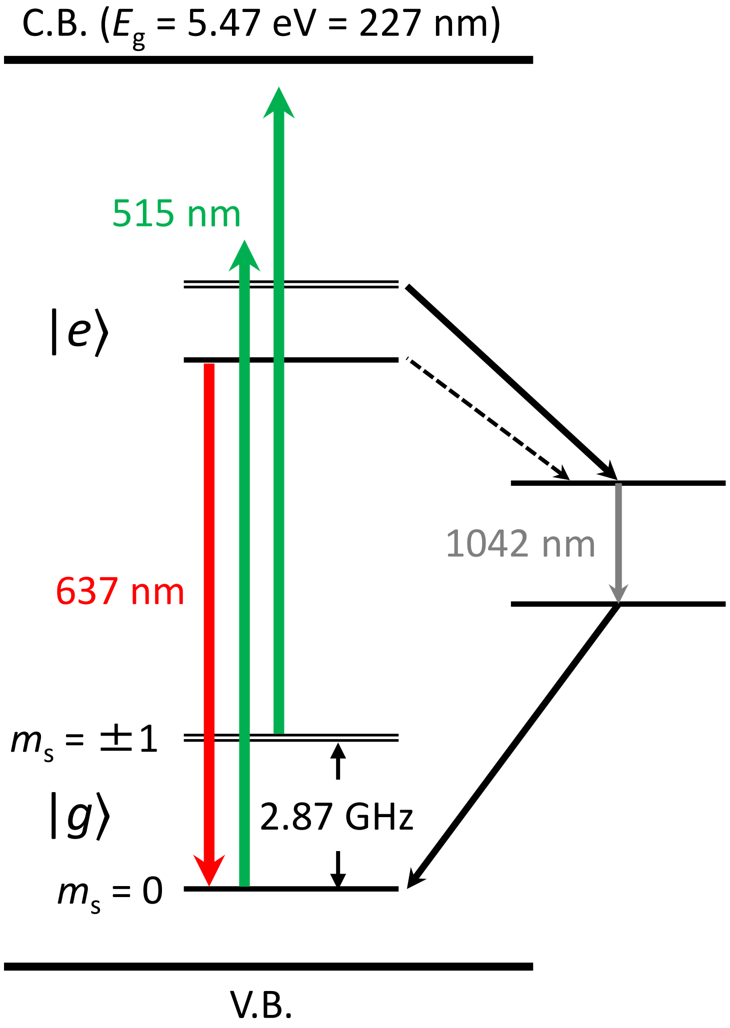
One photon at a time



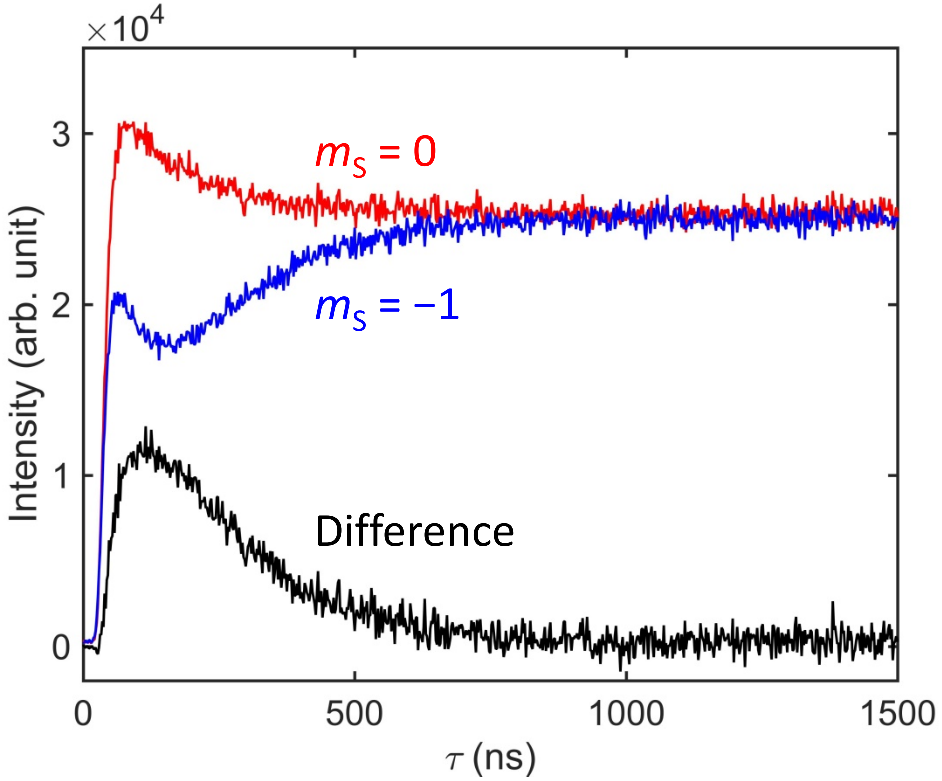
# Non-radiative path



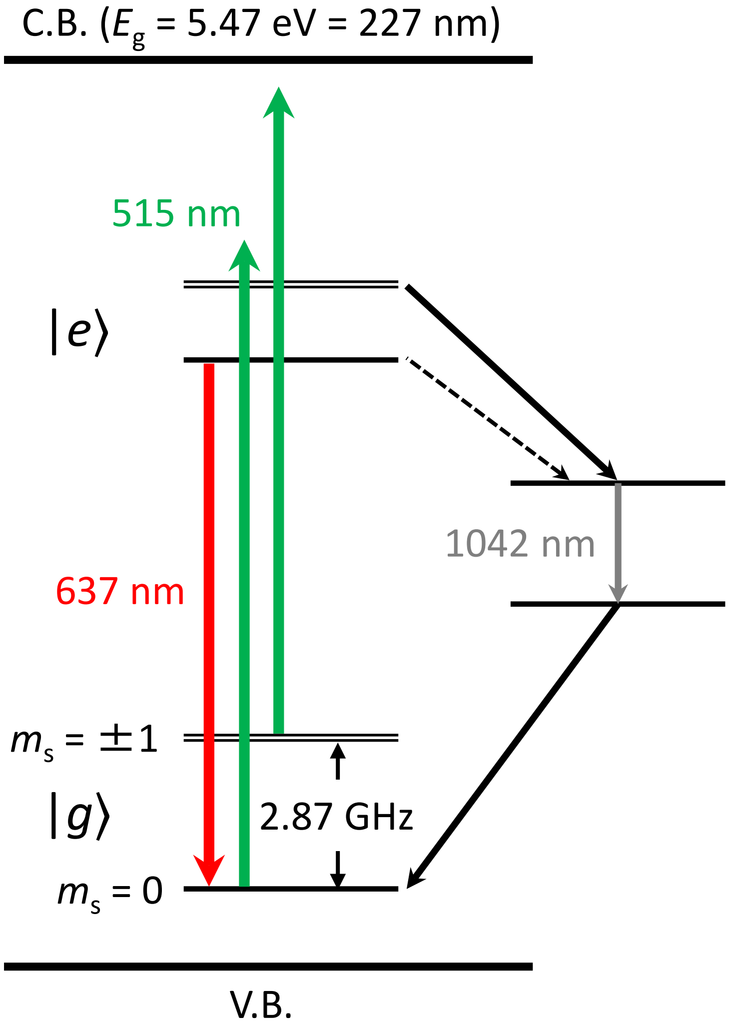
# Time-resolved fluorescence

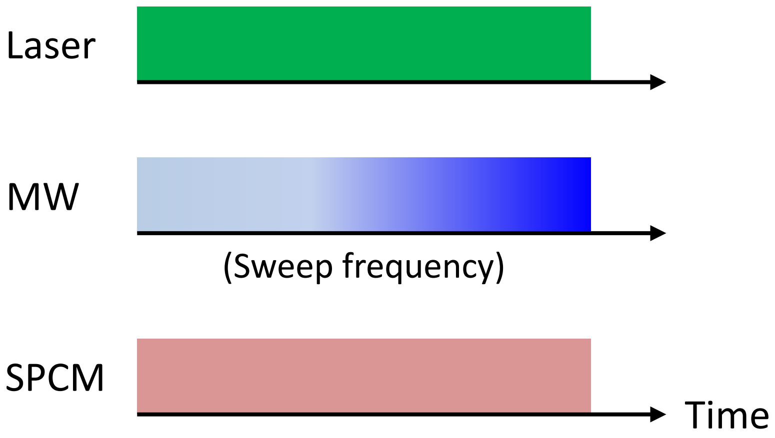


The NR channel provides a means to **read out** and **initialize** the NV spin

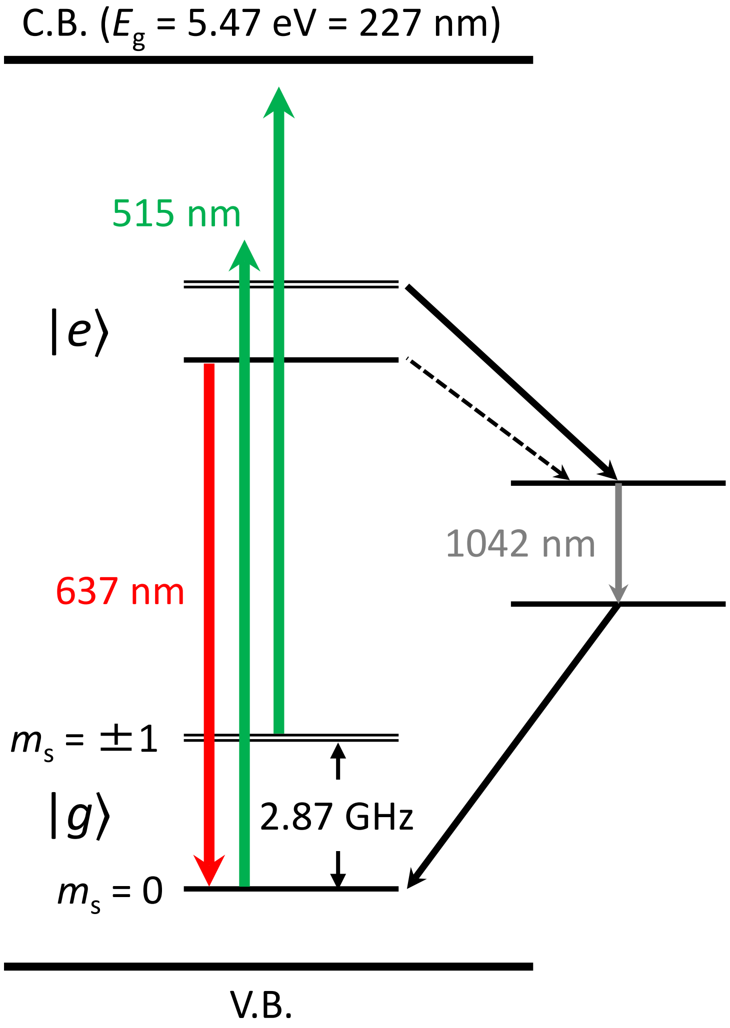


# CW ODMR


C.B. ($E_g$ = 5.47 eV = 227 nm)
515 nm
$|e\rangle$
1042 nm
637 nm
$m_s = \pm 1$
$|g\rangle$
2.87 GHz
$m_s = 0$
V.B.


Laser
MW
(Sweep frequency)
SPCM
Time

# CW ODMR at $B_0 = 0$



C.B. ($E_g$ = 5.47 eV = 227 nm)

515 nm

$|e\rangle$

637 nm

1042 nm

$m_s = \pm1$

$|g\rangle$

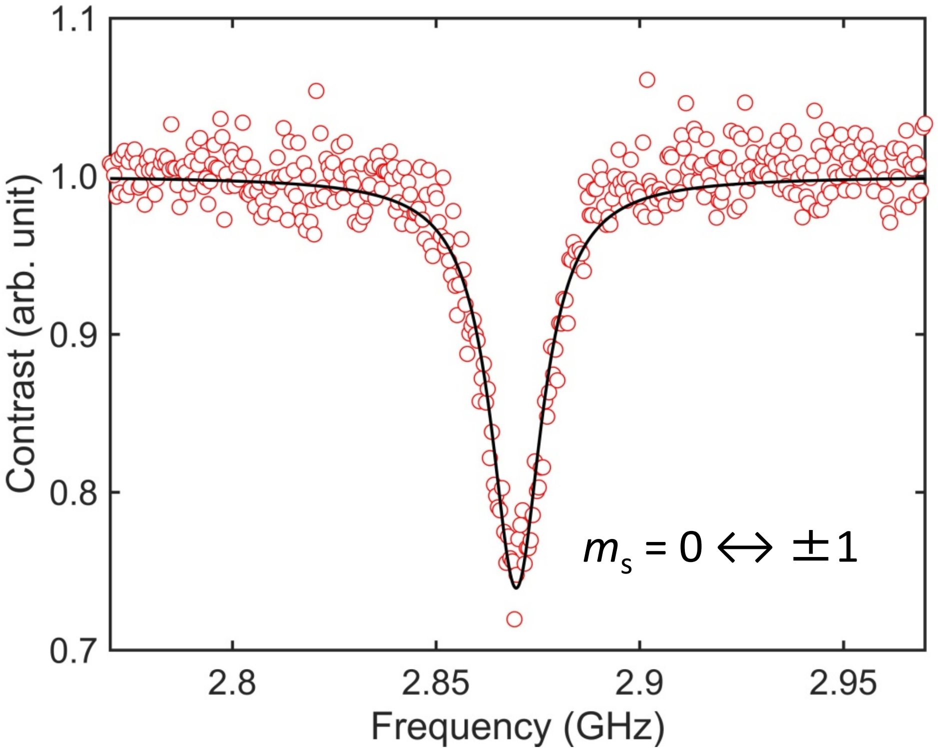
2.87 GHz

$m_s = 0$

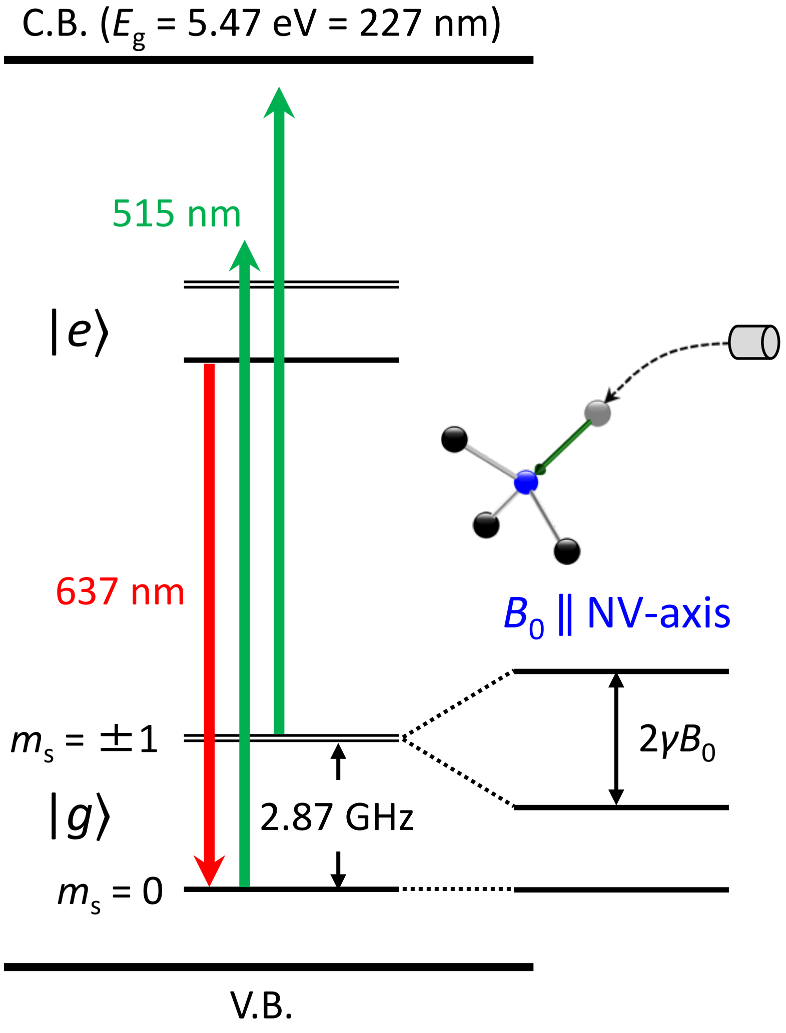
V.B.

**Zero-field splitting** $H = DS_z^2$

$D$ = 2.87 GHz

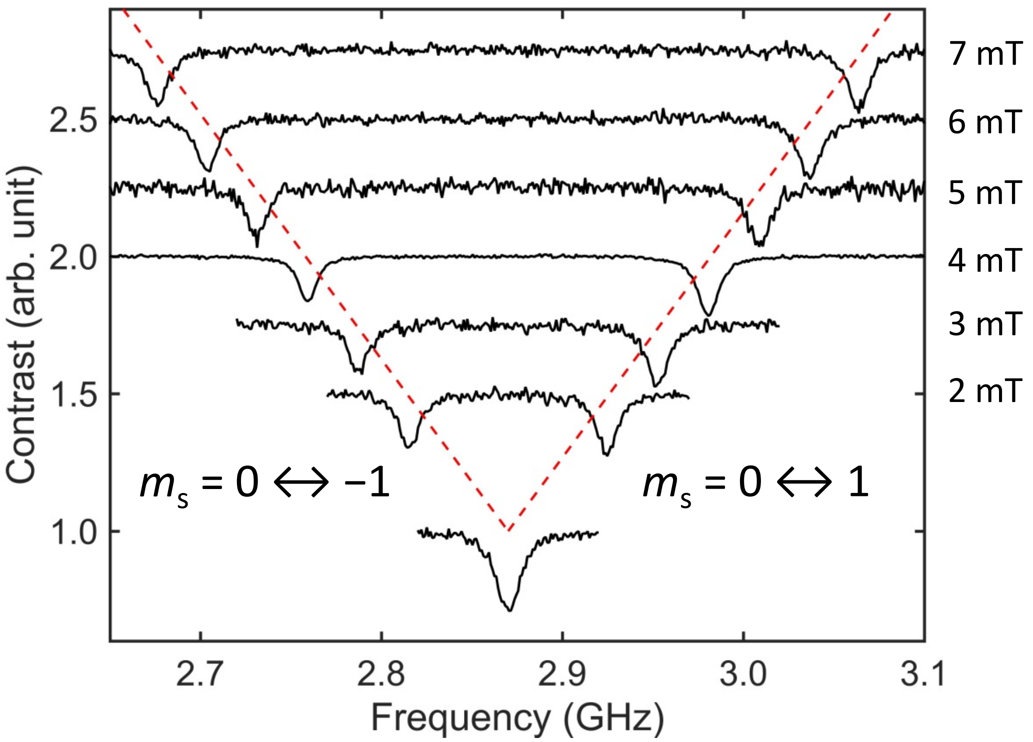


# CW ODMR at $B_0 \geq 0$

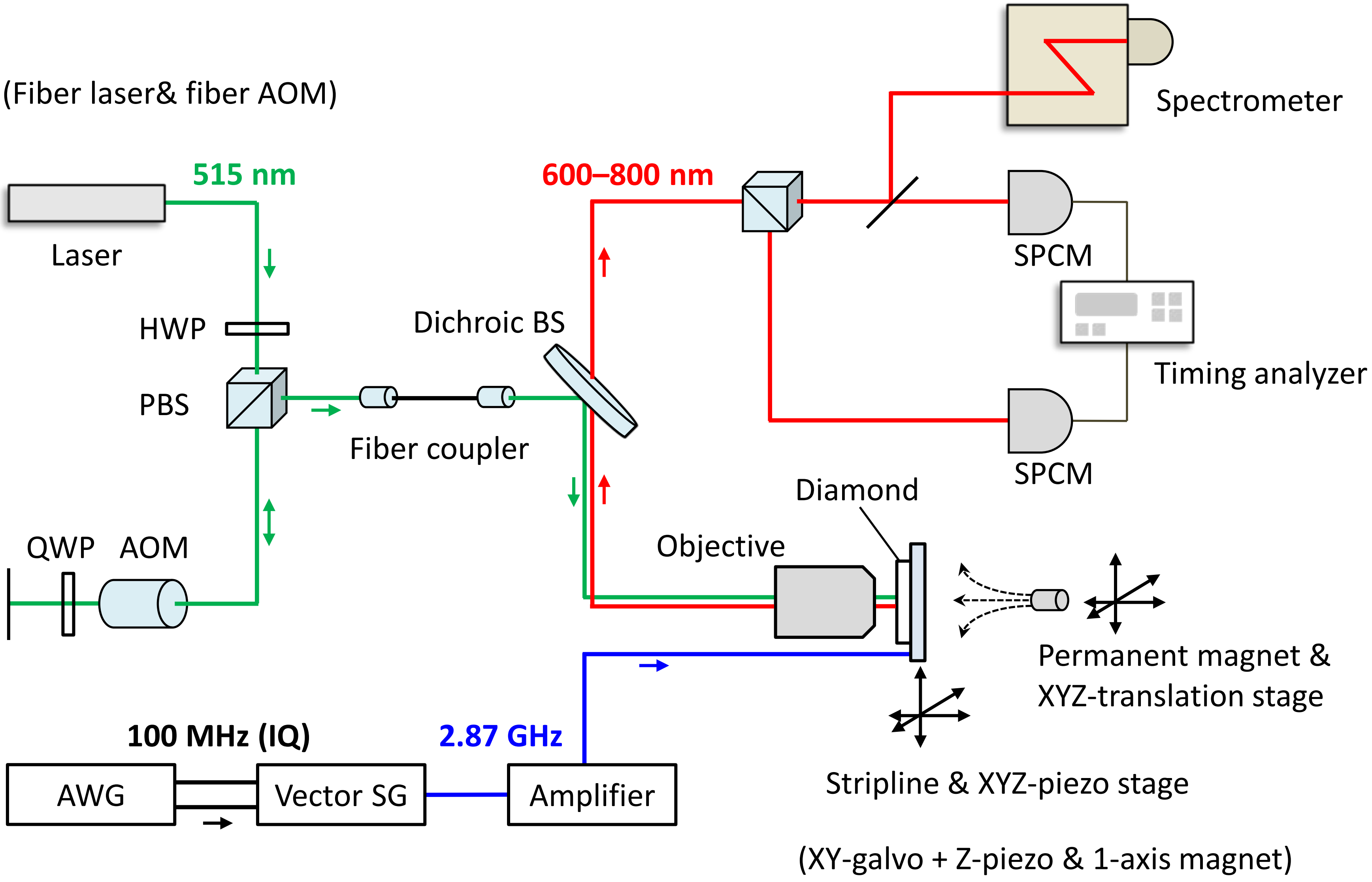


**Zeeman** $H = DS_z^2 + \gamma_e B_0 S_z$

$\gamma_e$ = 28 MHz/mT



# Experimental setup



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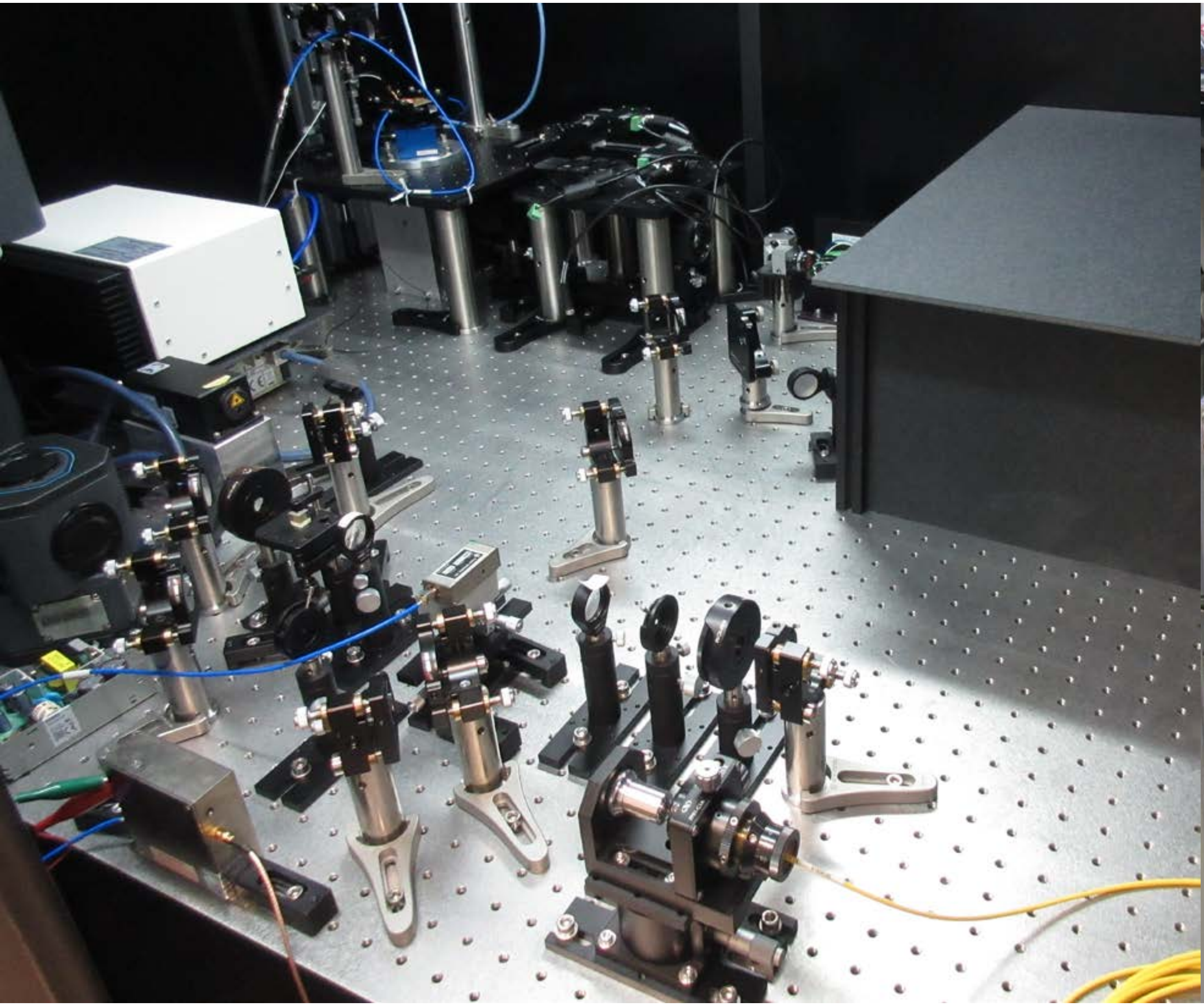

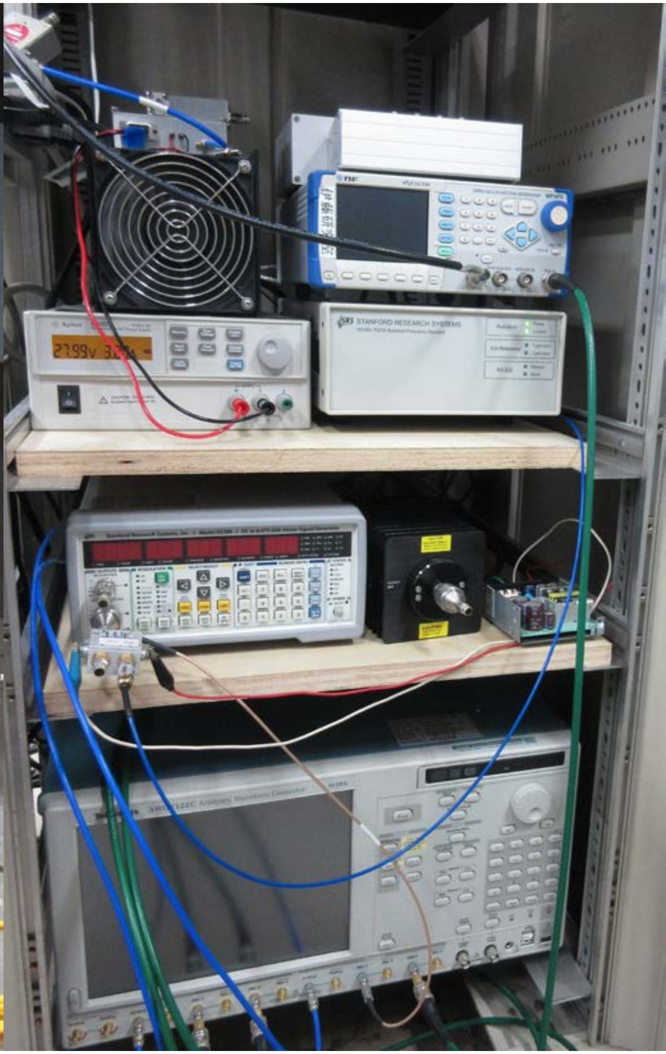

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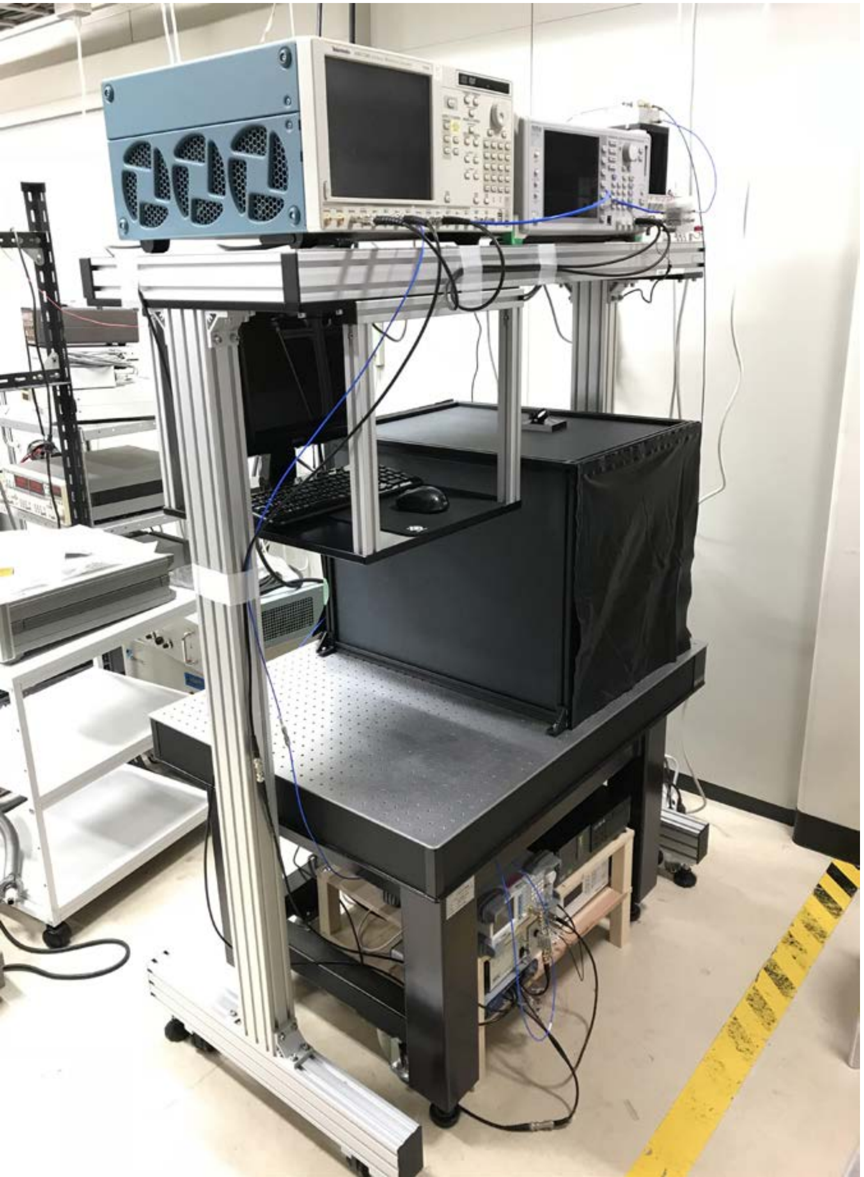
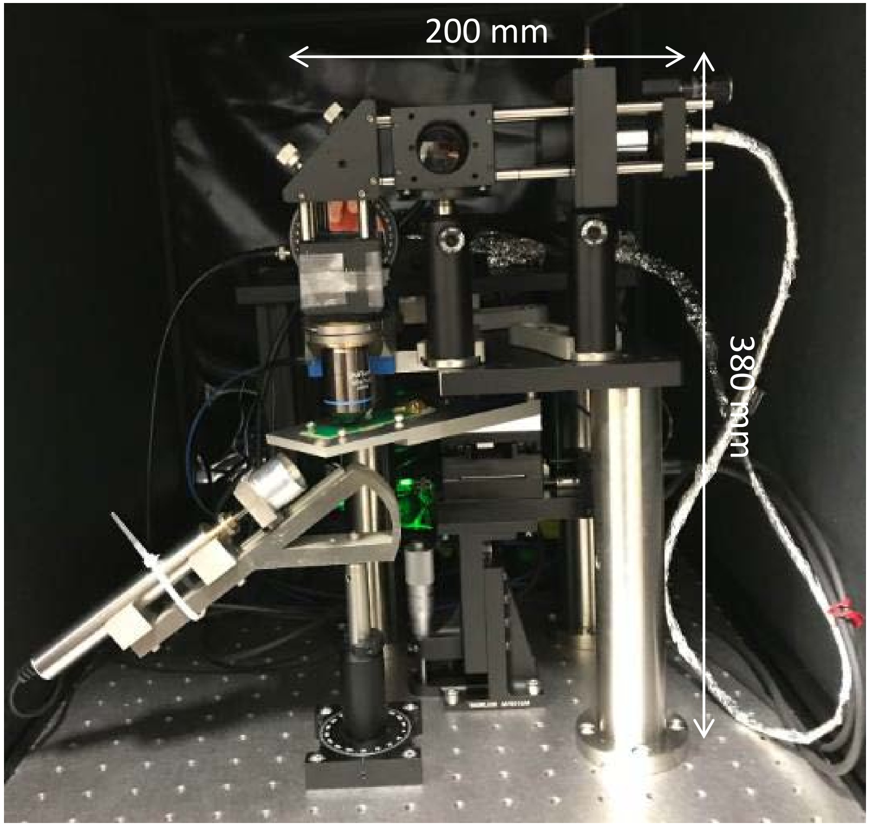
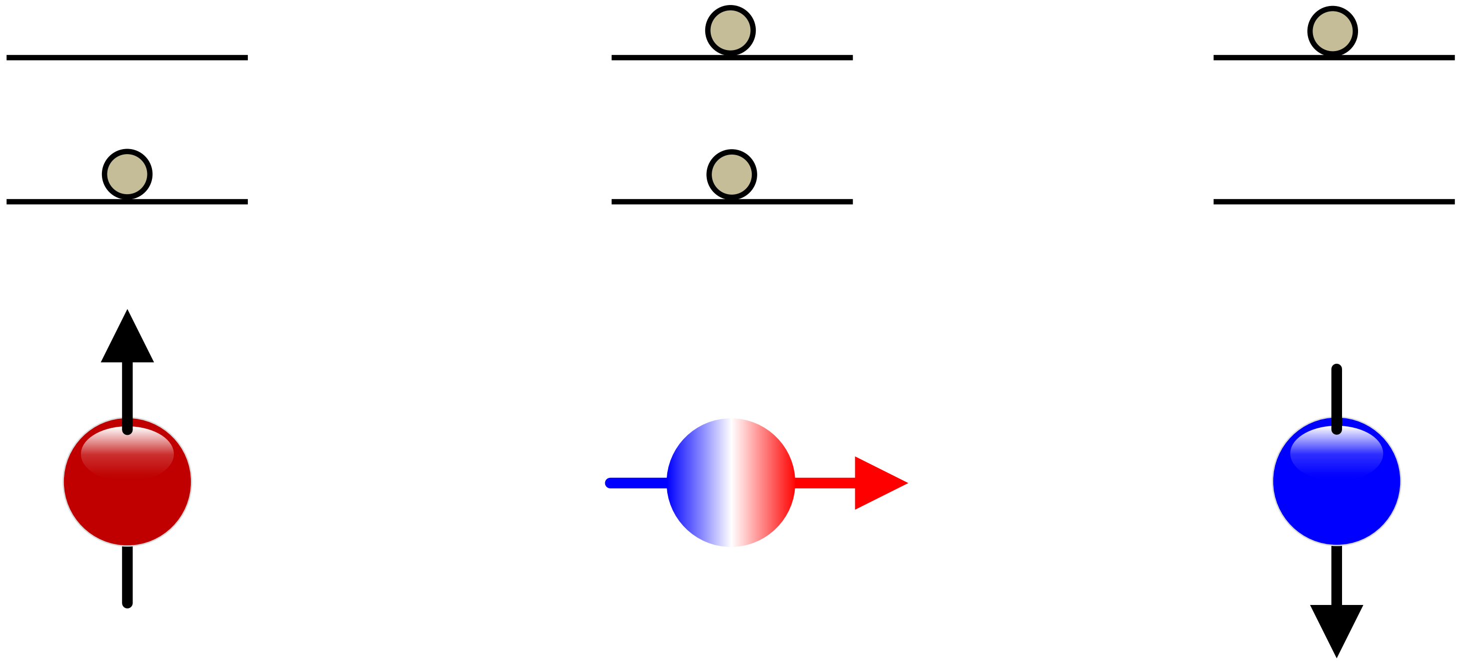




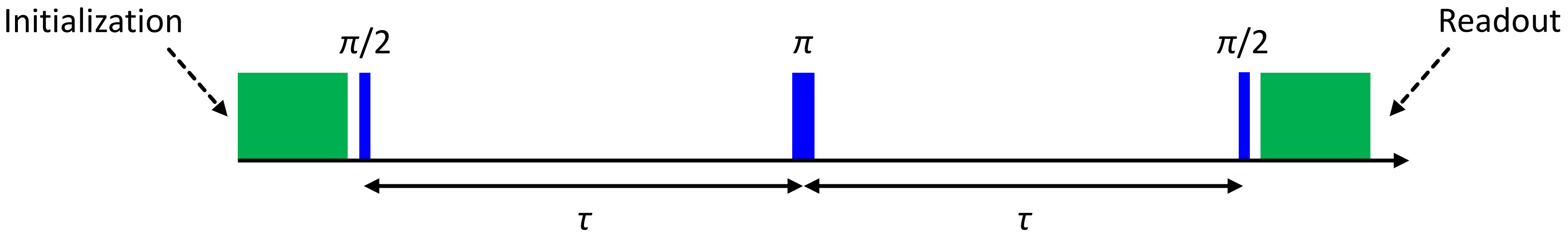
# Qubit & coherence



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

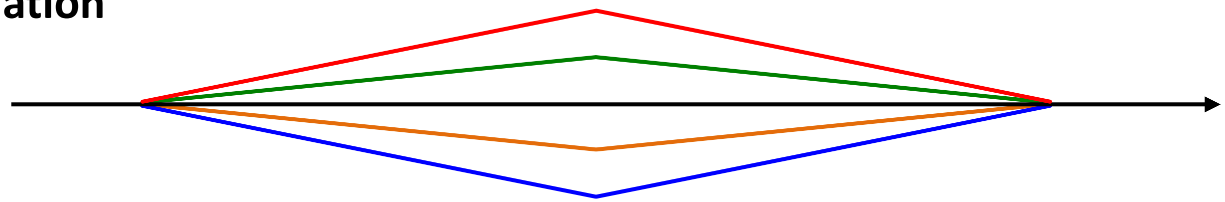
**$T_2$: measure of how long a superposition state is preserved**

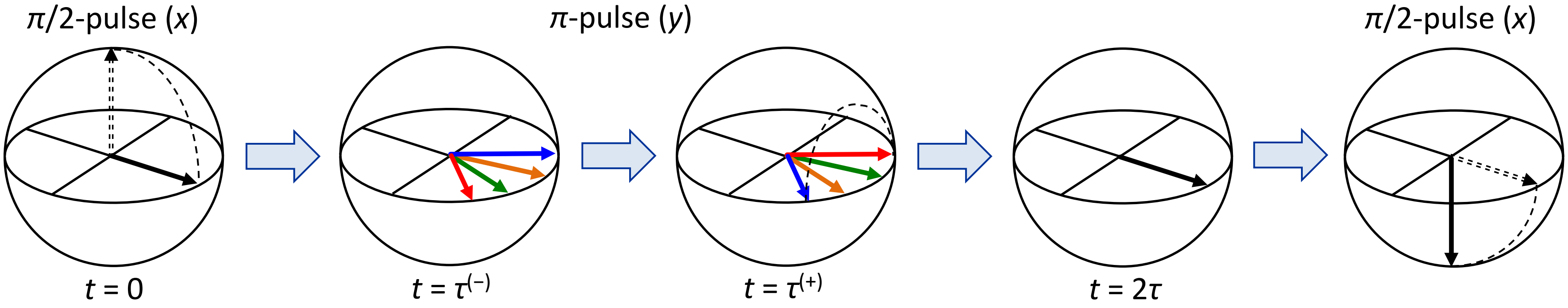
# Puled ODMR: Spin echo



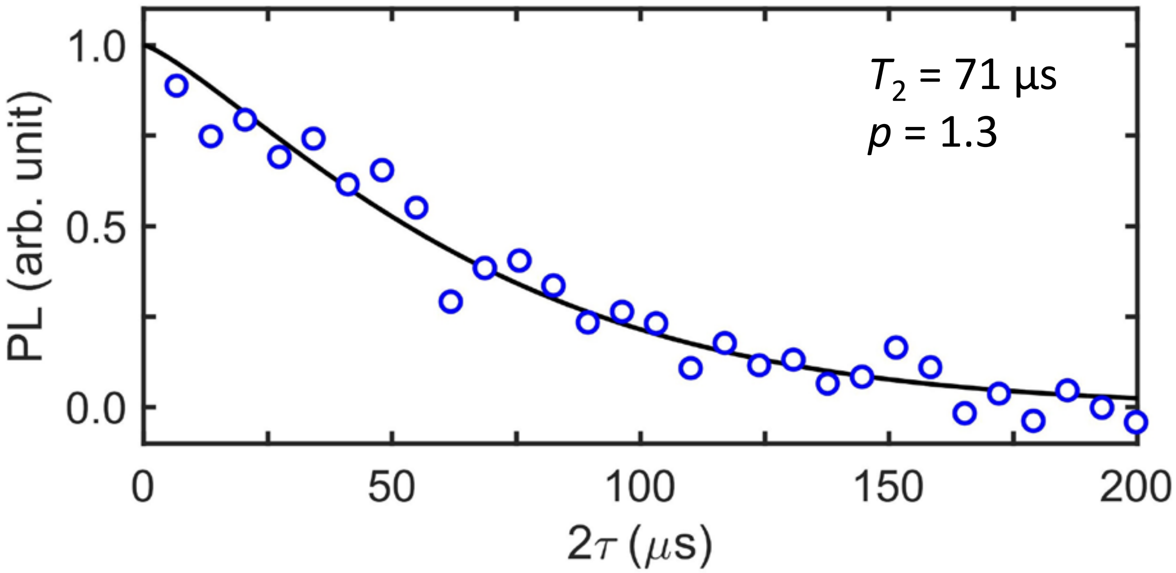
***Sign of phase accumulation***

**Phase accumulation by DC field**





# Coherence time



$T_2$ = 71 μs
$p$ = 1.3

**Stretched exponential decay**

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

**CVD growth of shallow single NV centers**

- Hydrogen-terminated
- ~5 nm from the surface
- [$^{12}$C] = 99.999%

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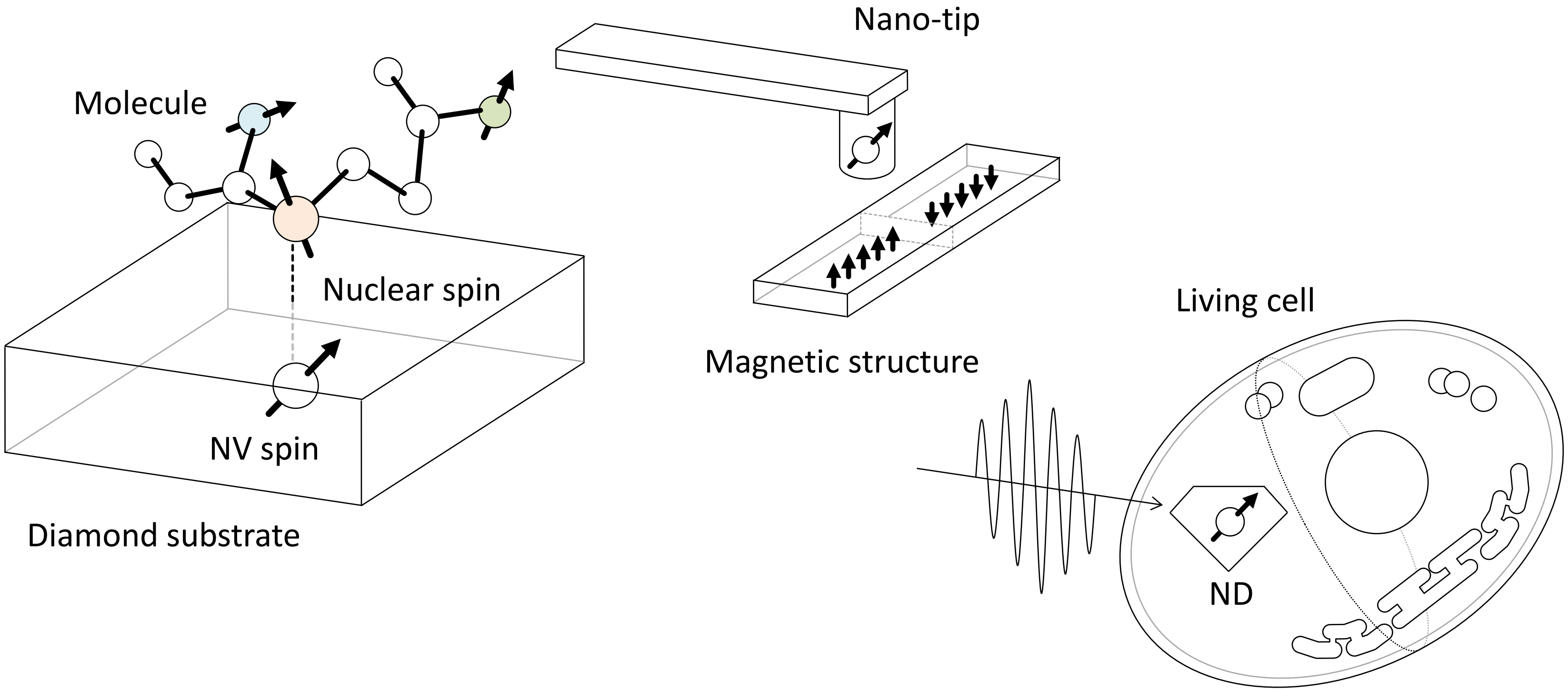
  - Optical properties
  - Spin properties

- **Quantum senisng**
  - Basics
  - Correlation spectroscopy and detection of nuclear spins
  - Ultrahigh resolution sensing
  - Determination of the position of a single nuclear spin

# Quantum sensing

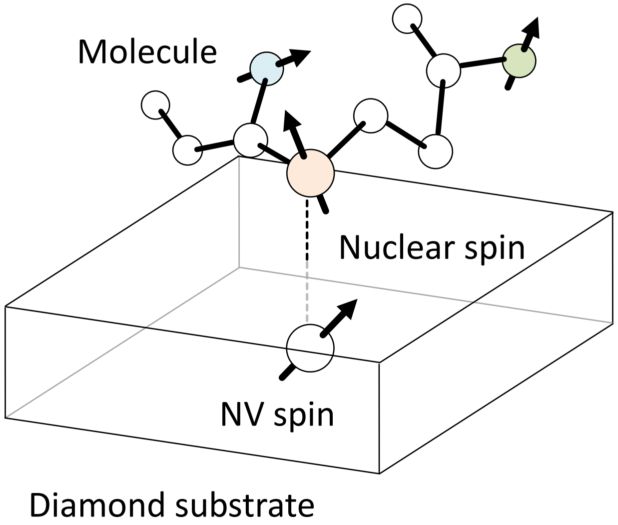


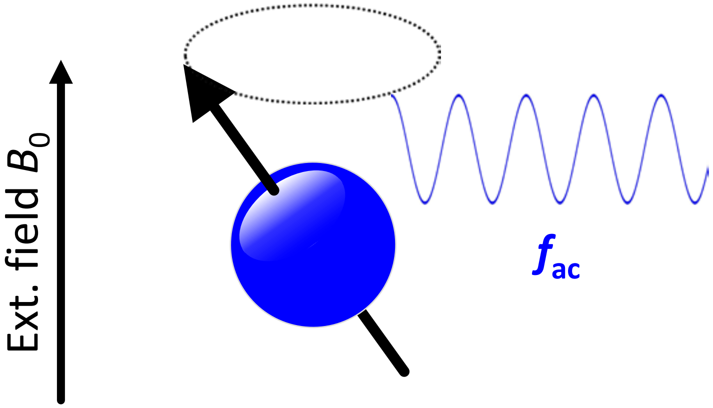
- Room T. operation
- High spatial resolution
- Nondestructive
- Various modalities

⇨

- Nano MRI
- Probe for CM systems
- Biology

# Nuclear spin sensing





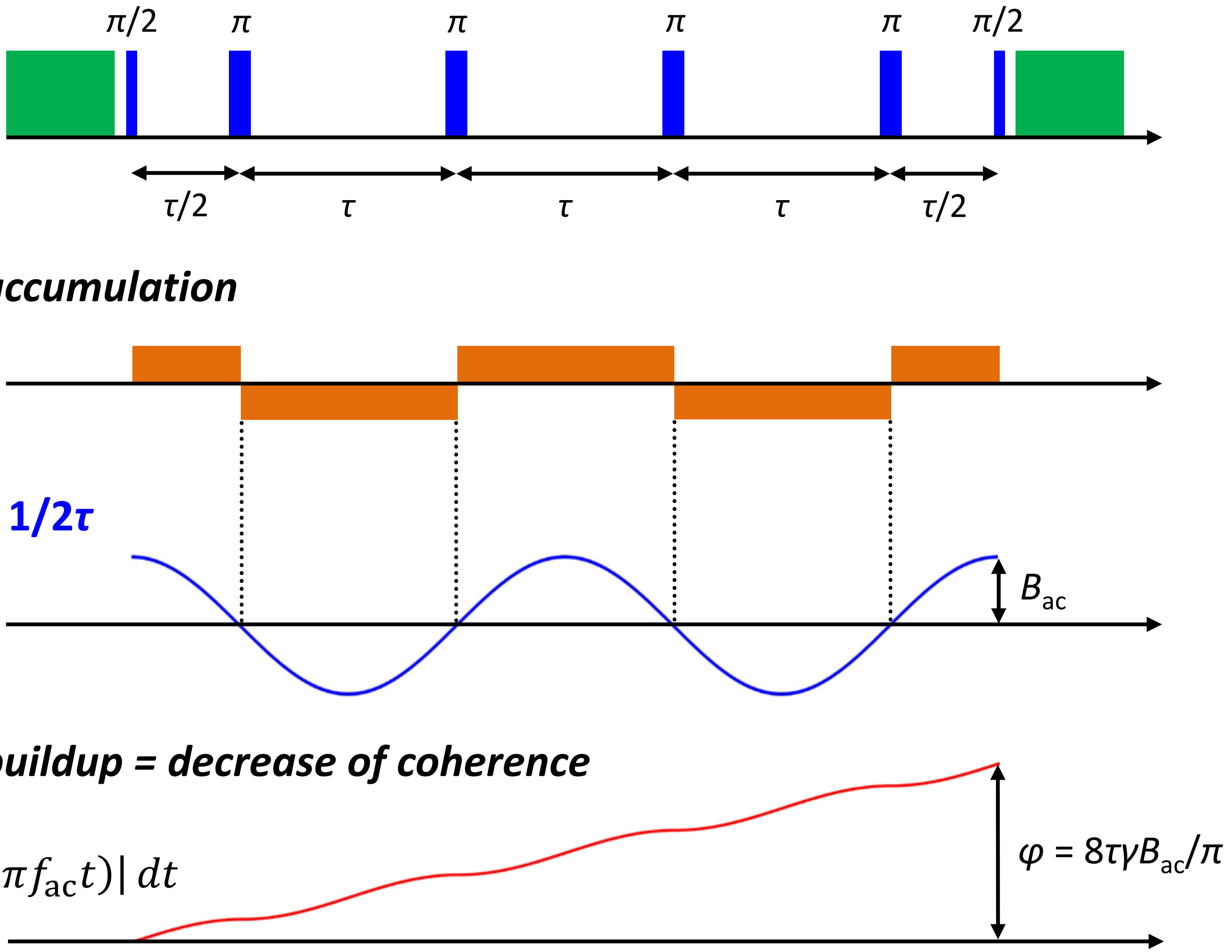
Nuclear spins **precess** at $f_{ac}$ = a few kHz–MHz under $B_0$

⇨ **Weak AC magnetic field** on the NV spin (11 nT@$d_{NV}$ = 5 nm)

⇨ Detect using **quantum coherence**

# AC magnetometry

**CP ($N$ = 4)**



***Sign of phase accumulation***

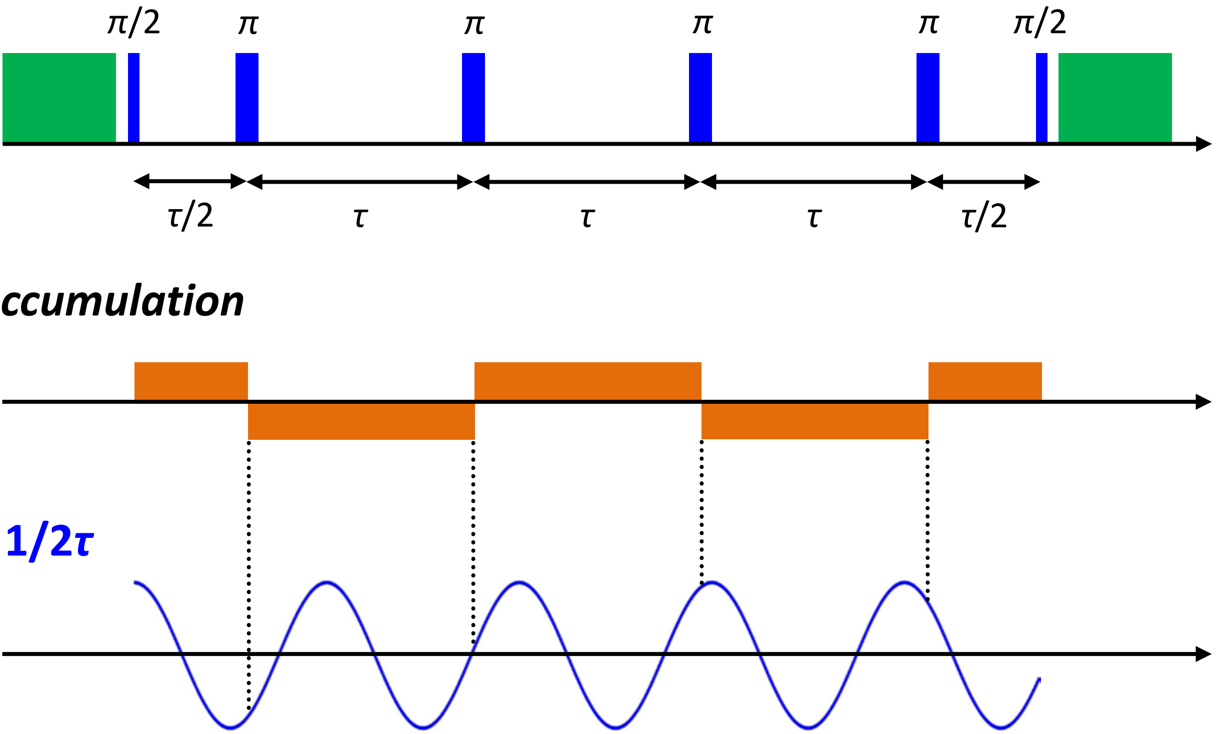
**AC field at $f_{ac} = 1/2\tau$**

***Sensor phase buildup = decrease of coherence***

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

Rev. Mod. Phys. **89**, 035002 (2017) Degen *et al.*

# AC magnetometry



**CP ($N$ = 4)**

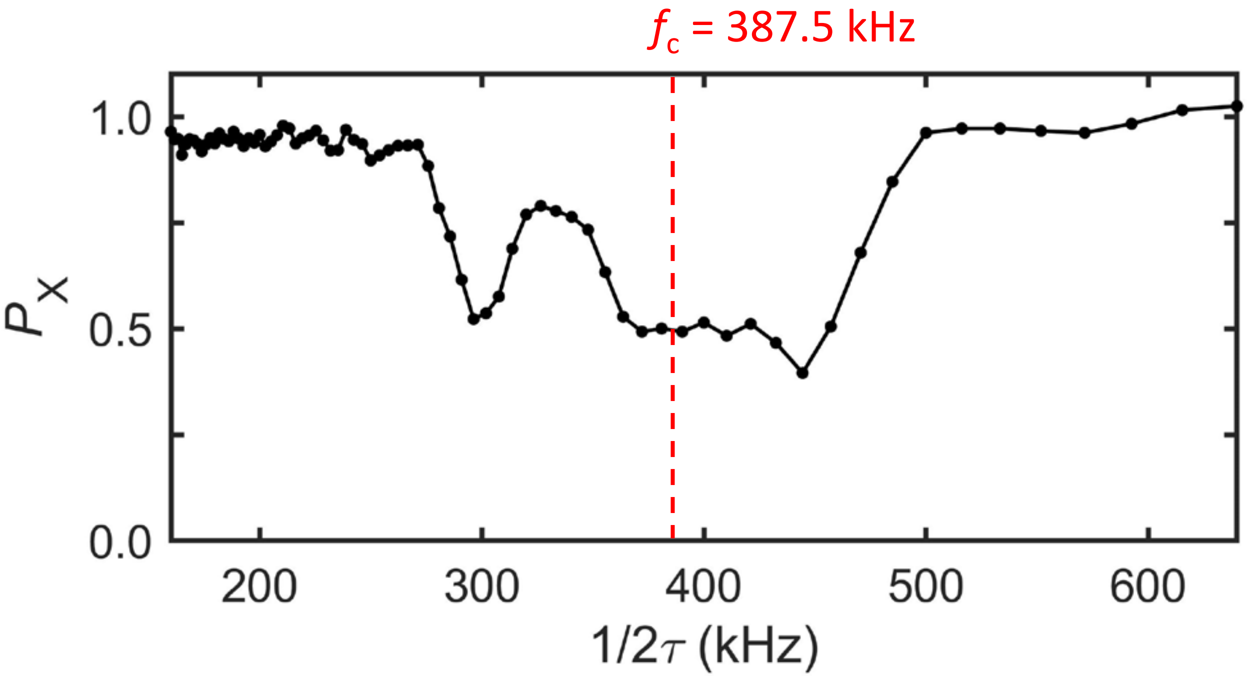
***Sign of phase accumulation***

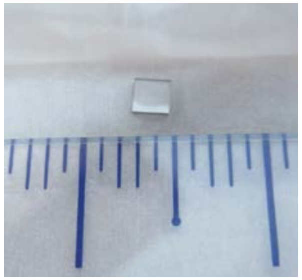
**AC field at $f_{ac} \neq 1/2\tau$**

Multiple oscillations between π-pulses average out the sensor phase

Rev. Mod. Phys. **89**, 035002 (2017) Degen *et al.*

# Nuclear spin sensing

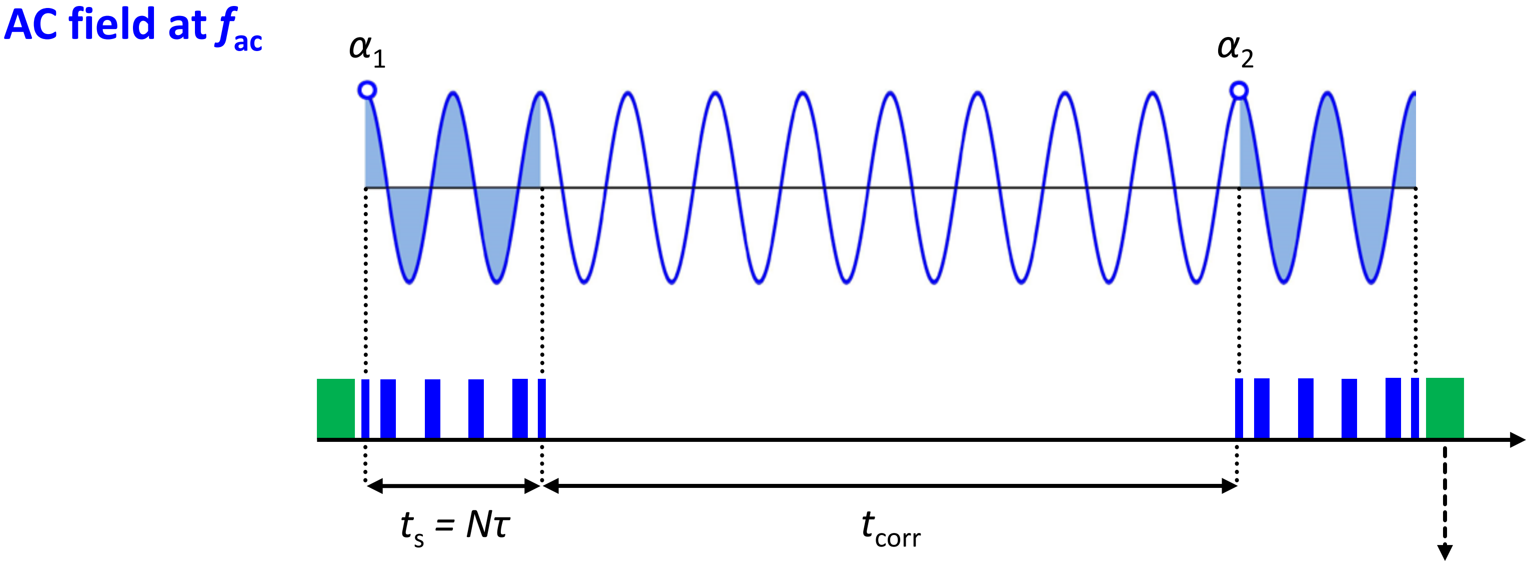




- Single NV center in a natural abundant diamond ([$^{13}$C] = 1.1%, $d_{NV}$ ~ 50 μm)
- **Sweep τ & repeat** ($f = 1/2\tau$, $\Delta\tau$ = 31.3 ns, $N$ = 16)
- $f_c = \gamma_C B_0$ = 10.705 kHz/mT x 36.2 mT

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

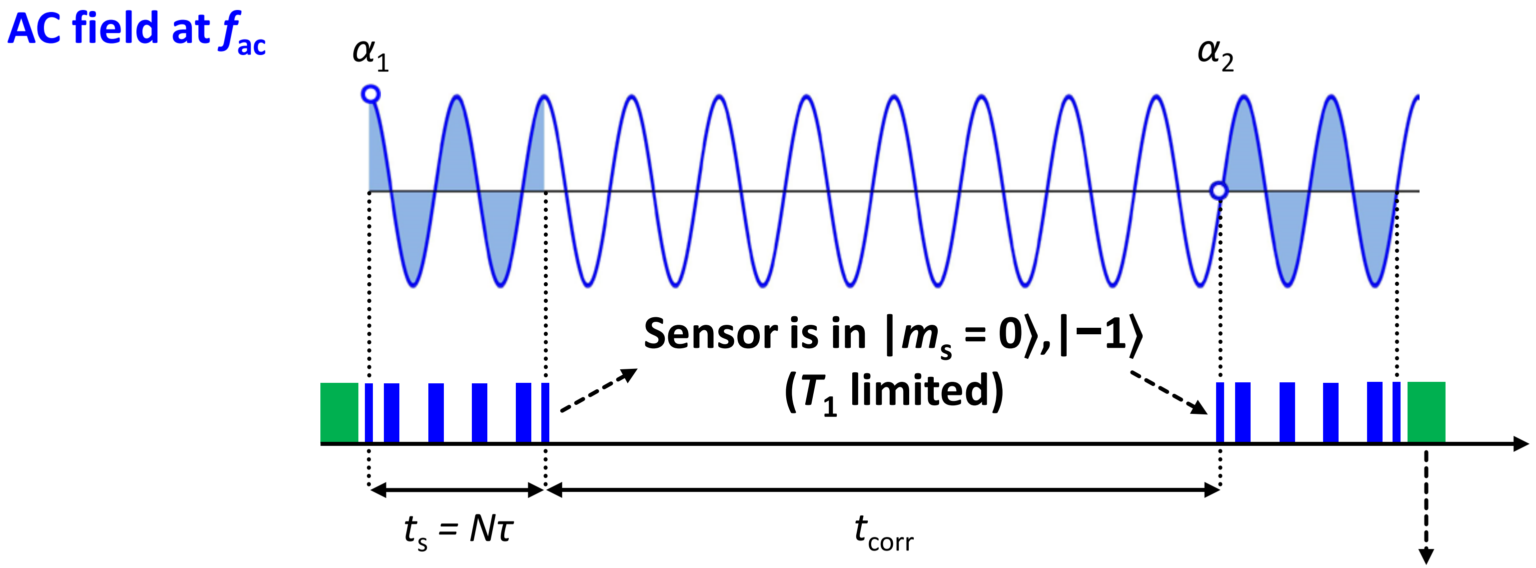
# Correlation spectroscopy



**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



**Sensor is in $|m_{\mathrm{s}} = 0\rangle, |-1\rangle$**
**($T_1$ limited)**

**No gain of the phase if**
**$t_{\mathrm{corr}} = (m+1/4)/f_{\mathrm{ac}}$**

**The transition probability for random phases**

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

Nature Commun. **4**, 1651 (2013) Laraoui *et al.*
Phys. Rev. Appl. **4**, 024004 (2015) Kong *et al.*
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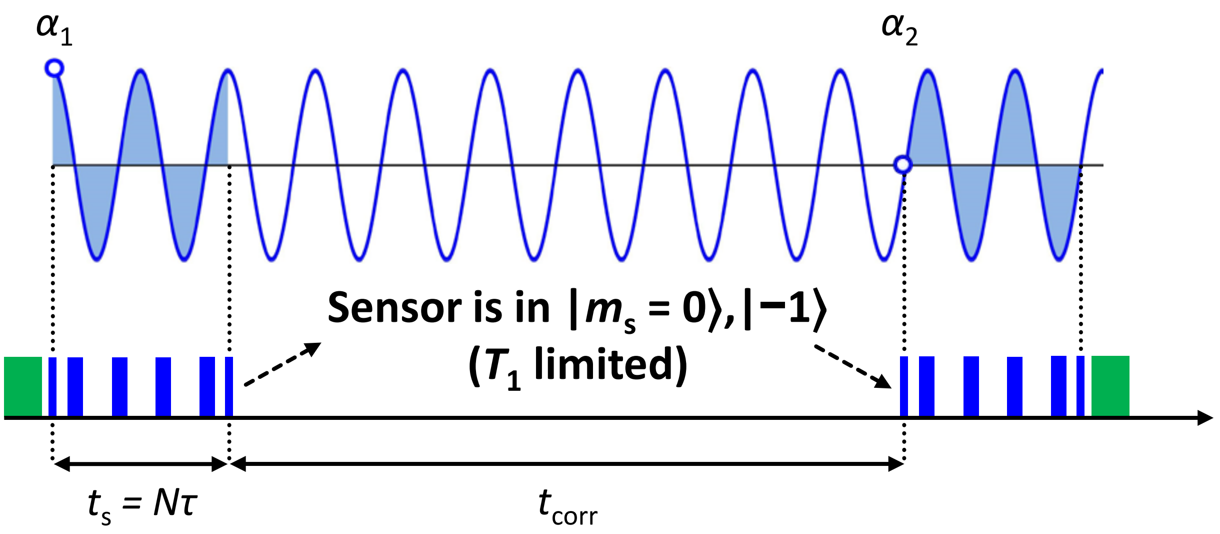
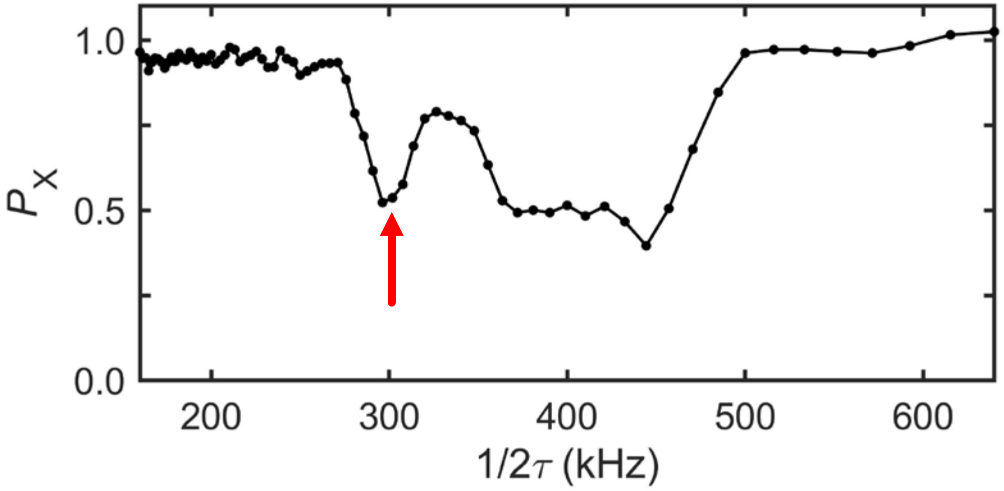
# Correlation spectroscopy

**AC field at $f_{ac}$**



**Sensor is in $|m_s = 0\rangle, |-1\rangle$ ($T_1$ limited)**

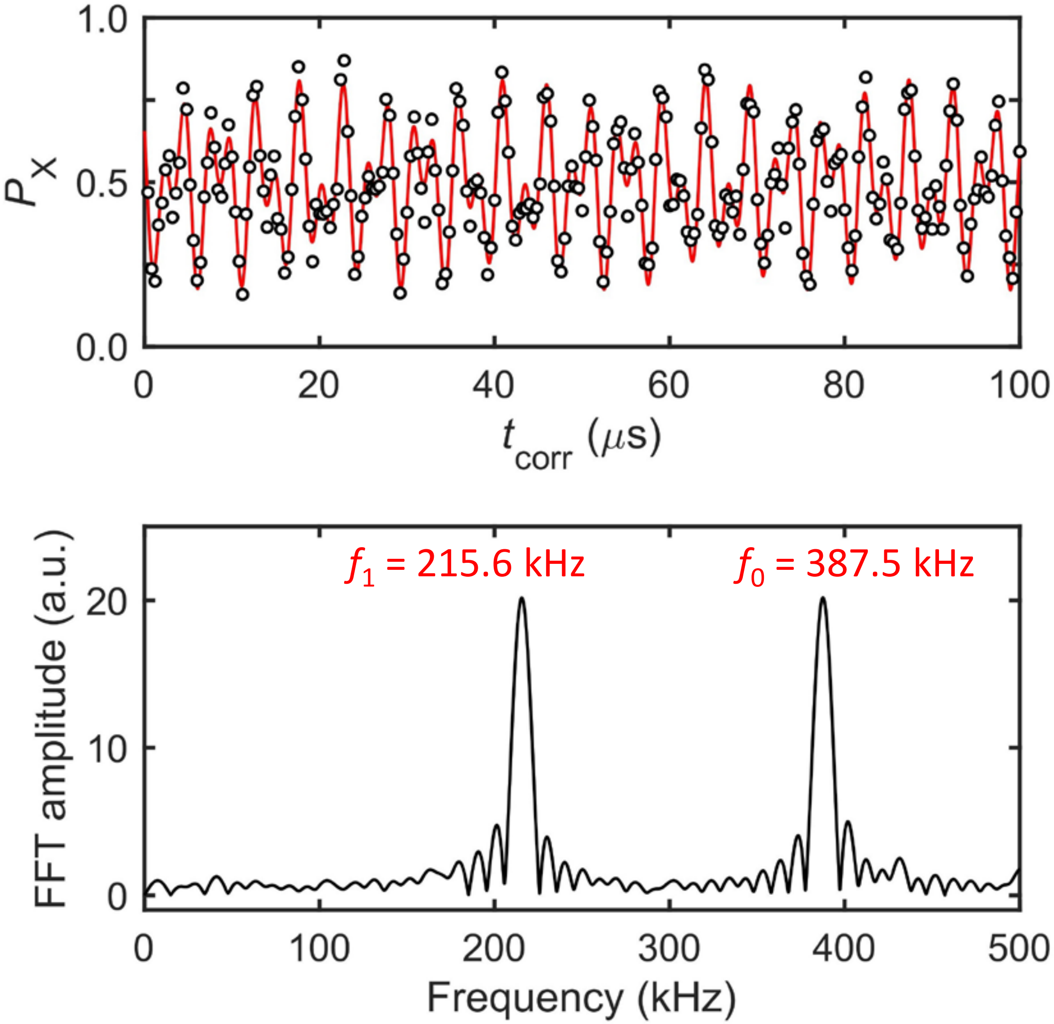


**Where to look at?**

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

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

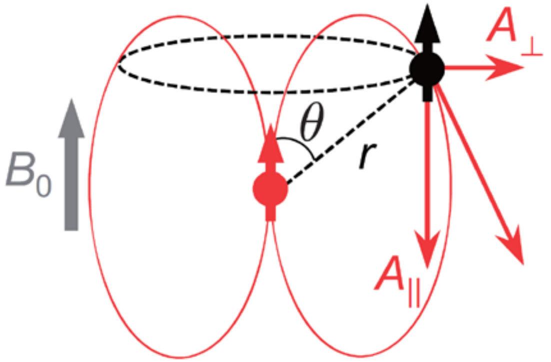
# Correlation spectroscopy of a nucleus



**No decay up to 100 μs**

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

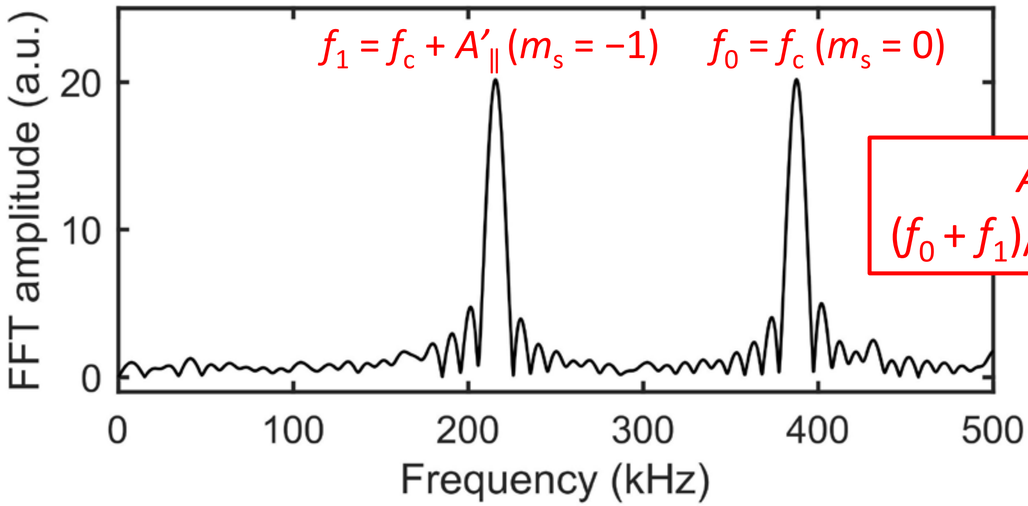
# Correlation spectroscopy of a nucleus



**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

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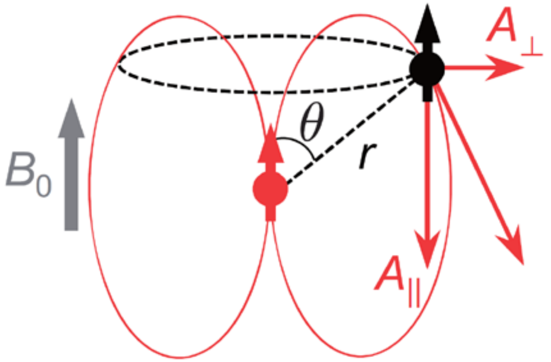
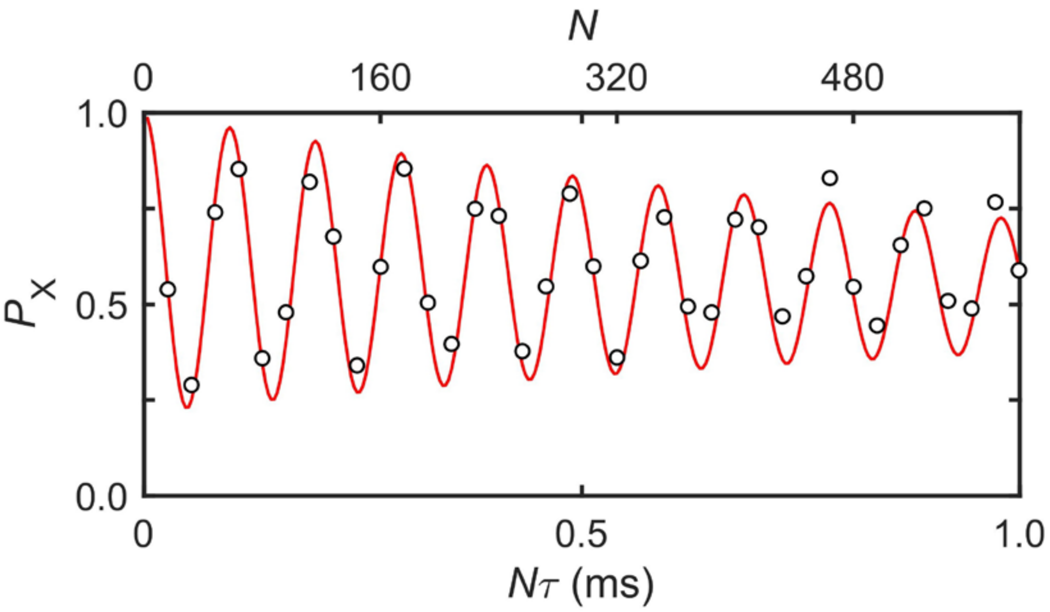
# Coherent control of a nuclear spin



**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**

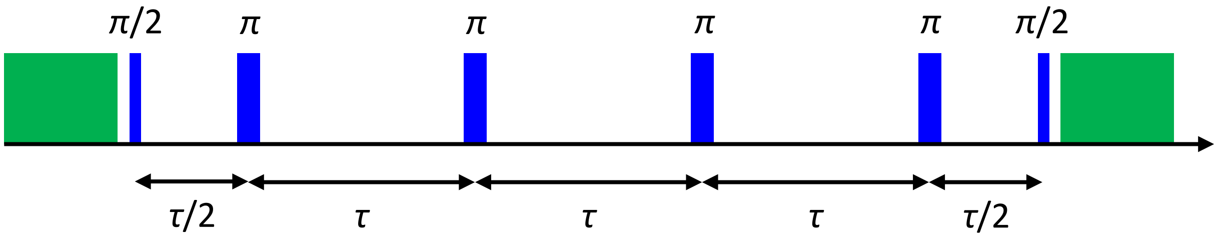


$$\tau \approx f_c + \frac{A_\parallel}{2}$$

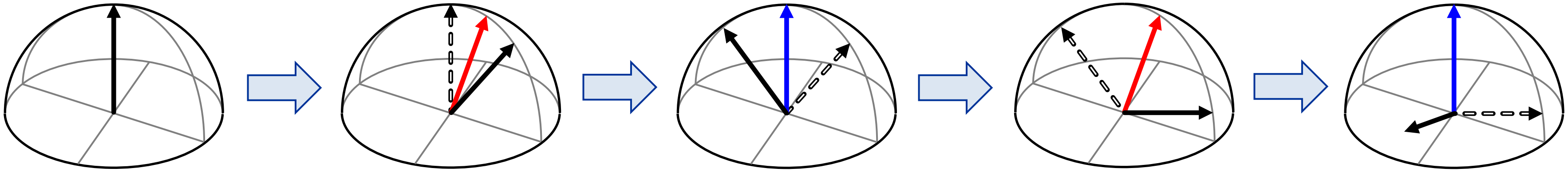
Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

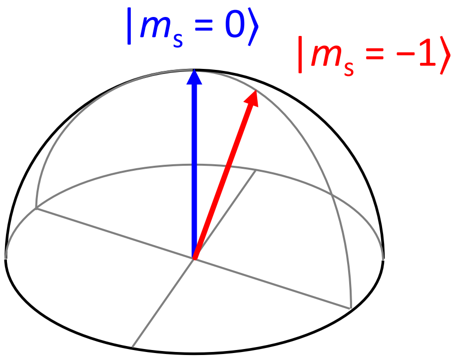
# Conditional rotation of a nuclear spin

**CP (*N* = 4)**



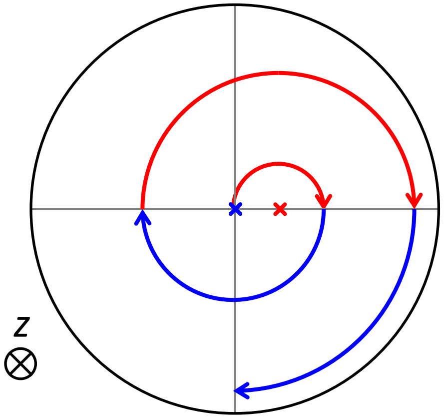
**Evolution of *n*-spin vector**



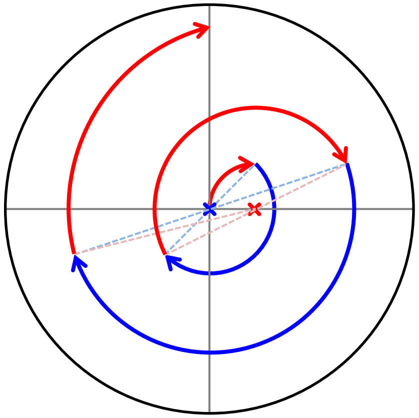


Q-axis of *n*-spin

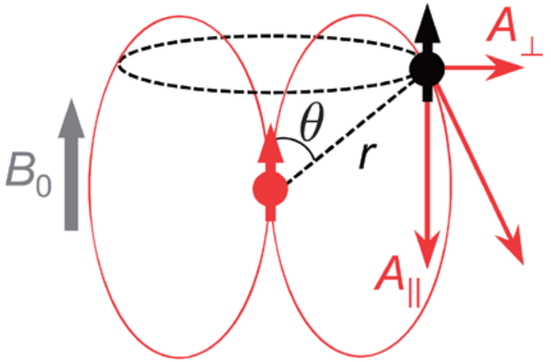
***Start from*** $|m_s = 0\rangle$



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



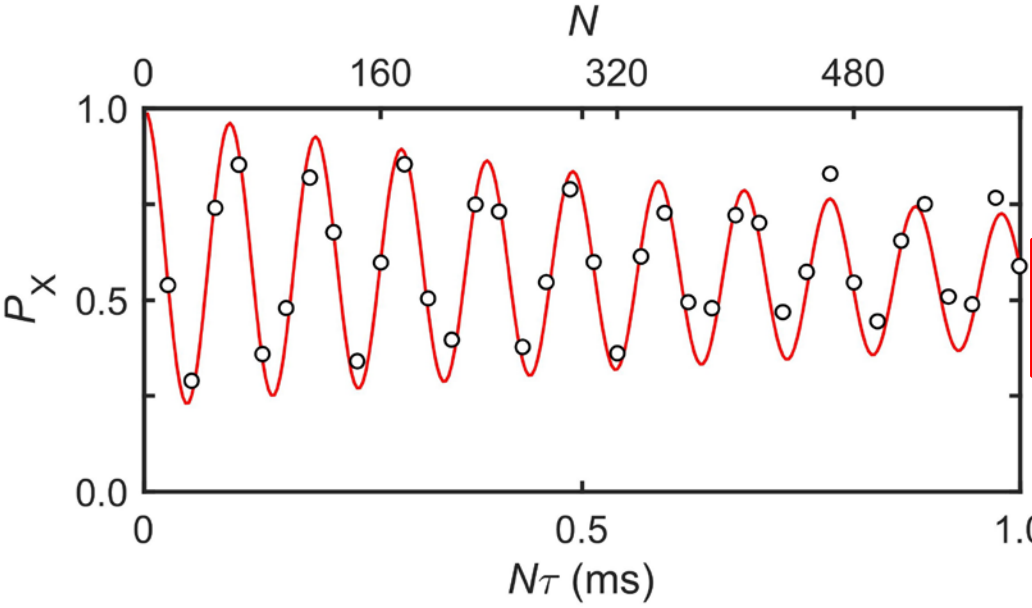
# Coherent control of a nuclear spin



**Transition probability of the NV spin**

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

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



$f_\mathrm{cp}$ = 10.2 kHz ≈ $A'_\perp/2$
$P_\mathrm{X} < 0.5$ → single

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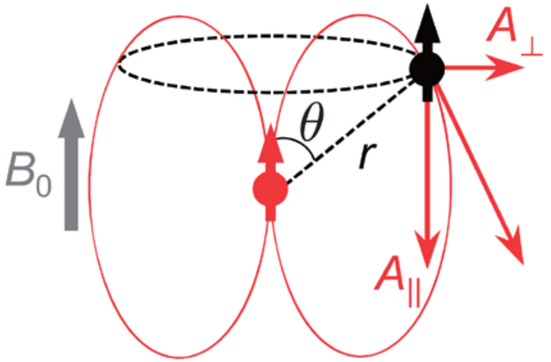
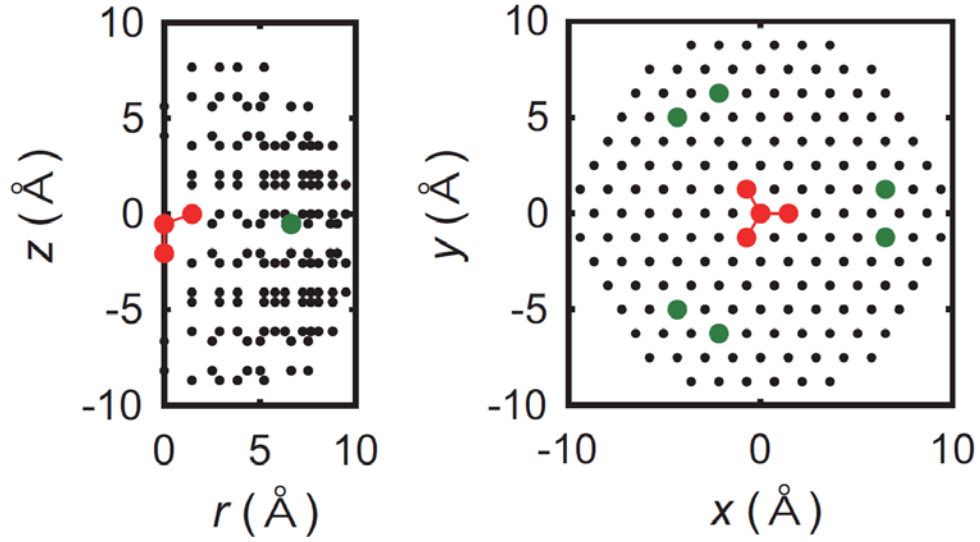
# Determination of hf constants



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

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



($r$, $\theta$) = (6.84 Å, 94.8°)

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

$A_\parallel = -175.1 \pm 2.1$kHz
$A_\perp = 21.9 \pm 0.2$ kHz

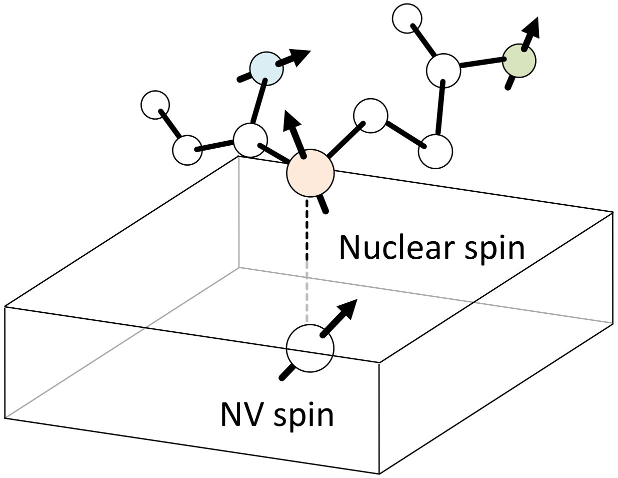
**DFT**: New J. Phys. **20**, 023022 (2018)
Nizovtsev *et al.*

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 ($A_{\parallel}$, $A_{\perp}$) ≈ ($r$, $\theta$)
  - → Lack of information on the azimuthal angle $\phi$

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



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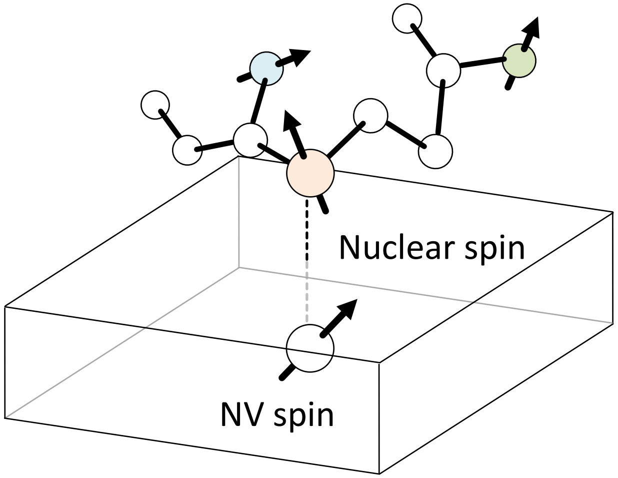
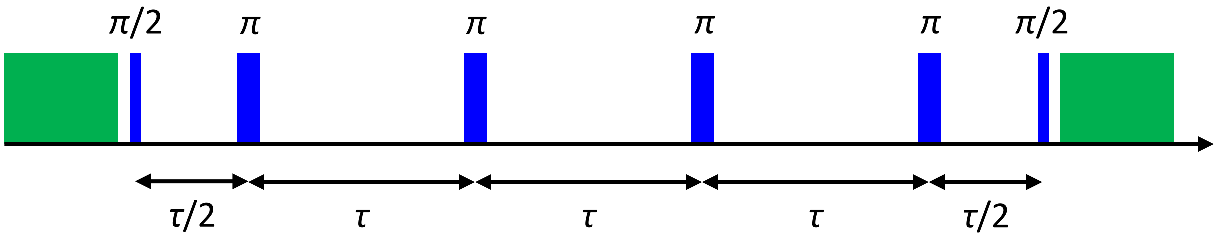


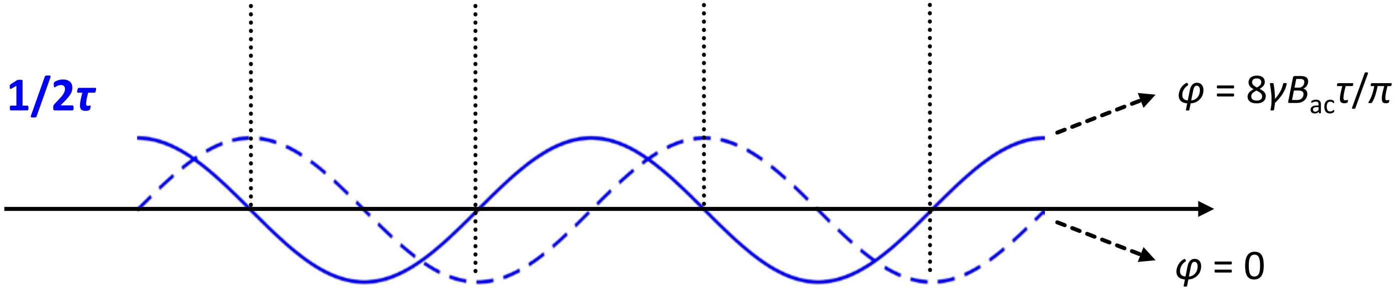
# AC magnetometry

**CP ($N$ = 4)**



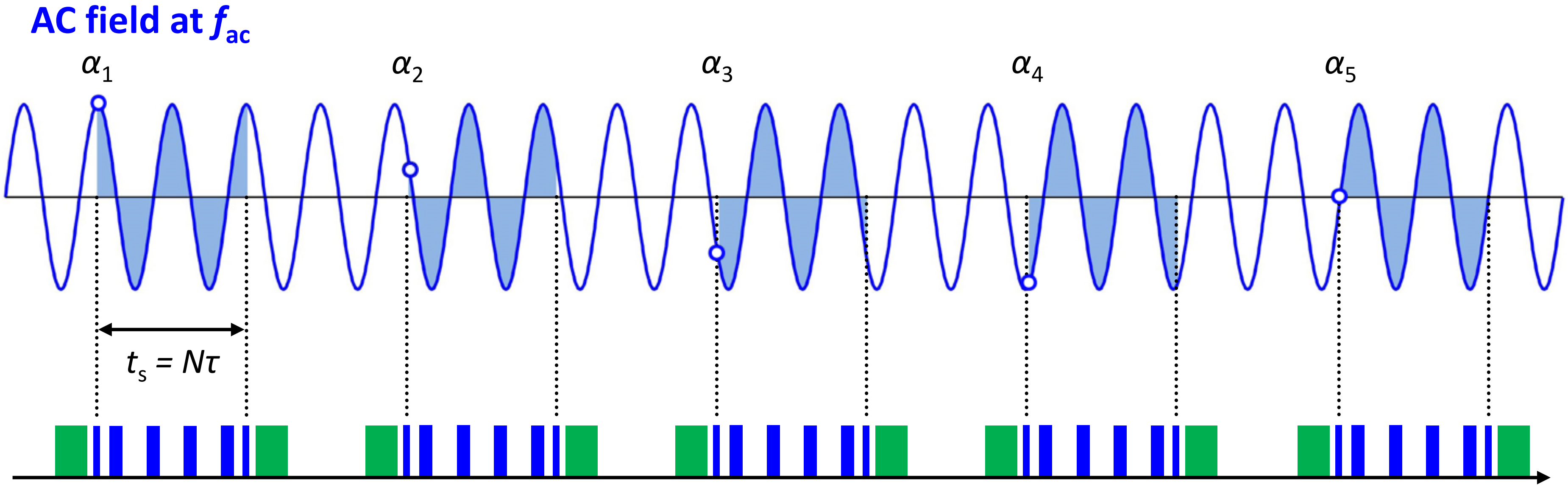
***Sign of phase accumulation***

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



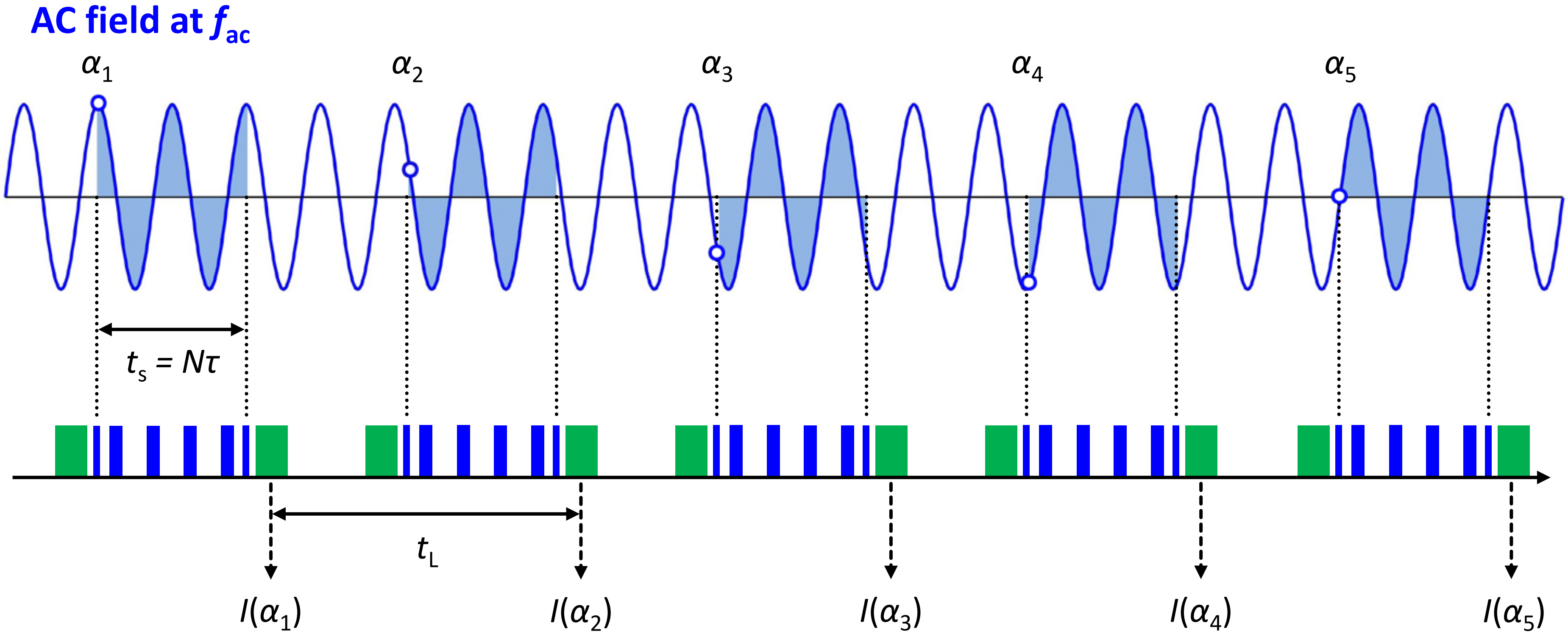
- $\varphi$ depends on the **initial phase $\alpha$ of the AC field** ($\varphi \propto \cos \alpha$)

# AC magnetometry



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

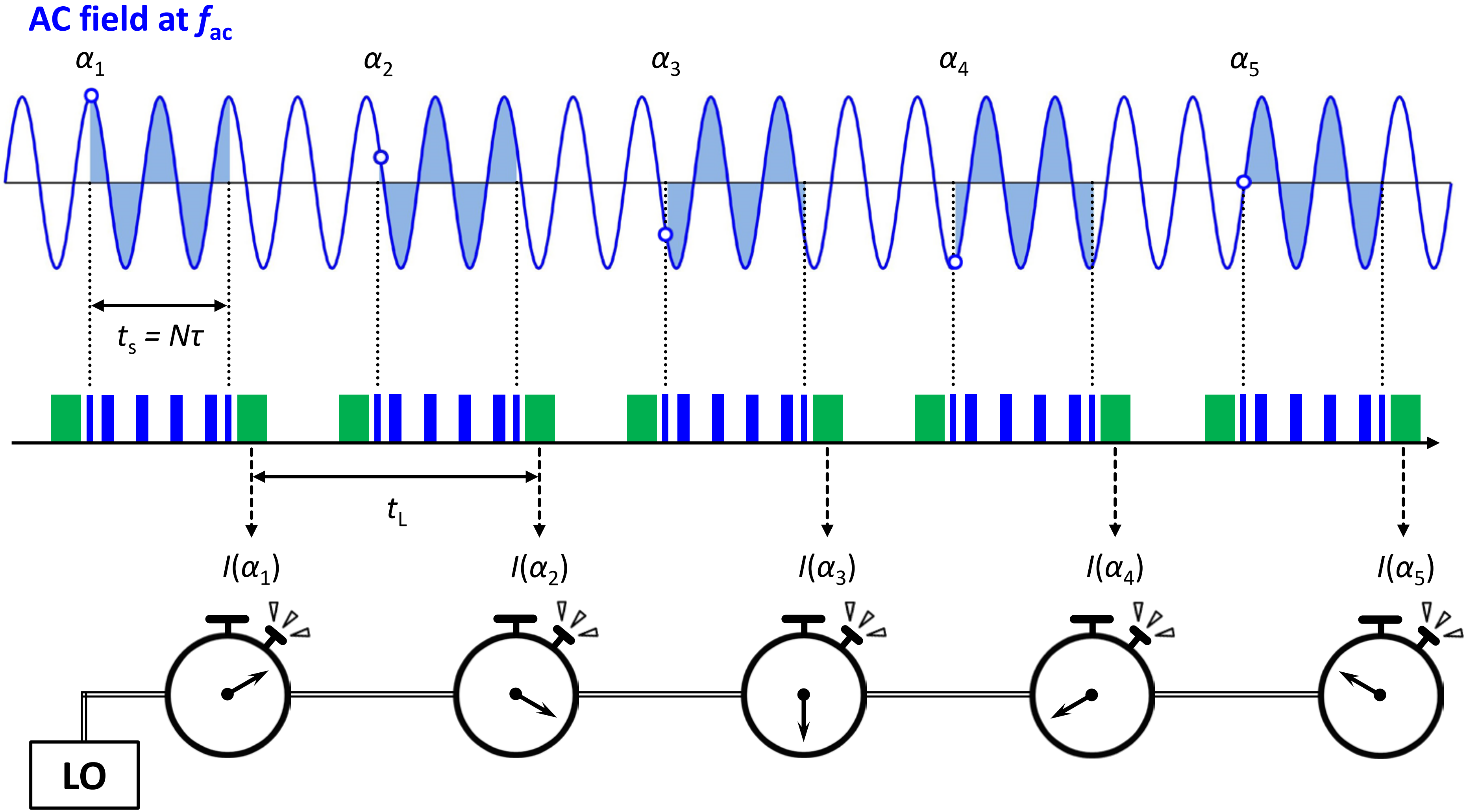
# Ultrahigh resolution sensing



- $\varphi$ 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.*

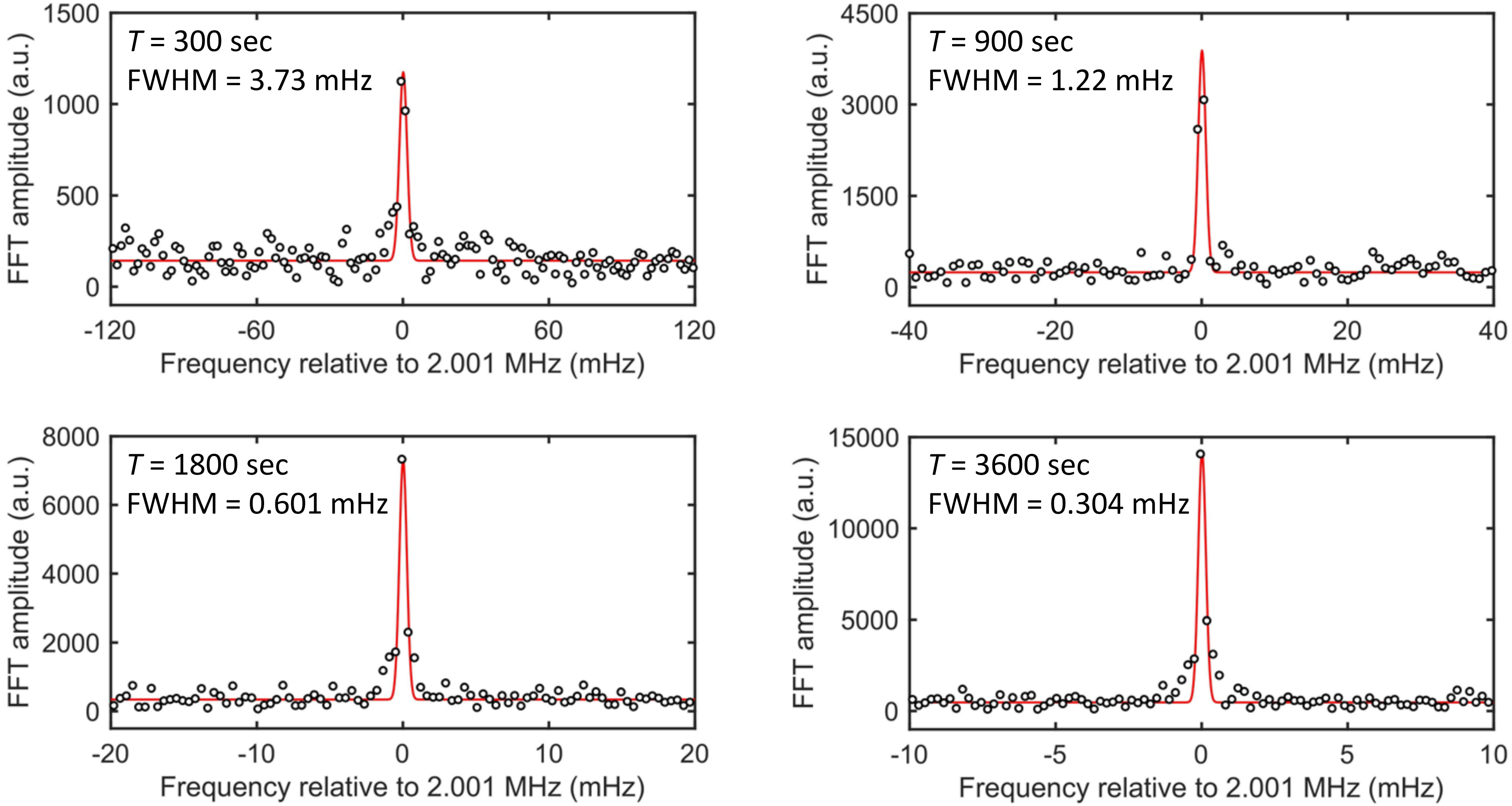
# Ultrahigh resolution sensing



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

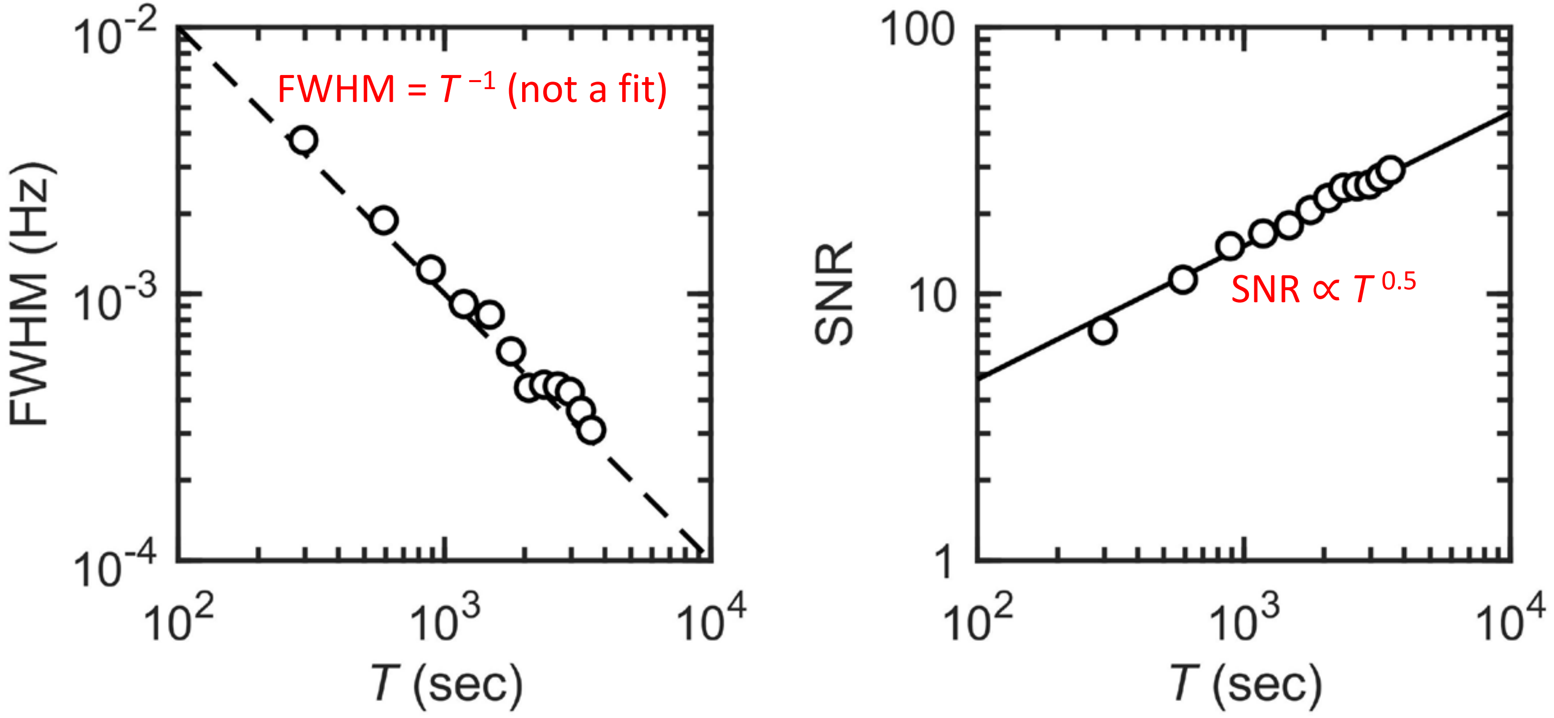
# Ultrahigh resolution sensing

**$B_{ac}$ = 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

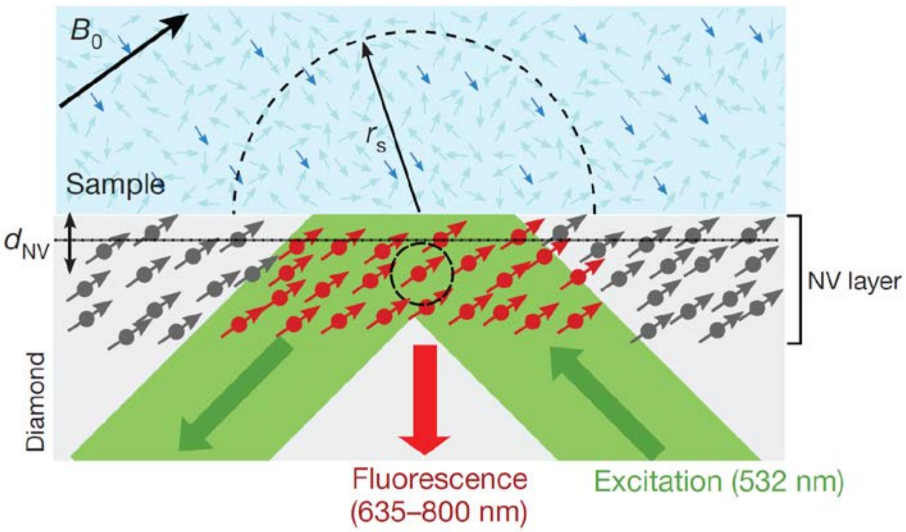


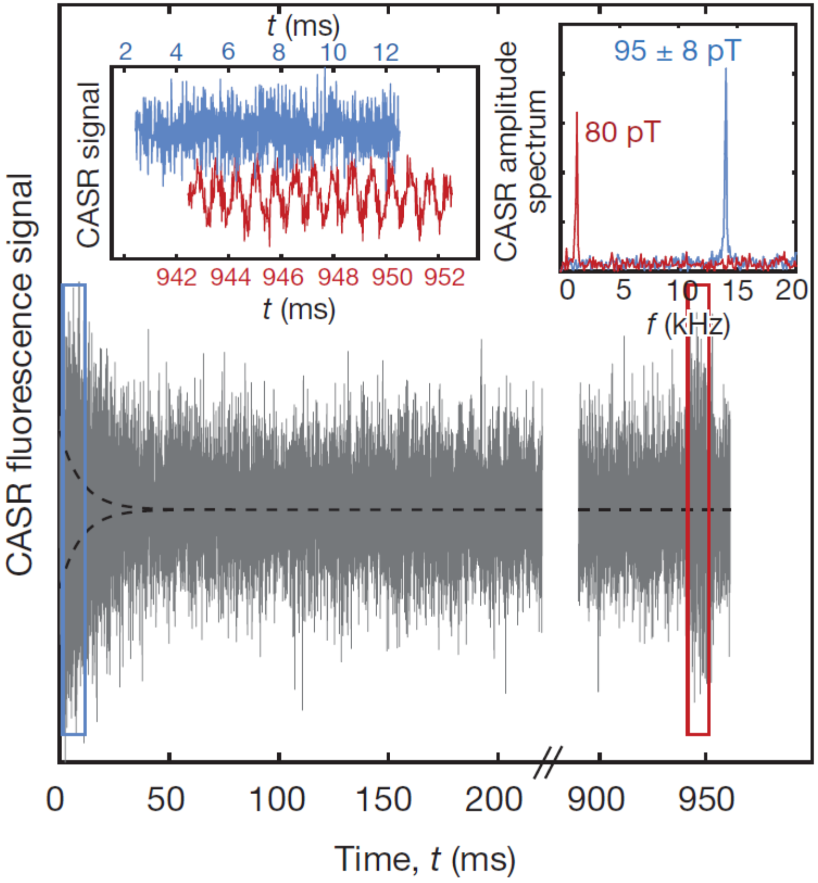
- Spectral resolution not limited by sensor/memory lifetimes ($T_{2e/n}$, $T_{1e/n}$)
- Only limited by the stability of LO (essentially infinite)
- Resolution = $T^{-1}$ & SNR ∝ $T^{0.5}$ → Precision ∝ $T^{-1.5}$

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 $\approx 5 \times 10^{9}$
- $V_{\text{detect}} \approx 25$ pL
- # of protons $\approx 2.5 \times 10^{15}$
- 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

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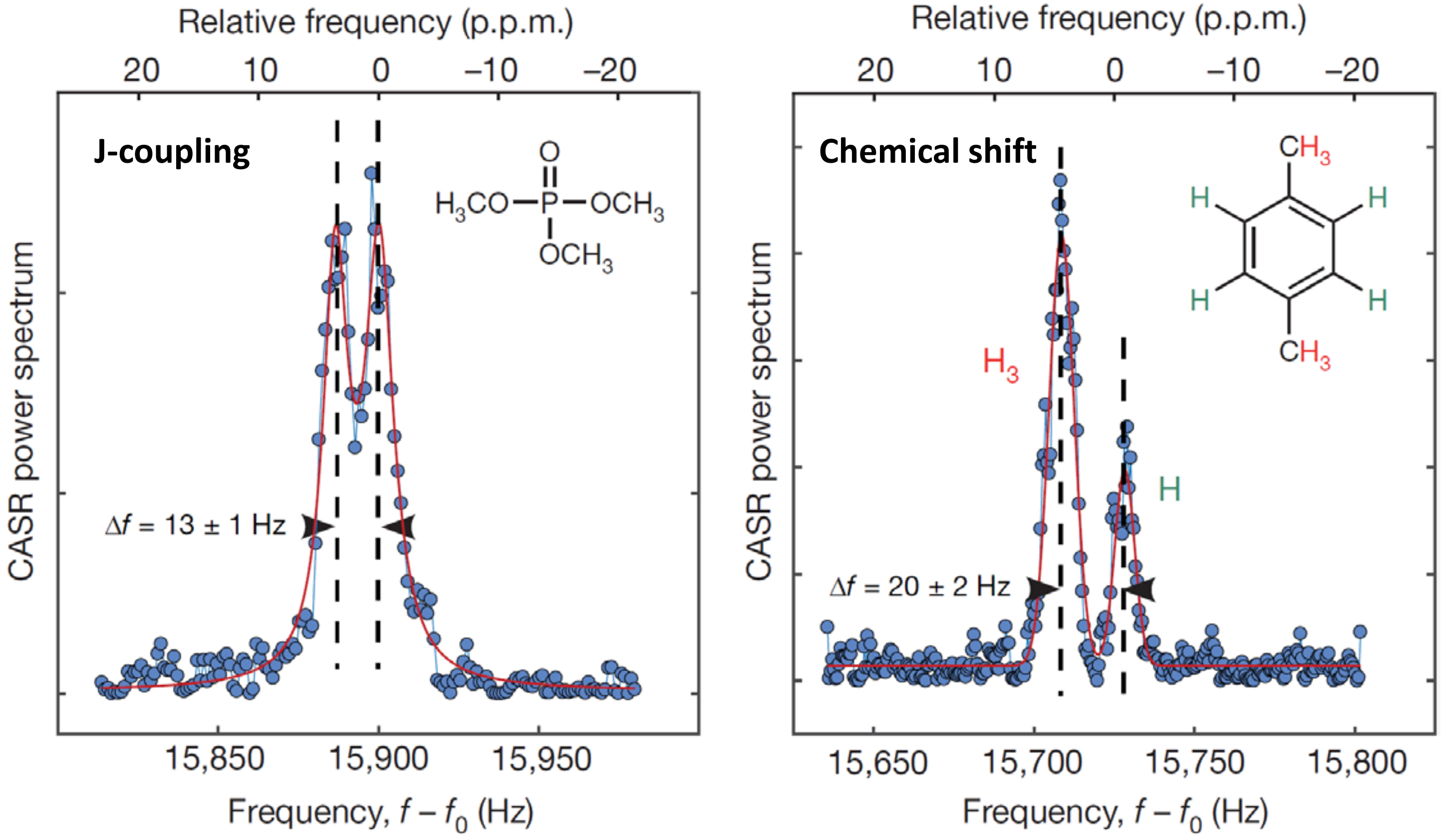

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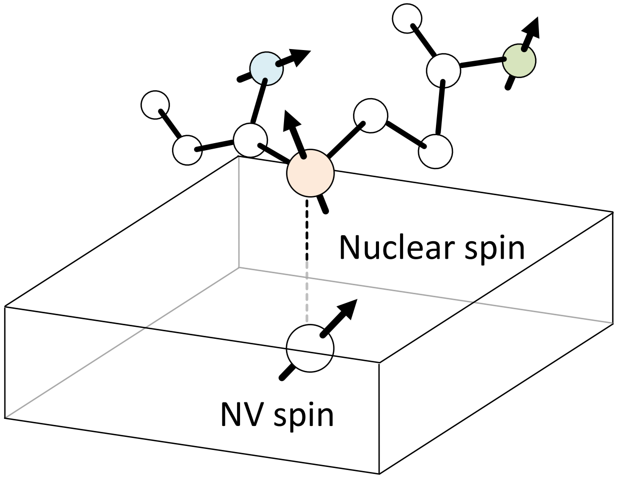
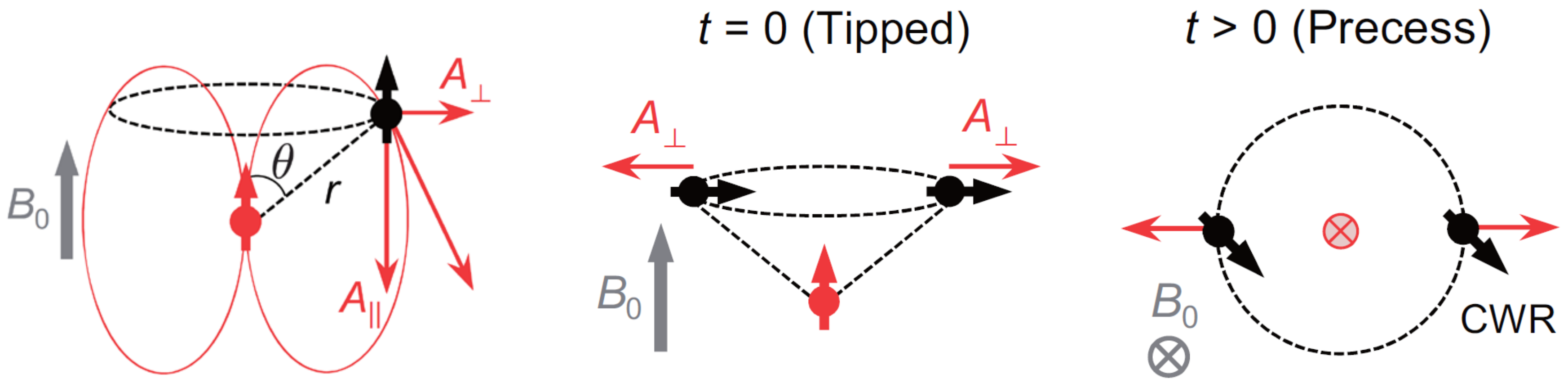


# How to determine $\phi$?



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

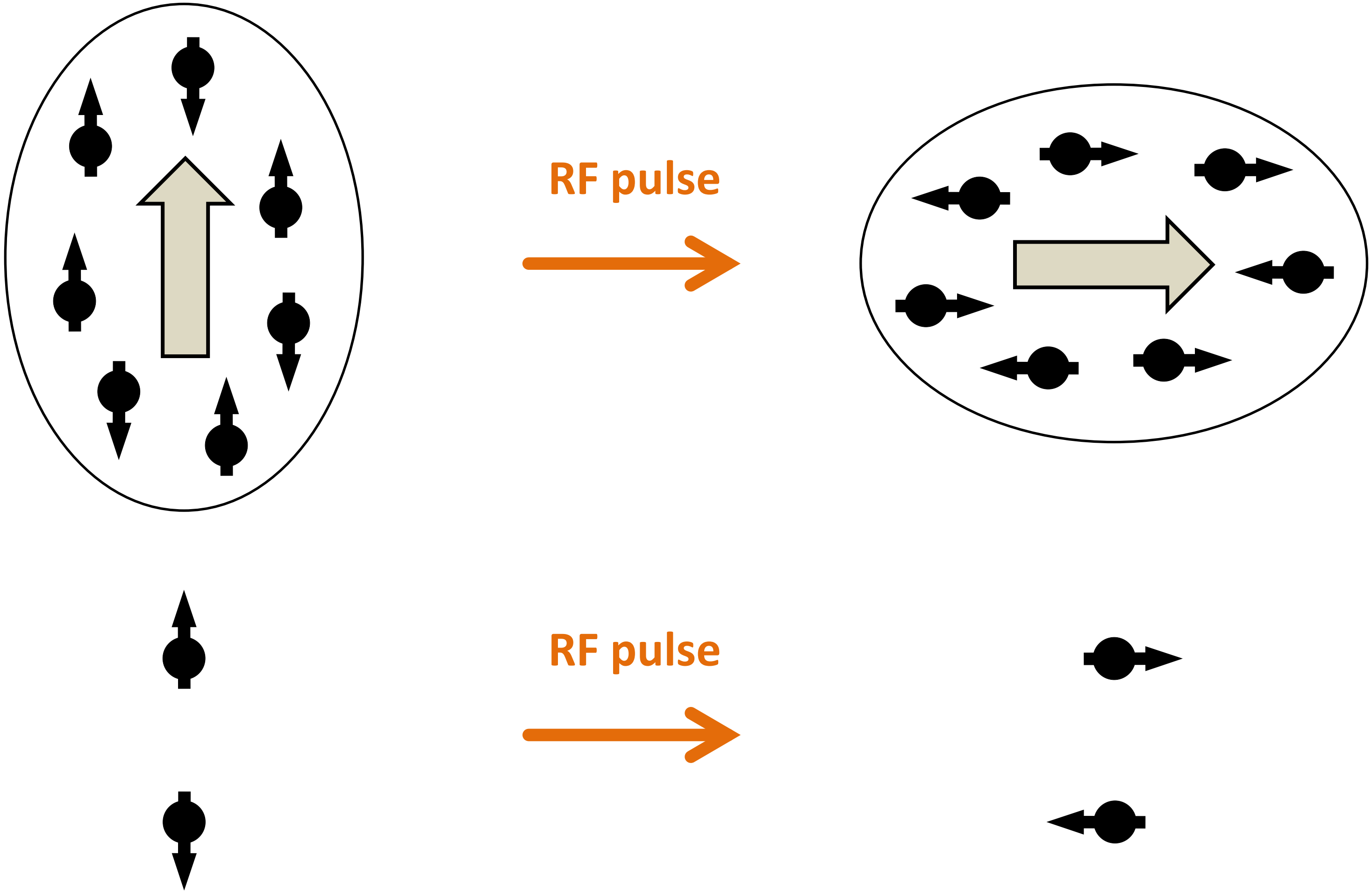
$$P_\mathrm{Y} = \frac{1}{2} - \frac{1}{2}\cos(\phi - \phi_\mathrm{n})\sin N\phi_\mathrm{cp}$$

↓

Azimuthal angle of the nuclear Bloch vector: $2\pi f_\mathrm{p} t + \phi_\mathrm{n}(0)$

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

# Ensemble vs. single

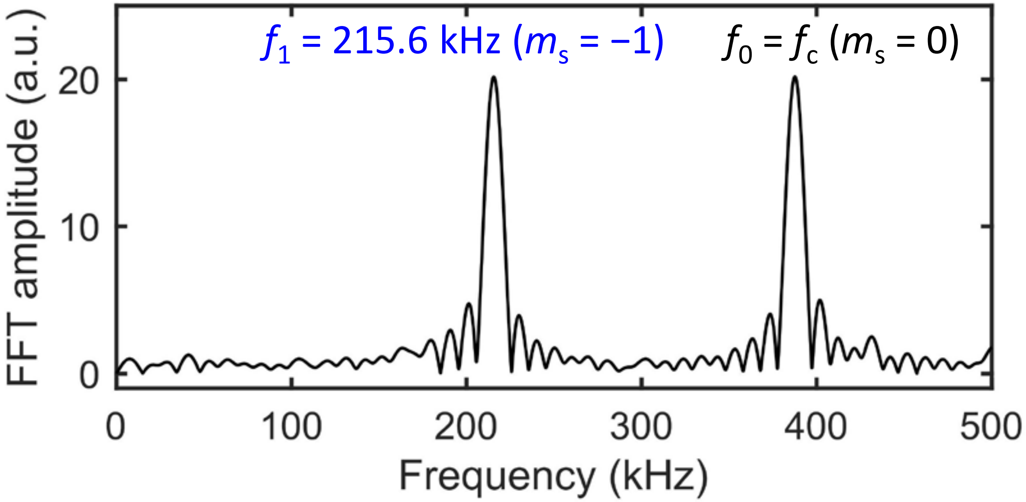


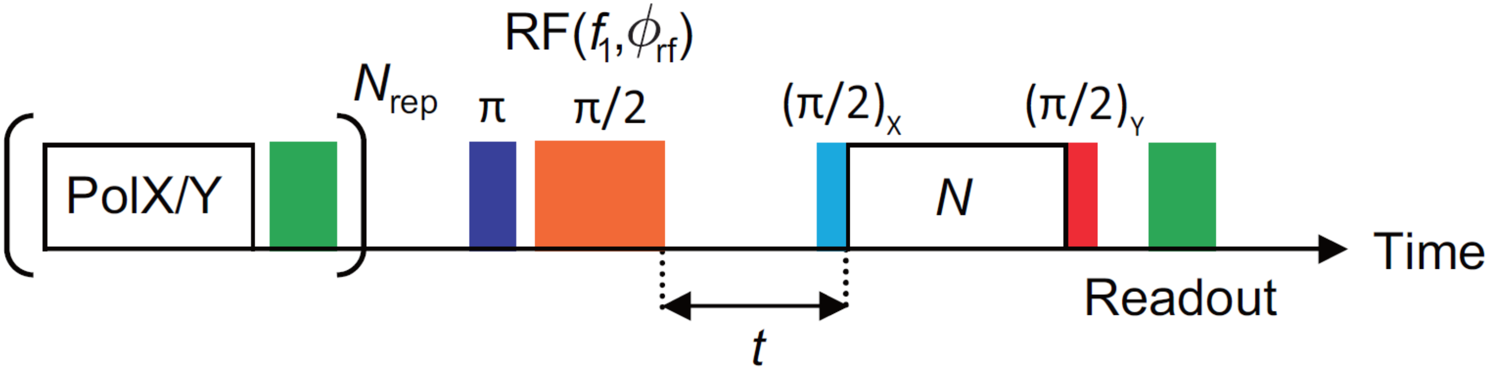
**The initial state matters**

→ Dynamic nuclear polarization (DNP)

# Determination of $\phi$ of a $^{13}$C *n*-spin

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



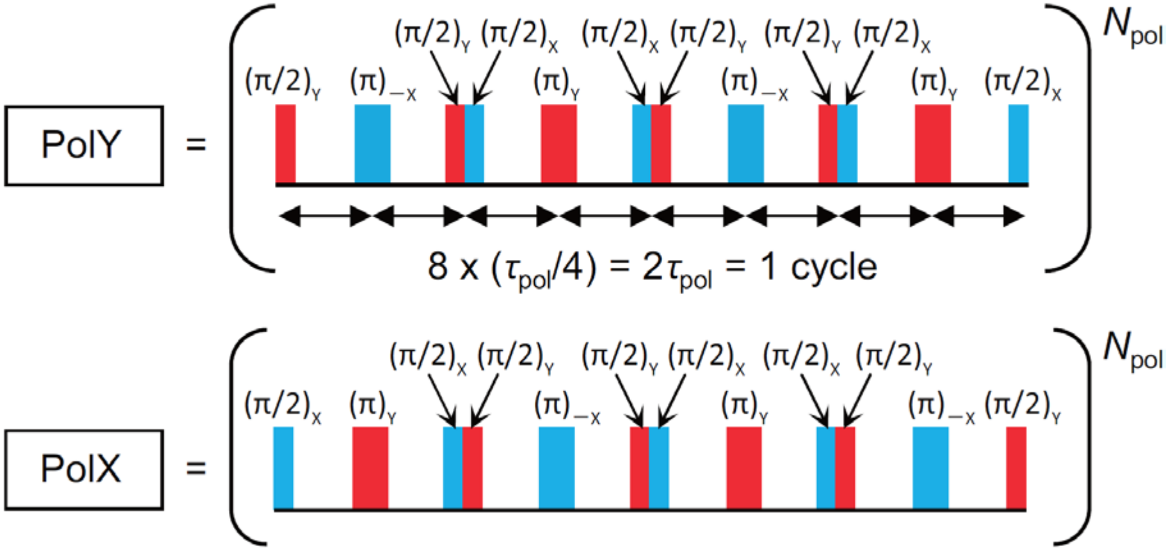


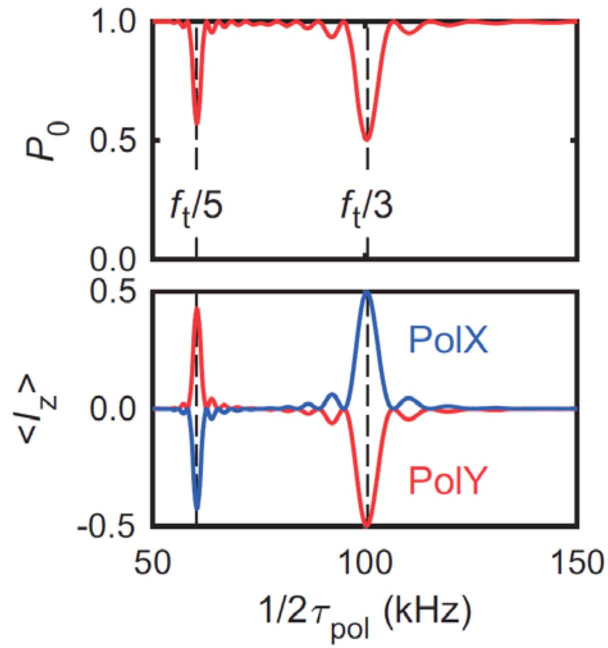
Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

# PulsePol

**Hamiltonian engineering**

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

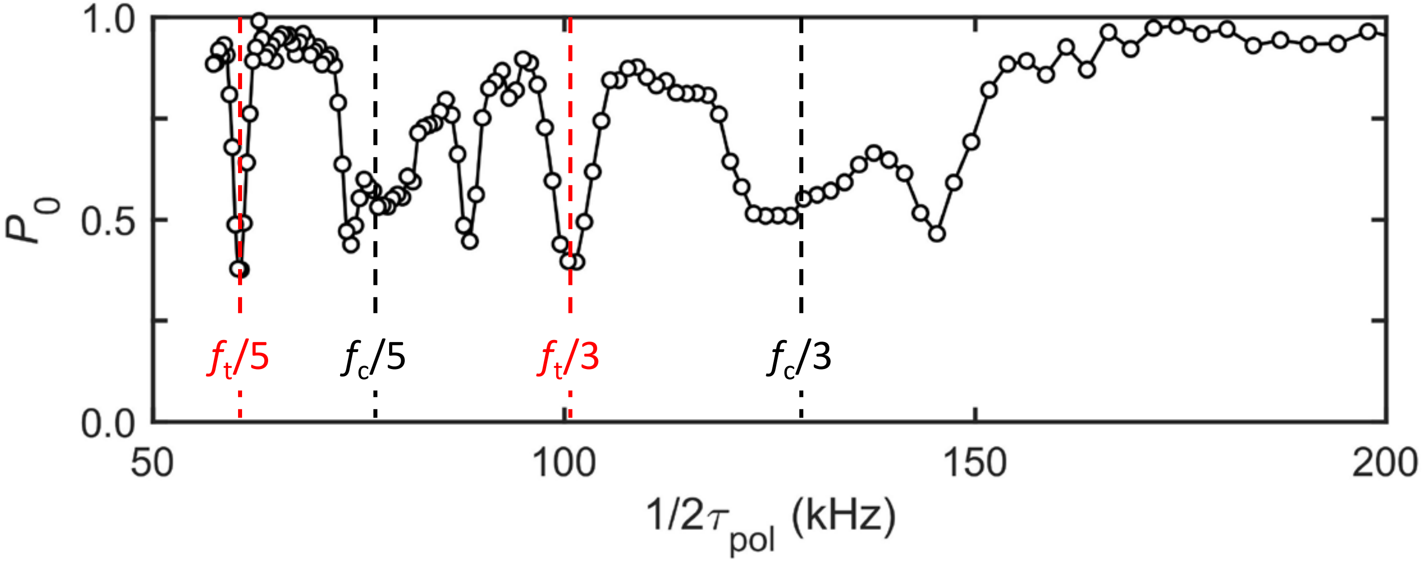


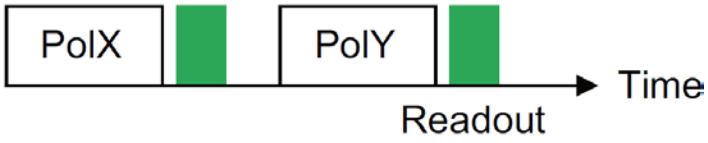


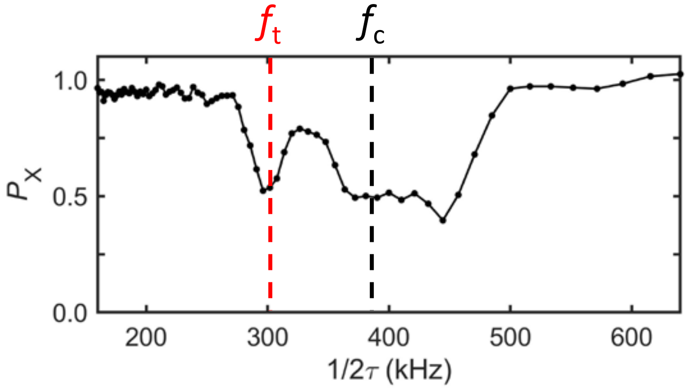
**[PulsePol]** Sci. Adv. **4**, eaat8978 (2018) Schwartz *et al.*

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

# PulsePol







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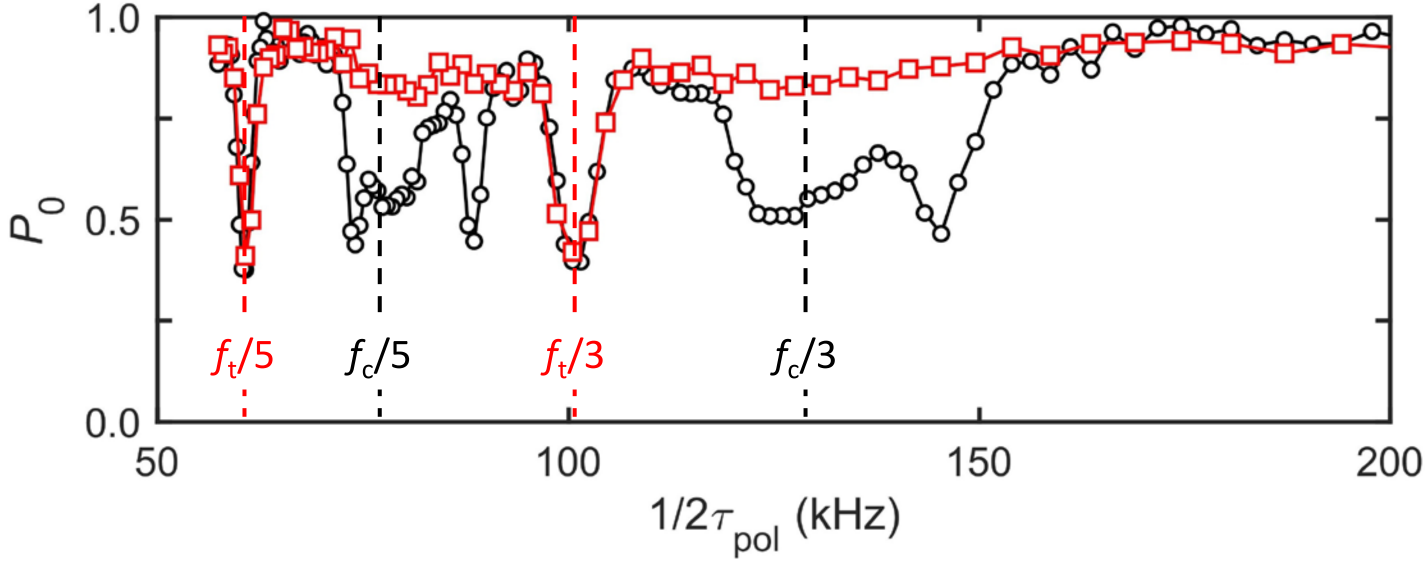
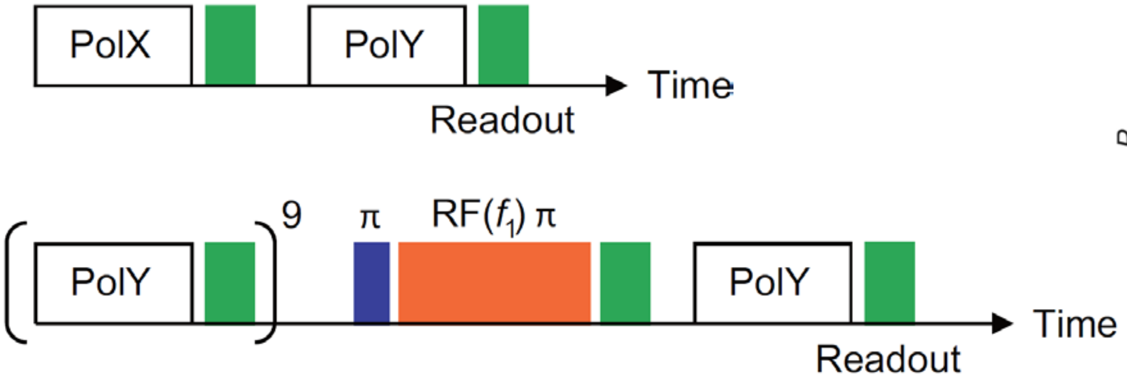
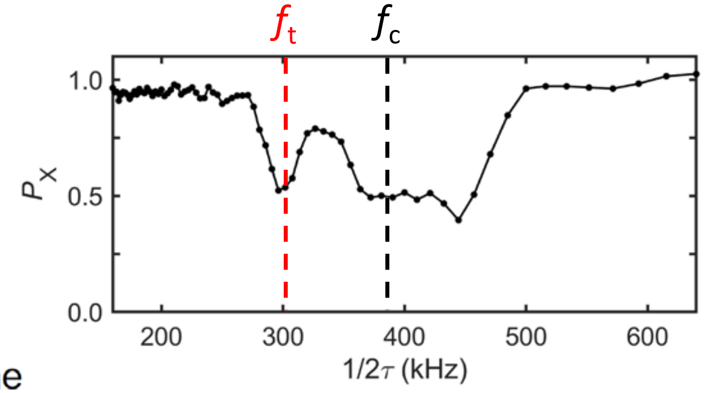
# PulsePol







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

# Determination of $\phi$ of a $^{13}$C *n*-spin

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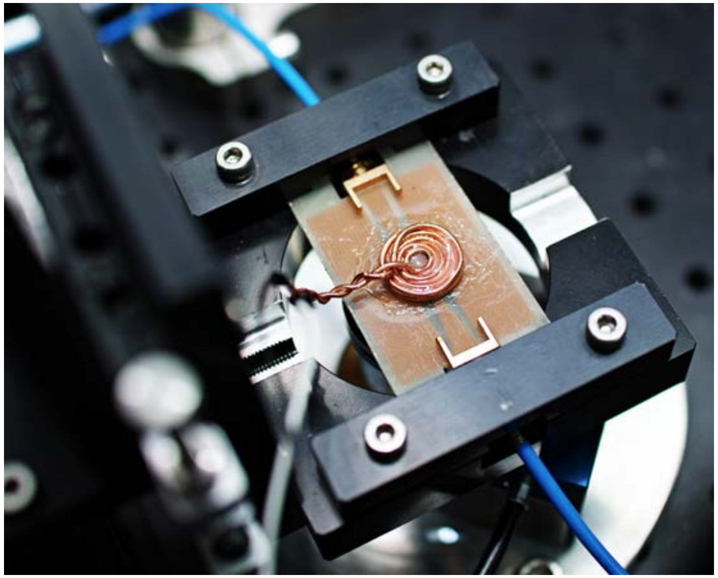
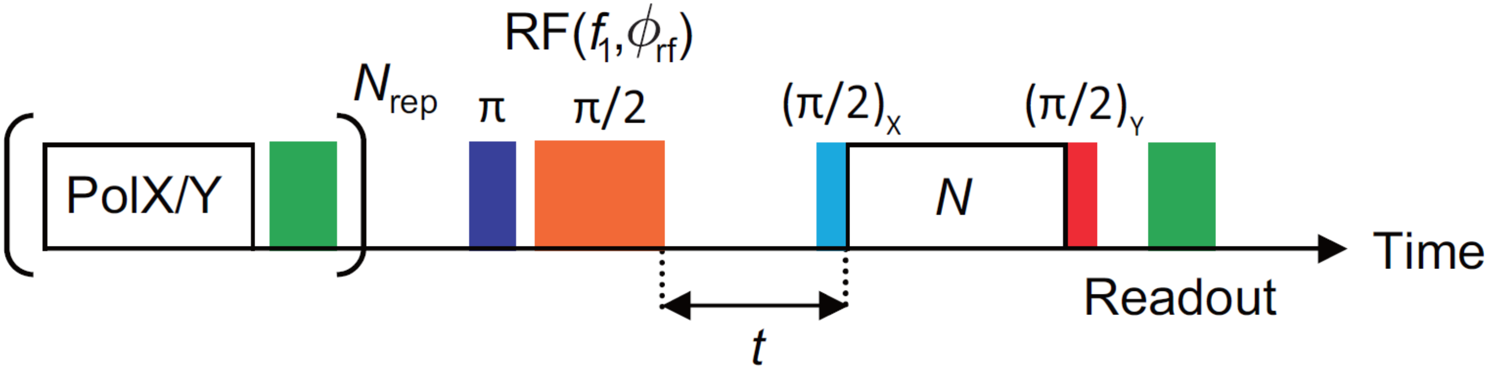
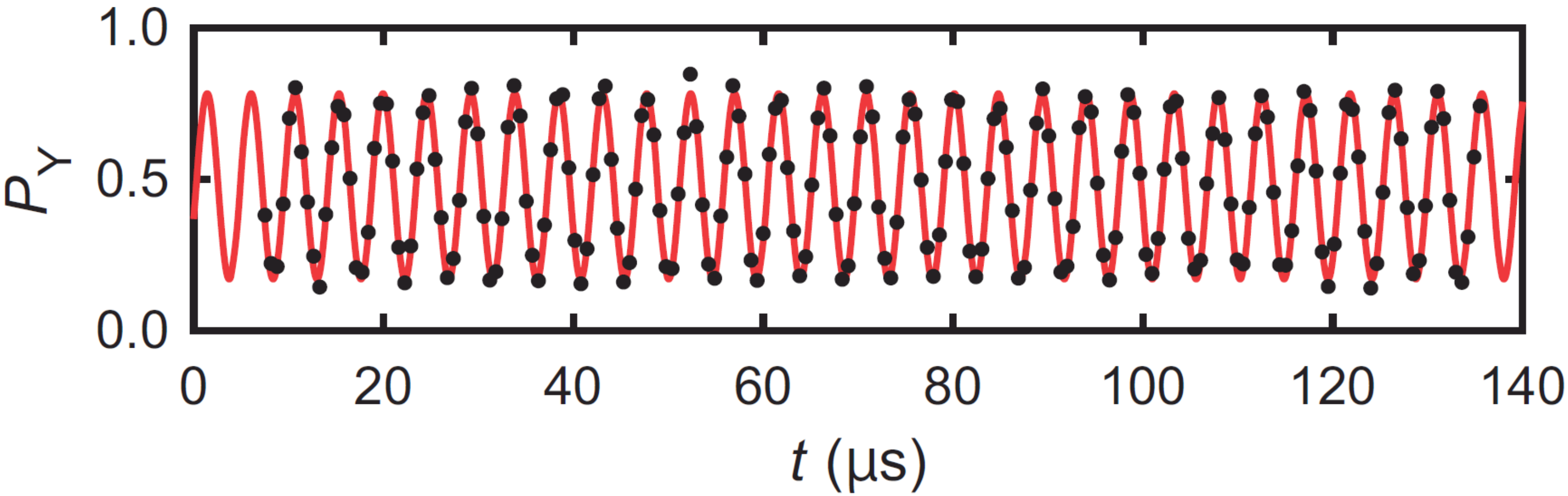




Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

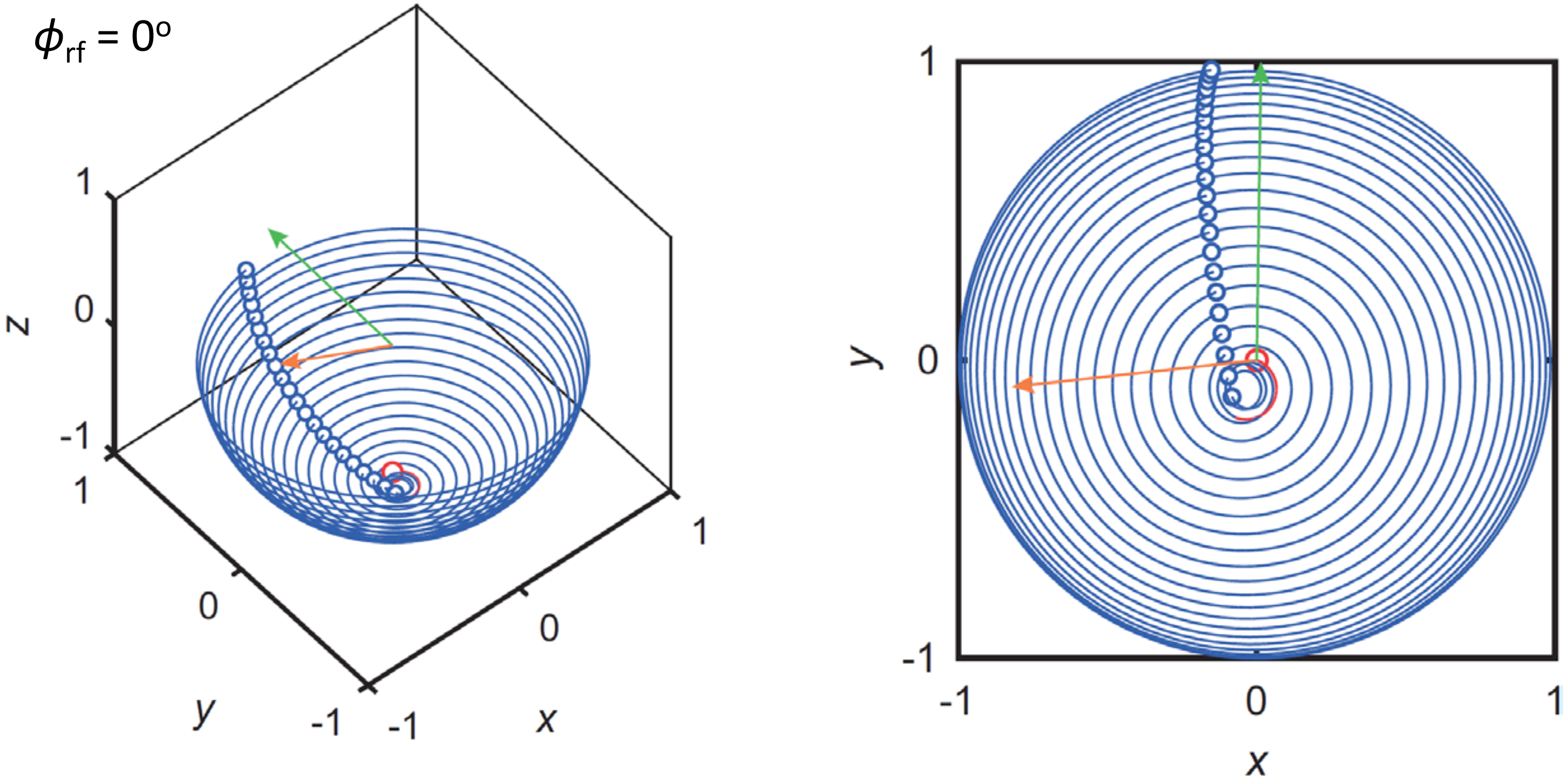
# Determination of $\phi$ of a $^{13}$C $n$-spin



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

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

# $\phi_n(0)$: Real-space *n*-spin trajectory



⟶ Direction of the RF field

⟶ Bloch vector@$t$ = 0 (Considering the rotation axis of the n-spin & detuning)

— Full simulation based on the Bloch equation (Tilt of q-axis, pulse delay...)

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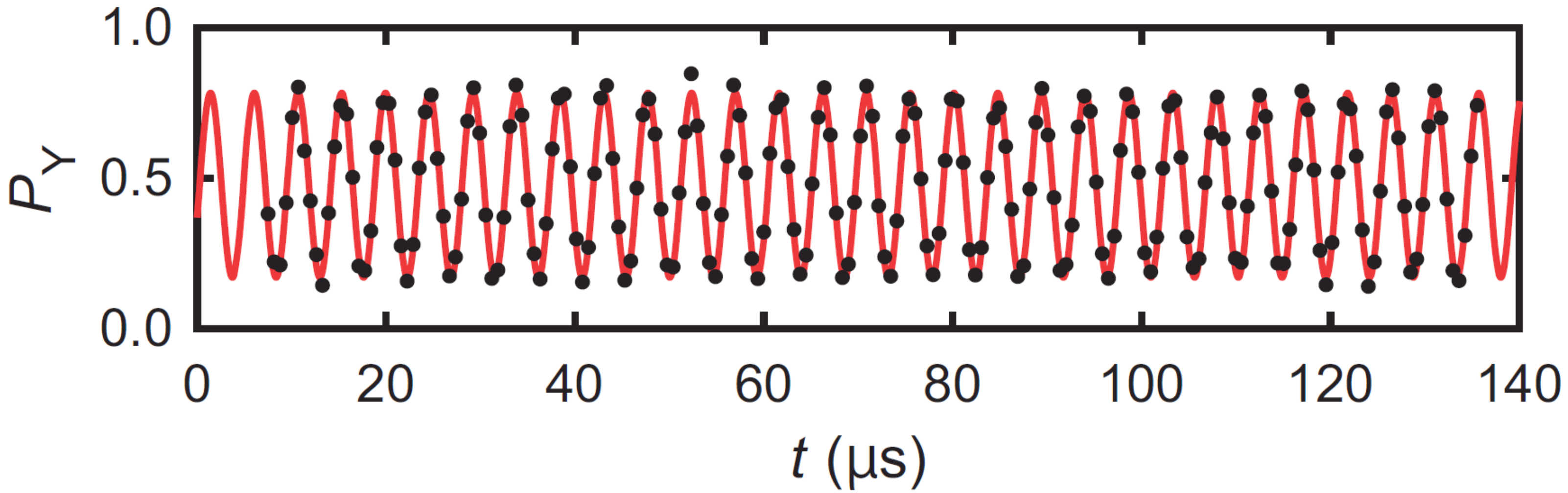
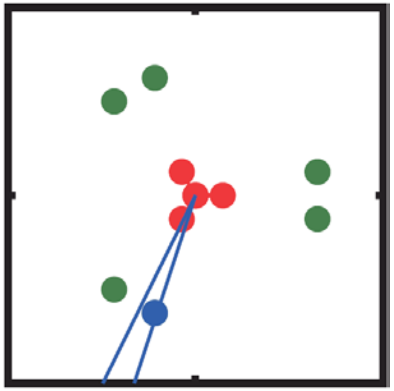
# Determination of $\phi$ of a $^{13}$C *n*-spin



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

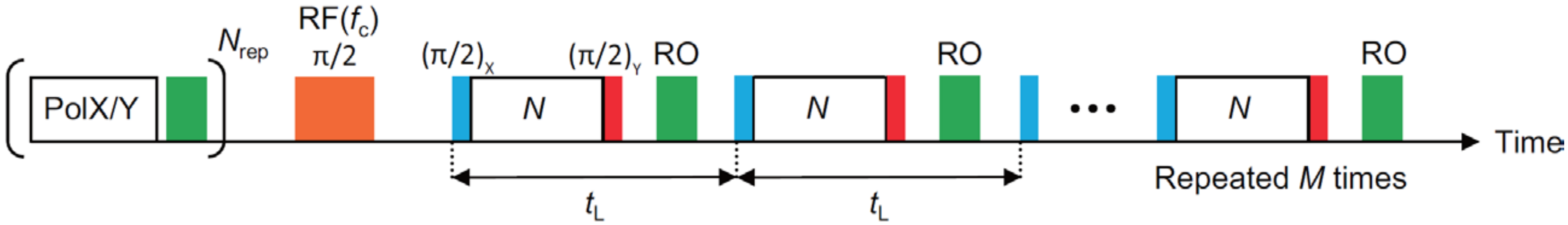
→ $\phi = 247.8 \pm 4.1^\circ$

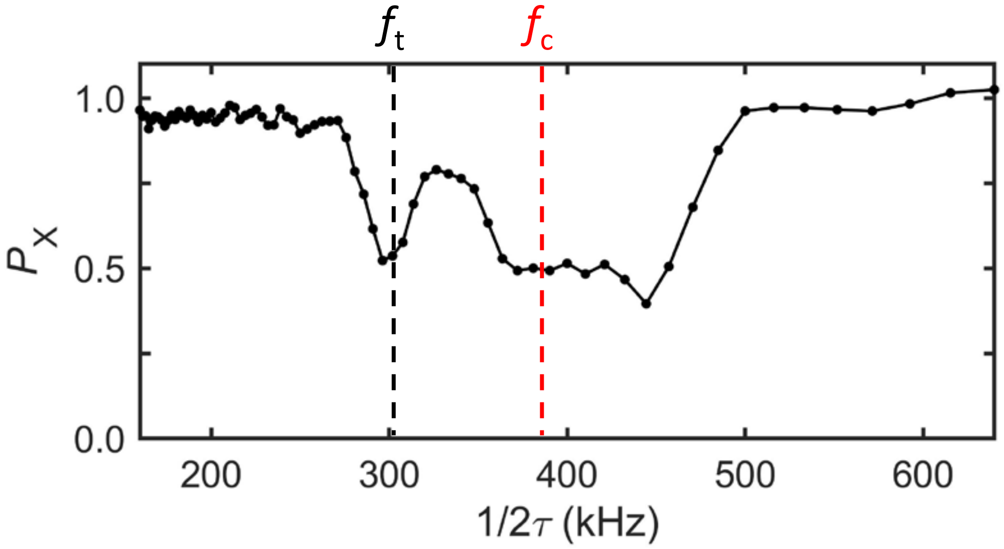


Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

# Observation of weakly coupled $^{13}$C *n*-spins

**Ultrahigh resolution sensing (*N* = 2)**





- $f_c$ = 387.5 kHz
- RF pulse@$m_s$ = 0
- $N$ = 2 to minimize **back actions** from NV

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

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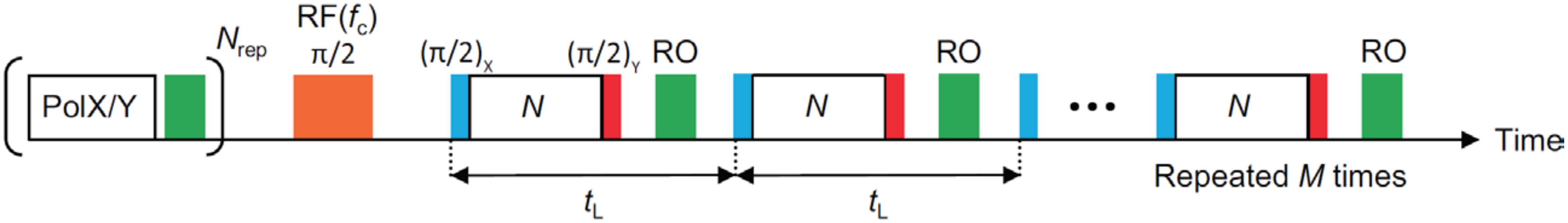

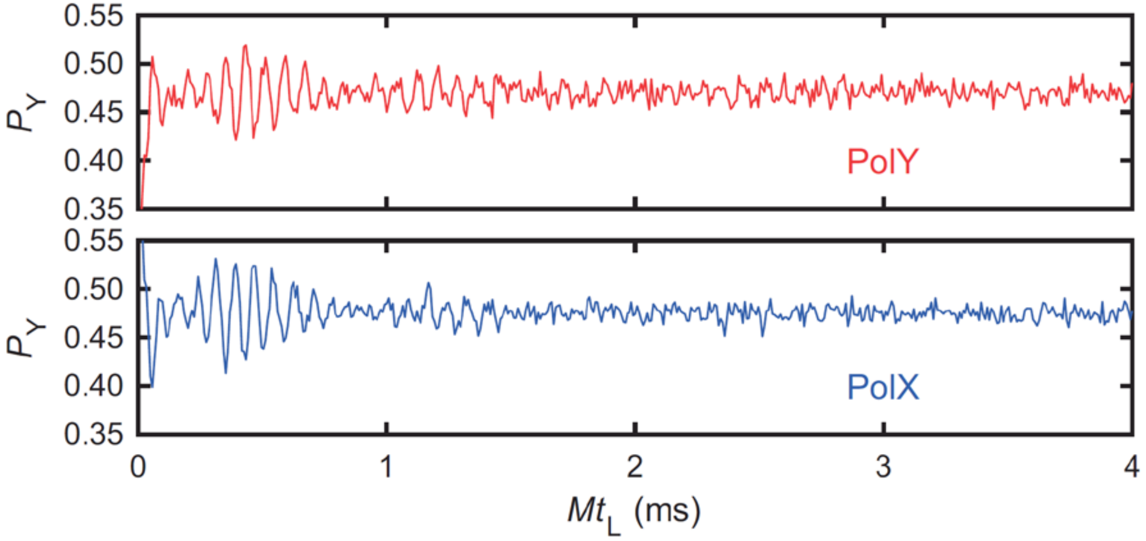

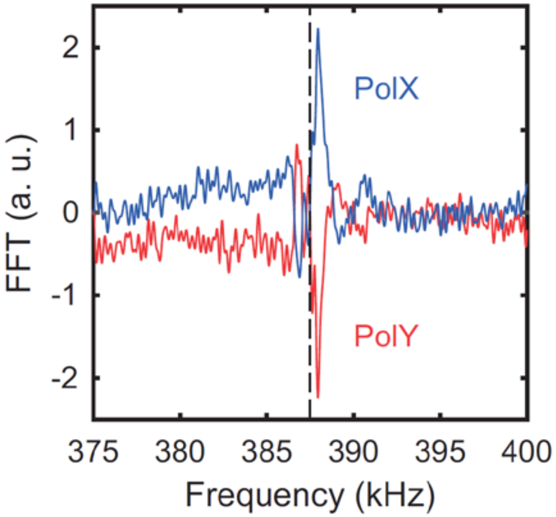

Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

# Summary

- **Tools for single-molecule imaging/structural analysis are being developed**

  → Determination of the position of a single *n*-spin[1,2]
  → Ultrahigh resolution sensing on single *n*-spins[1,3,4]

- **Other issues:** Create high-quality "shallow" NVs, accurately position single molecules/proteins near the sensor etc

[1] Phys. Rev. B **98**, 121405 (2018) Sasaki, Itoh & Abe (arXiv.1806.00177)
[2] Phys. Rev. Lett. **121**, 170801 (2018) Zopes *et al.* (arXiv.1807.04559)
[3] arXiv.1806.02181 Pfender *et al.*
[4] arXiv.1806.08243 Cujia *et al.*

**→ Suppressing back actions by weak measurement**