# Quantum sensing of proton spins with a single NV center

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2022.3.9

Physics Frontiers with Quantum Science and Technology

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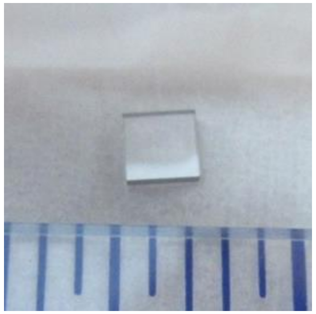
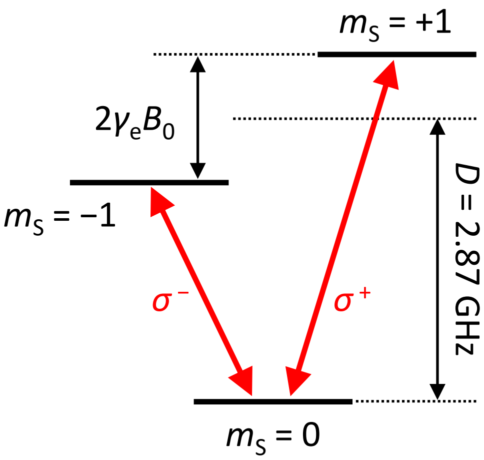
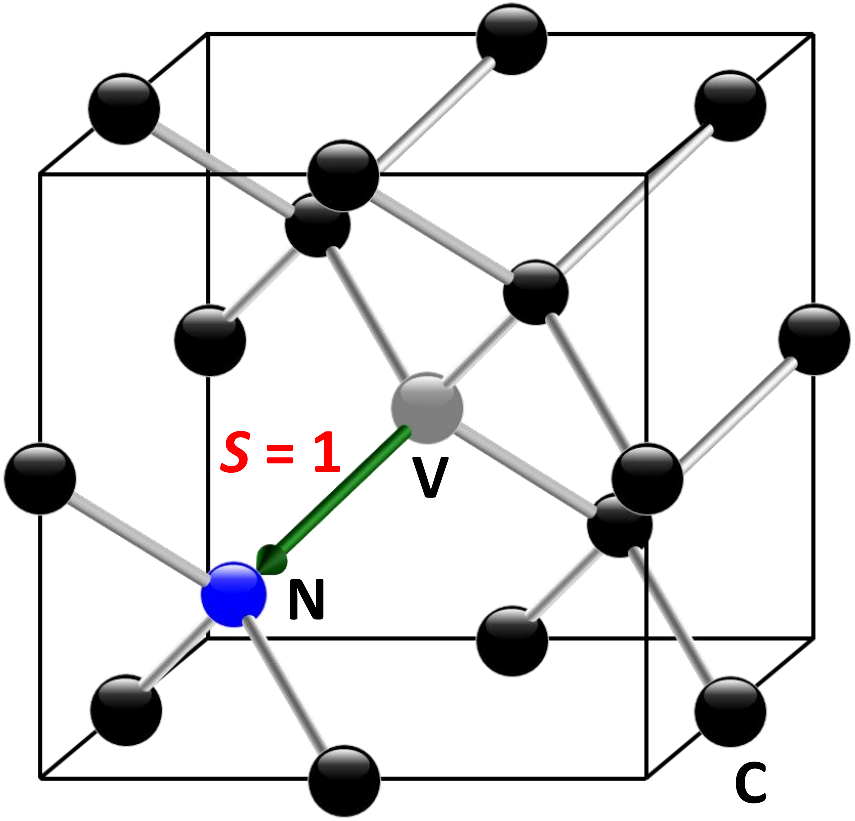
# NV center in diamond

**Synthetic (CVD) diamond**
[N] < 5 ppb, [NV] < 0.03 ppb





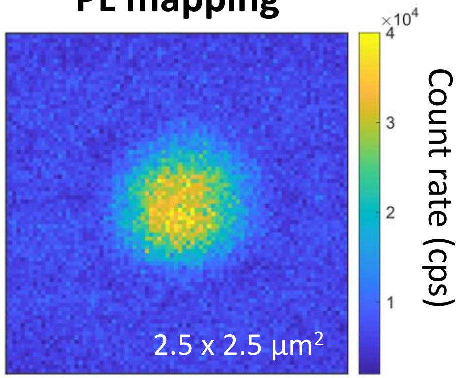




$\rho_C = 1.77 \times 10^{23}$ cm$^{-3}$

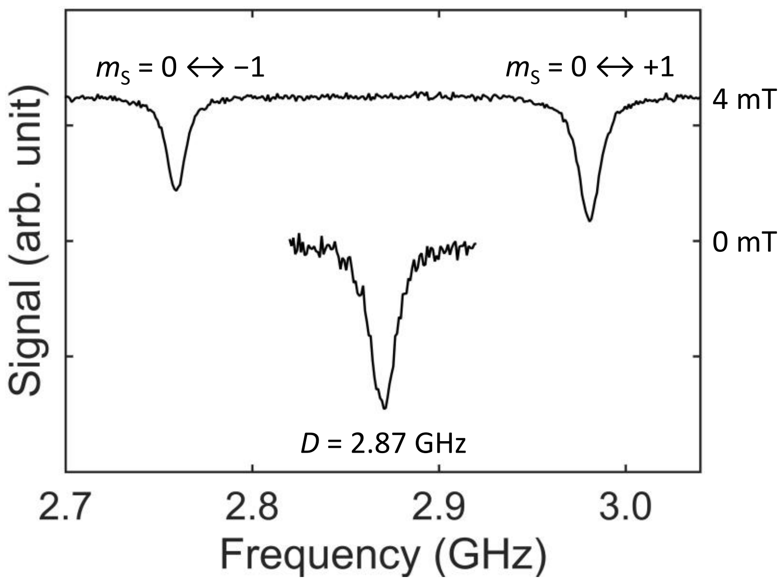
# NV center in diamond

- Optical detection & initialization of single spins
- Microwave control of single spins
- Room temperature operation

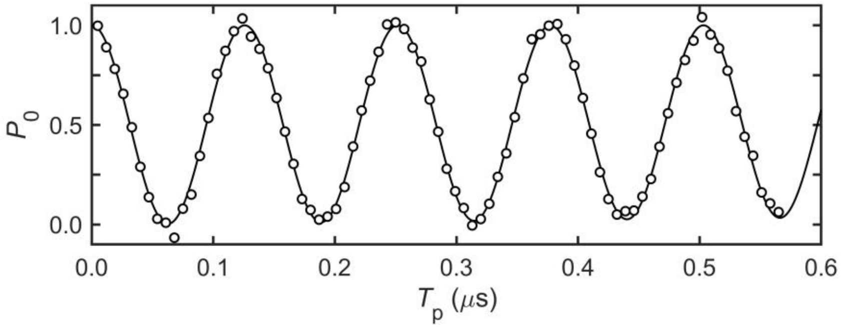
**PL mapping**



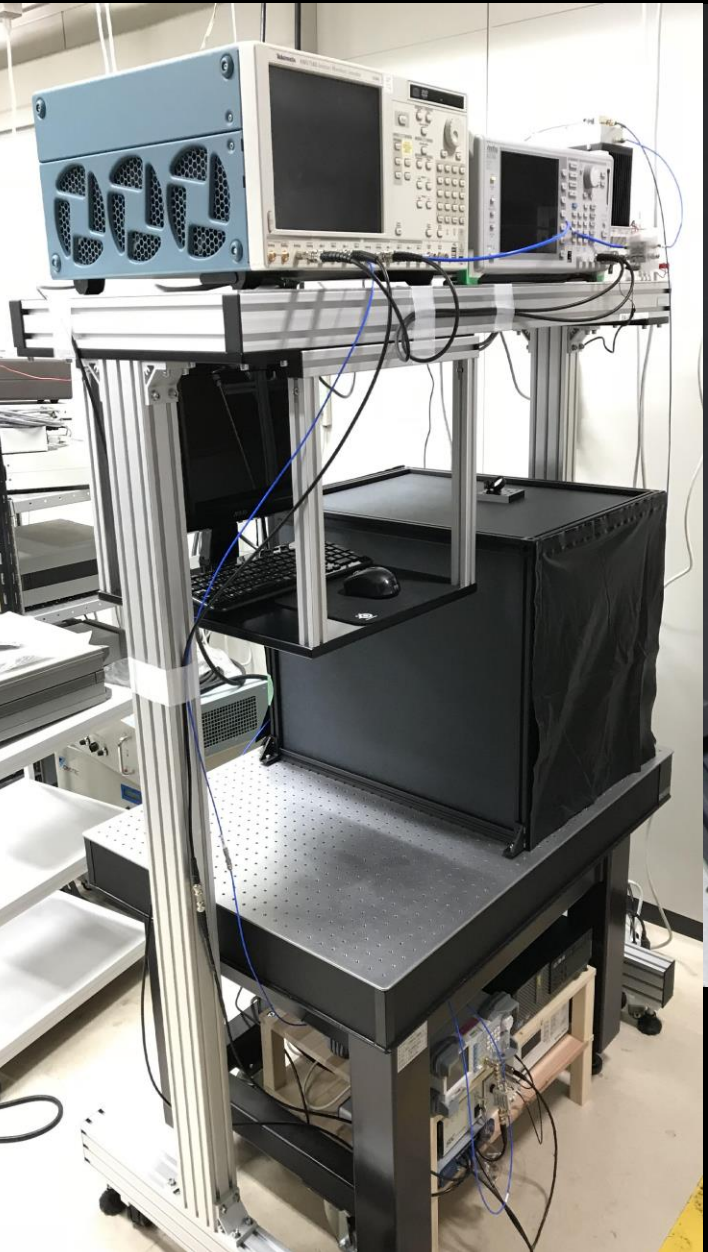

**Optically detected magnetic resonance**

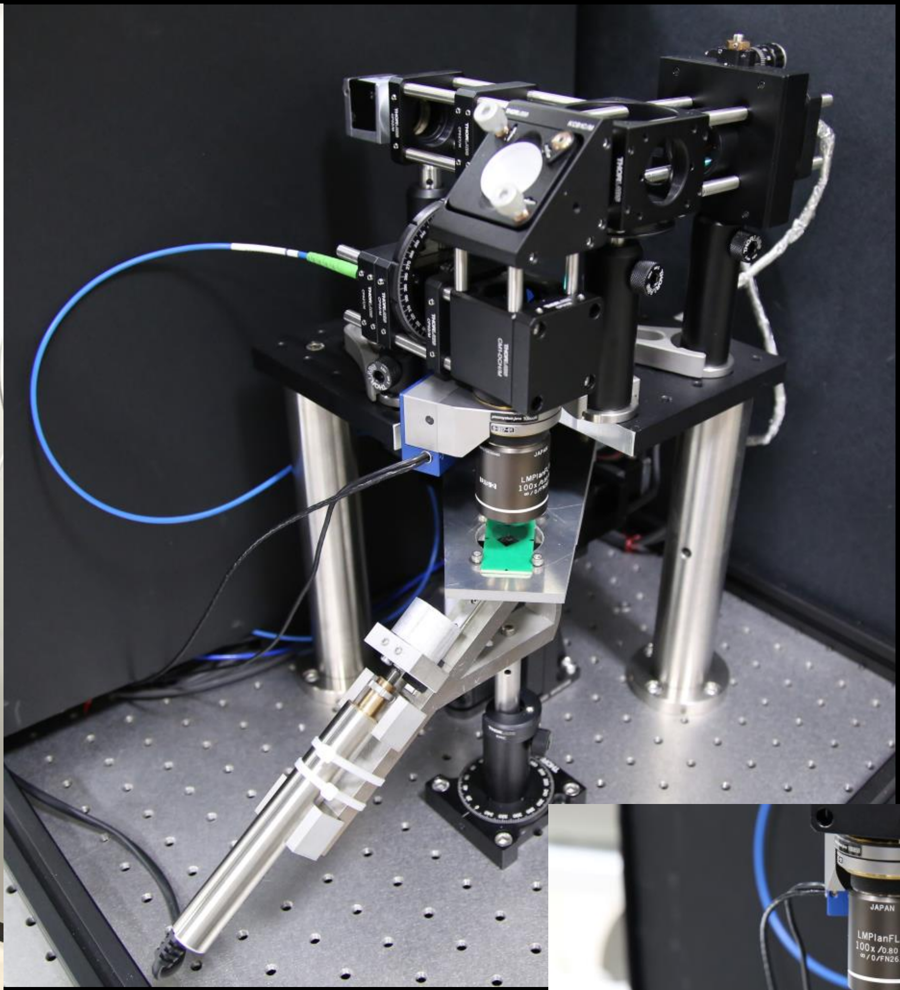


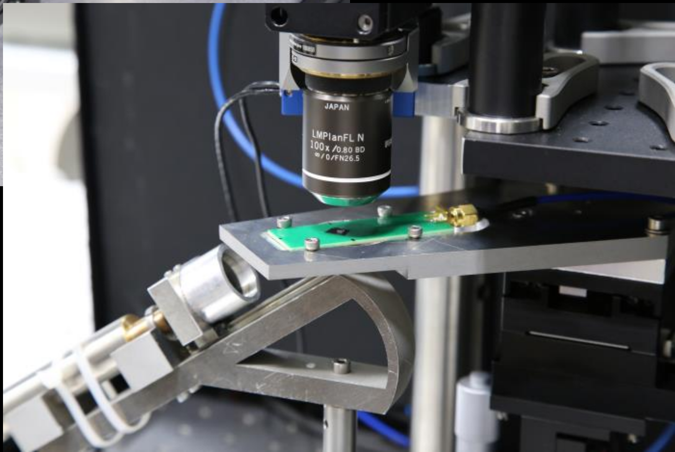

**Rabi oscillation**



# Experimental setup





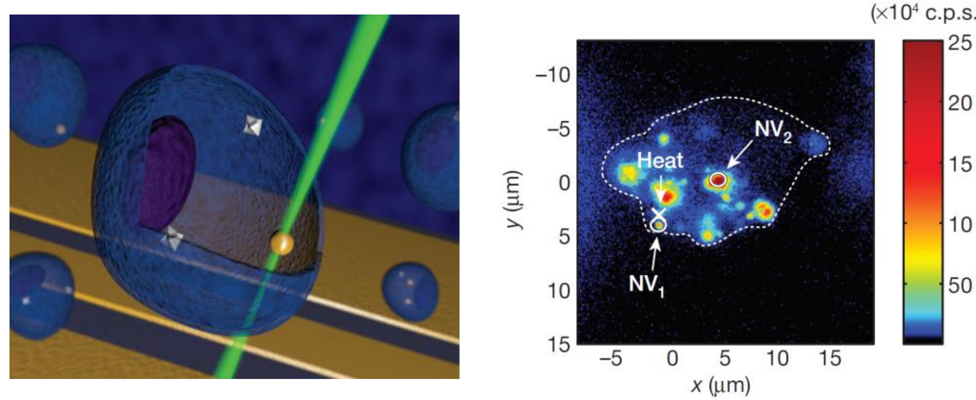



AIP Adv. **10**, 025206 (2020)
Misonou *et al.*

# Quantum sensing with NV centers

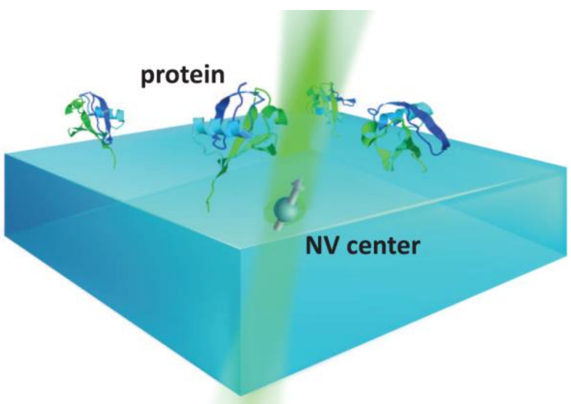
- *B*, *E*, *T*, *S*…
- DC & AC modes
- Wide temperature range
- Nondestructive
- High spatial resolution
- Various modalities

**Nanodiamond & biology**



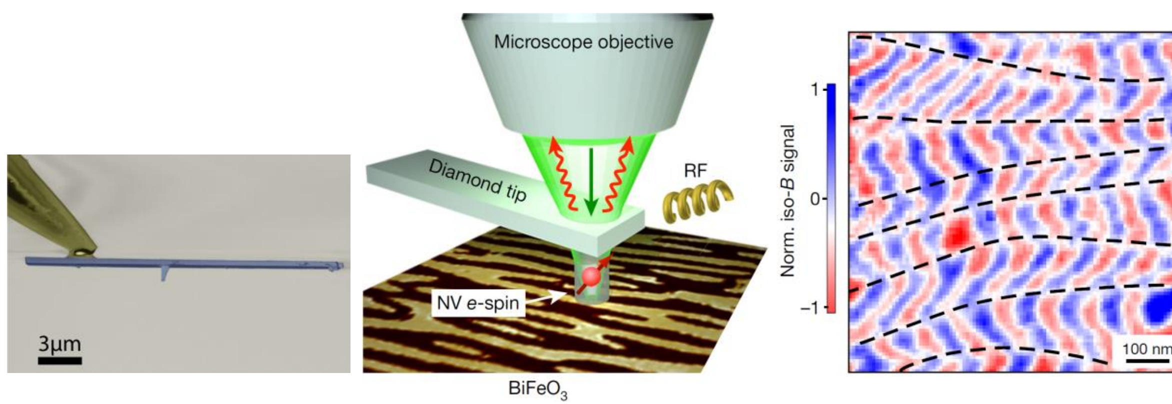

Nature **500**, 54 (2013)

**Near-surface NV center & NMR**




Science **351**, 836 (2016)

**Scanning probe & condensed matter**




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

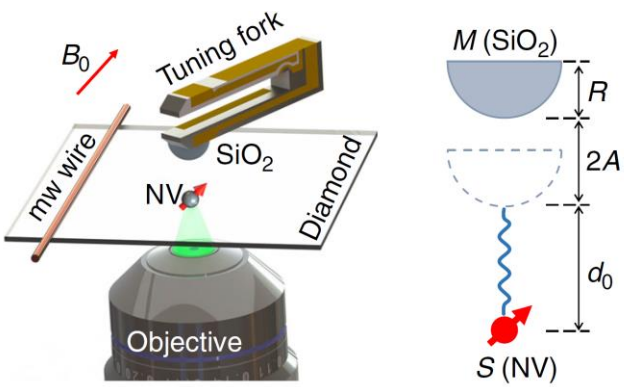
# Quantum sensing with NV centers

**Fundamental physics: search for exotic interactions & dark matter candidates**

DOI: 10.1038/s41467-018-03152-9 OPEN

## Searching for an exotic spin-dependent interaction with a single electron-spin quantum sensor

Xing Rong[1,2,3], Mengqi Wang[1,2,3], Jianpei Geng[1,2], Xi Qin[1,2,3], Maosen Guo[1,3], Man Jiao[1,3], Yijin Xie[1,3], Pengfei Wang[1,2,3], Pu Huang[1,2,3], Fazhan Shi[1,2,3], Yi-Fu Cai[4,5], Chongwen Zou[6] & Jiangfeng Du[1,2,3]




Nature Commun. **9**, 739 (2018) Rong *et al.*

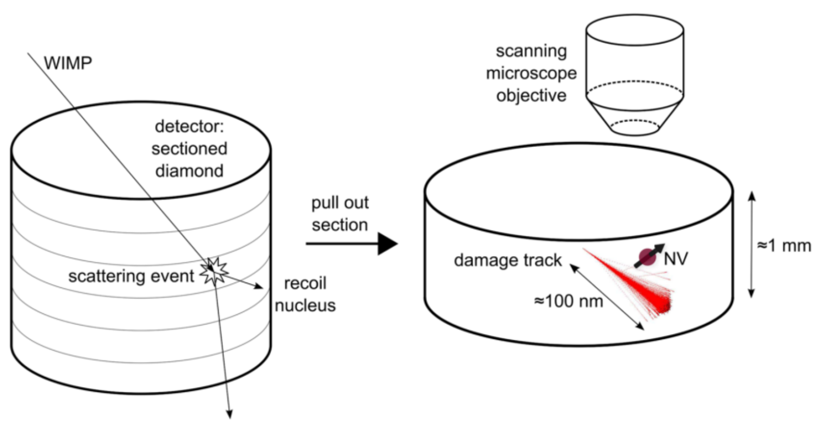
Related works from Jiangfeng Du's group at USTC:

- Phys. Rev. Lett. **121**, 080402 (2018) Rong *et al.*
- Phys. Rev. Lett. **127**, 010501 (2021) Jiao *et al.*
- arXiv: 2201.04408 Liang *et al.*

PHYSICAL REVIEW D **96**, 035009 (2017)

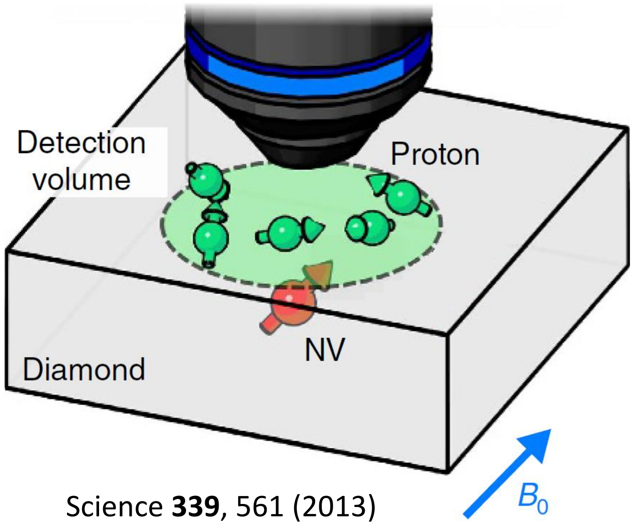
## A method for directional detection of dark matter using spectroscopy of crystal defects

Surjeet Rajendran,[1] Nicholas Zobrist,[2] Alexander O. Sushkov,[3,4] Ronald Walsworth,[5] and Mikhail Lukin[6]

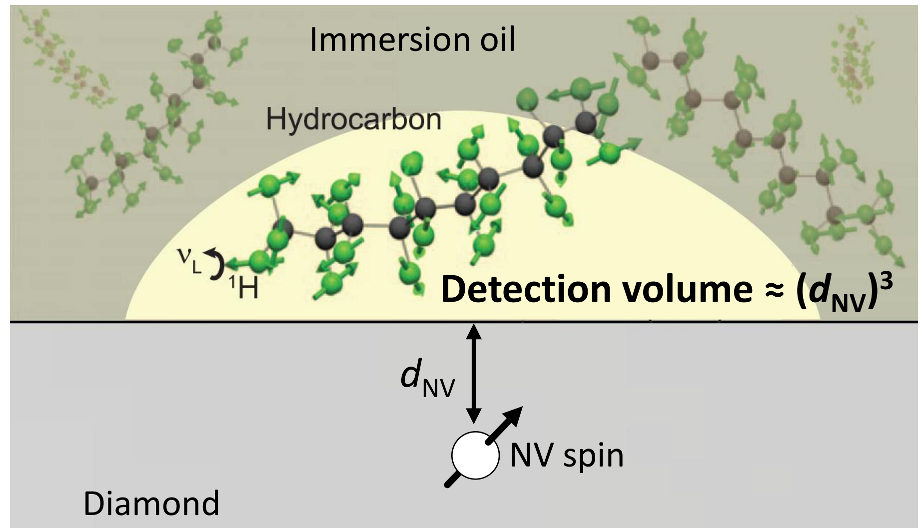



Phys. Rev. D **96**, 035009 (2017) Rajendran *et al.*

# Quantum sensing of nuclear spins




Science **339**, 561 (2013)



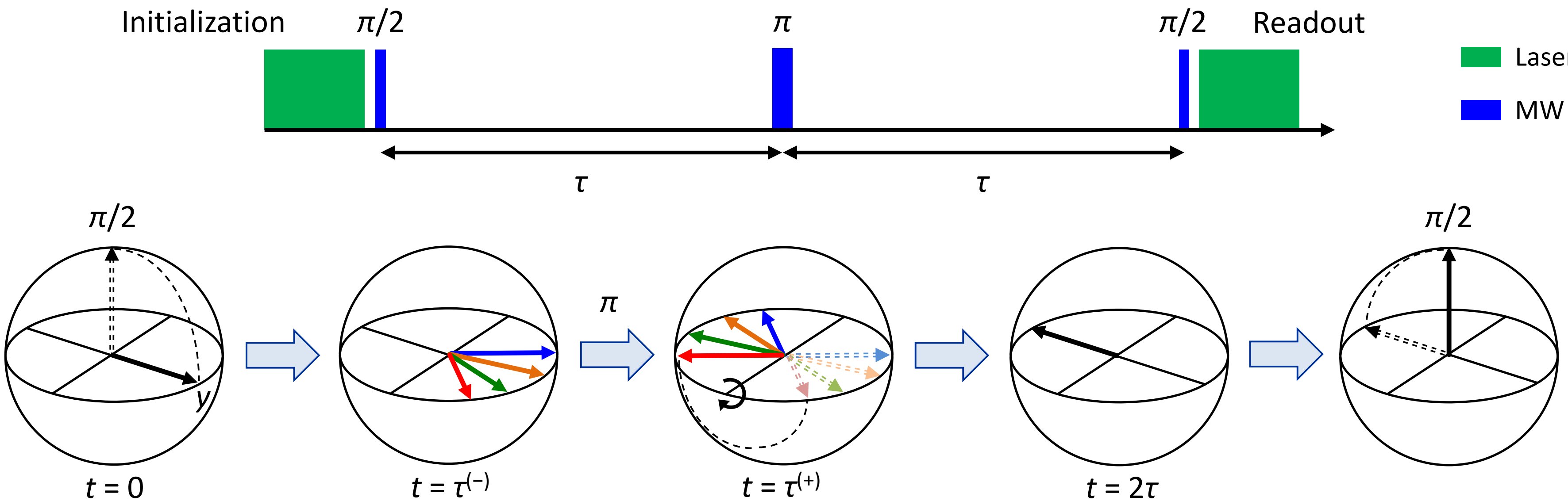

Nature Commun. **6**, 8527 (2015)

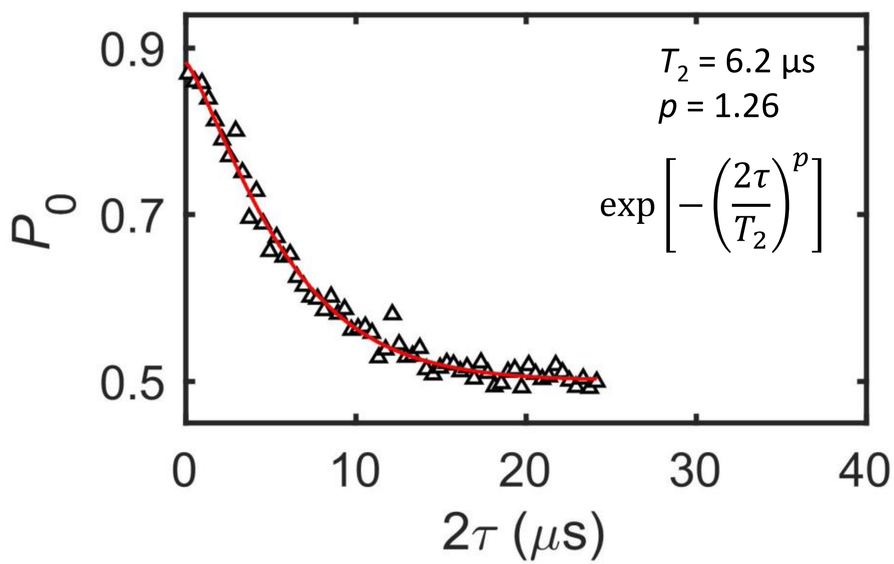
Nuclear spins **precess** at $f_{ac}$ = a few kHz–MHz under $B_0$

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

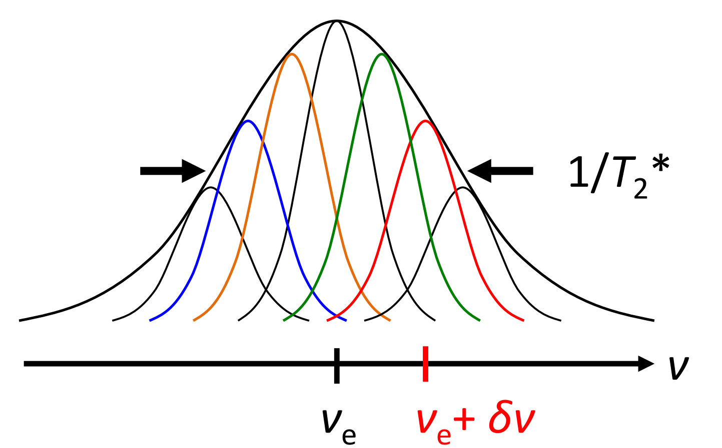
⇨ Detect using **quantum coherence** of the NV spin

# Coherence time of NV spin: $T_2$



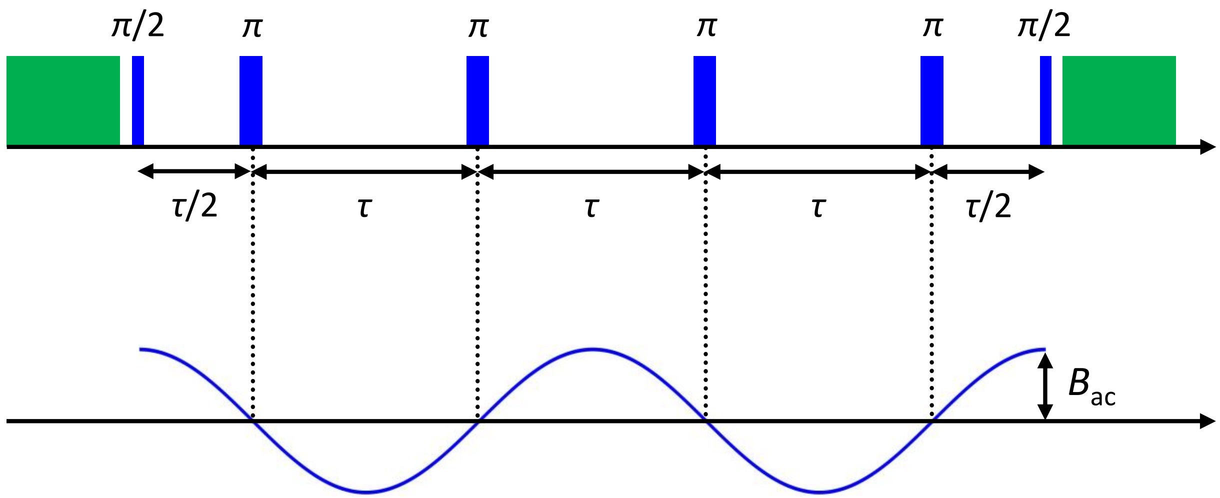




Static DC shifts cancelled (refocusing)



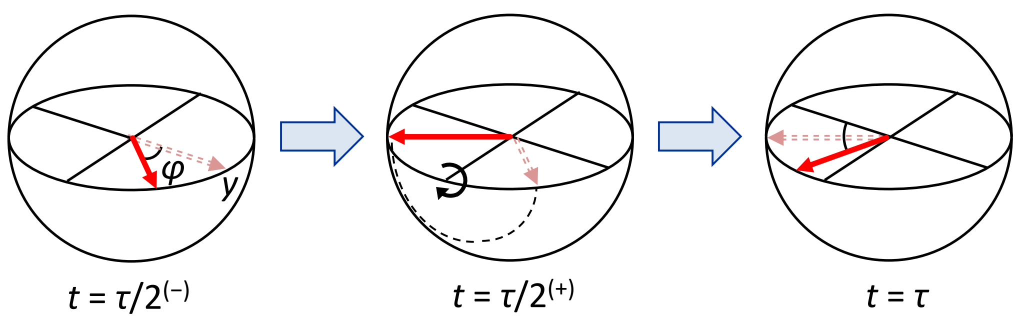
# AC magnetometry

***N* = 4**

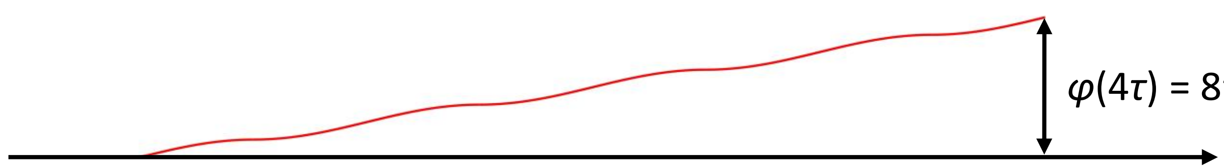



**AC field ($f_{ac} = 1/2\tau$)**

**Sensor phase buildup (deviation from *y* axis):** ***loss of coherence***

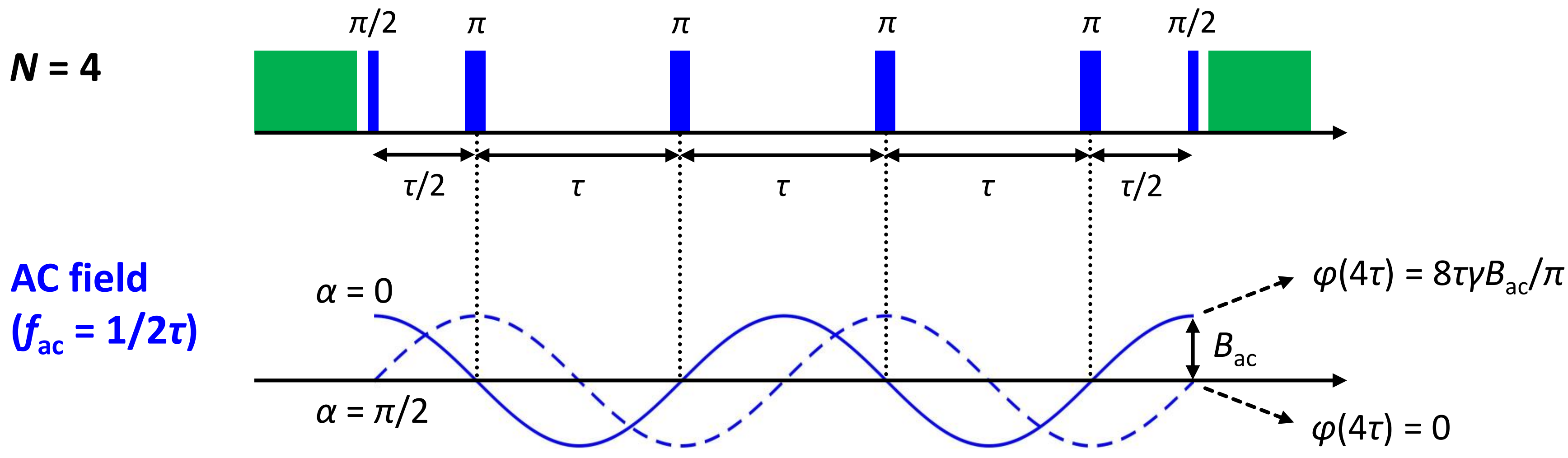



$\varphi(\tau) = 2\varphi(\tau/2)$

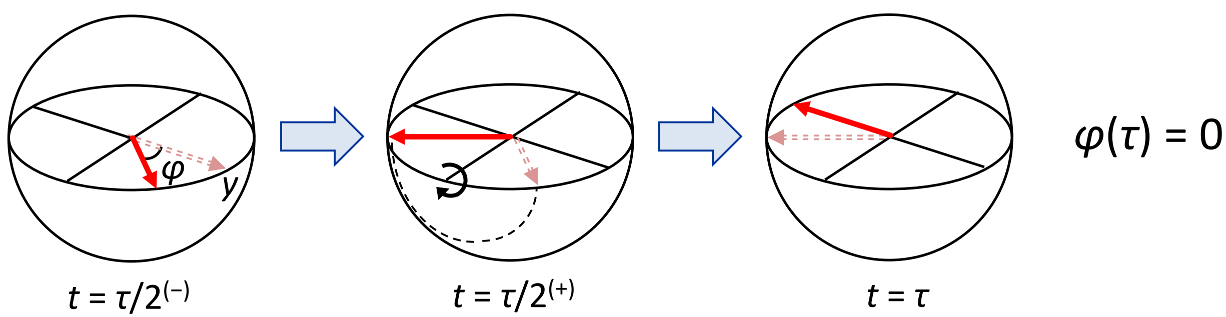


$\varphi(4\tau) = 8\tau\gamma B_{ac}/\pi$

# AC magnetometry

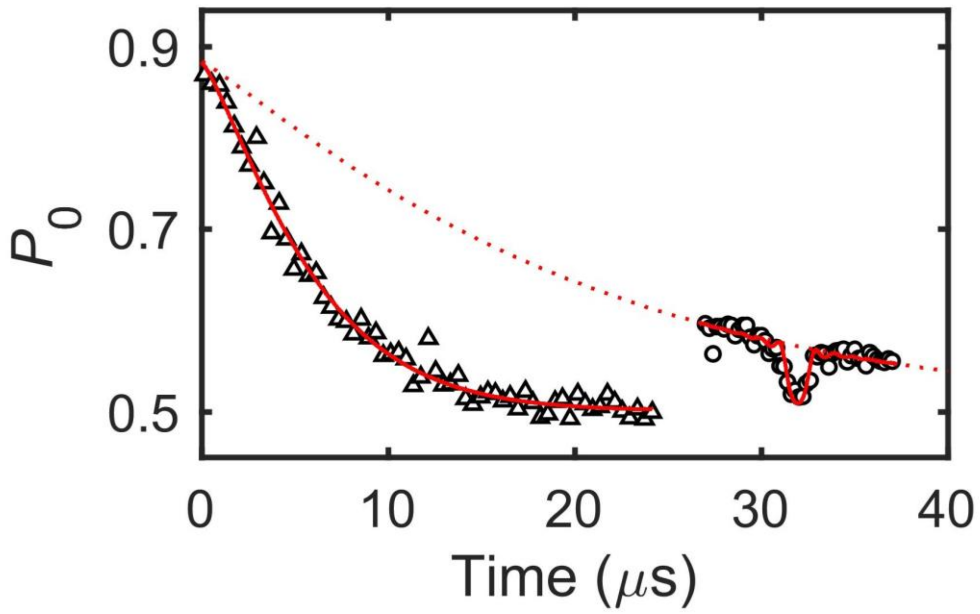


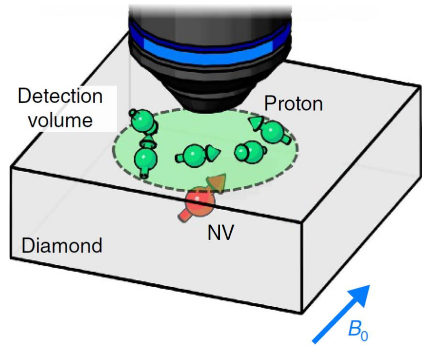

**Sensor phase buildup (deviation from *y* axis):** ***the initial phase α matters***




- $\varphi \propto \cos \alpha$
- Usually, we average over **random** $\boldsymbol{\alpha}$

# Sensing of ensemble *n*-spins

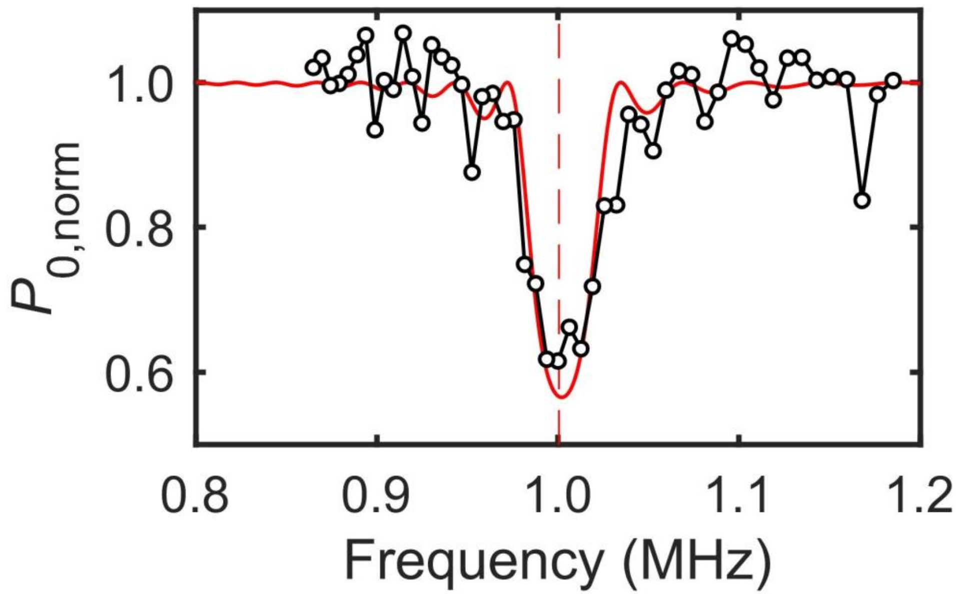



- $T_2$ = 6.2 μs @$B_0$ = 23.5 mT
- $N$ = 64
- 2$\tau$ = 2 x 32 μs/64 = 1 μs
  → $\gamma_H B_0$ = (42.577 kHz/mT) x $B_0$ = 1.00 MHz

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

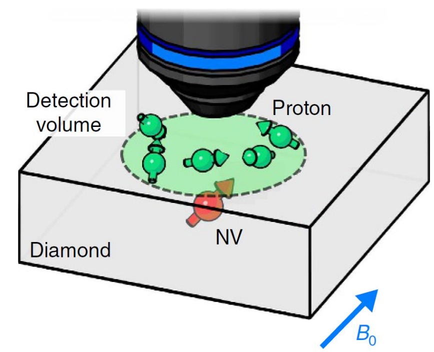
# Sensing of ensemble *n*-spins




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

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

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



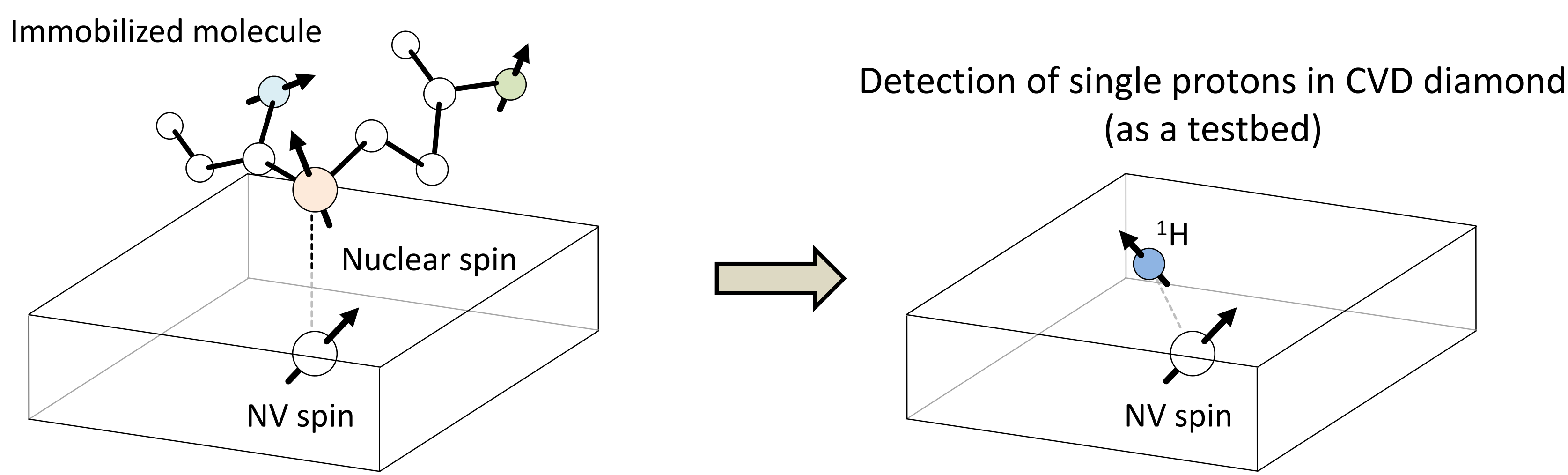

- Proton density $\rho$ = 6 x $10^{28}$ $m^{-3}$ (known)
- $d_{\mathrm{NV}}$ = 6.26 nm
- $B_{\mathrm{rms}}$ ≈ 560 nT
- Detection volume $(d_{\mathrm{NV}})^3$ ≈ **0.25 zL** (zepto = $10^{-21}$)
- # of protons $\rho(d_{\mathrm{NV}})^3$ ≈ 1500
- Thermal polarization ($10^{-7}$) vs. statistical fluctuation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

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

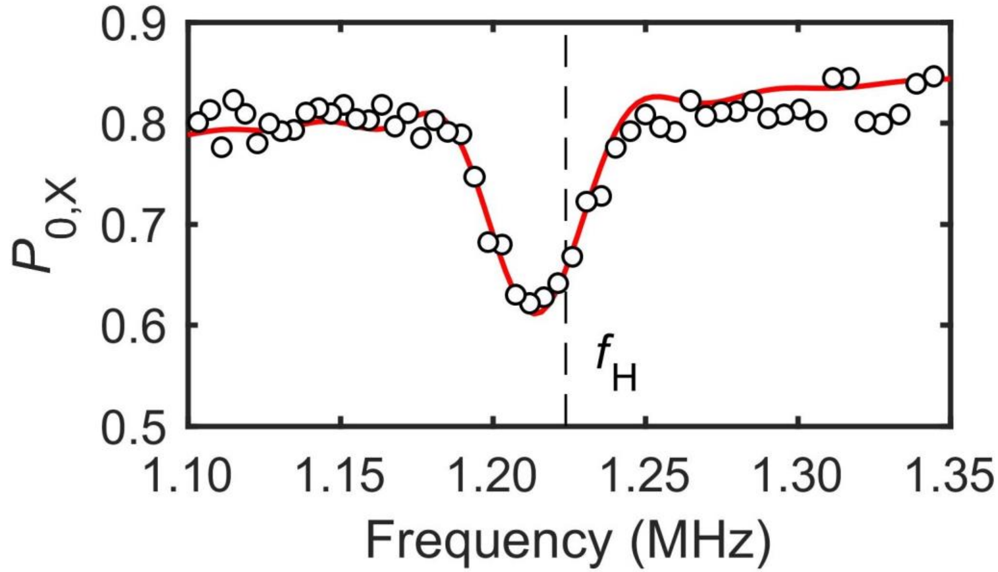
# Toward single-molecular imaging

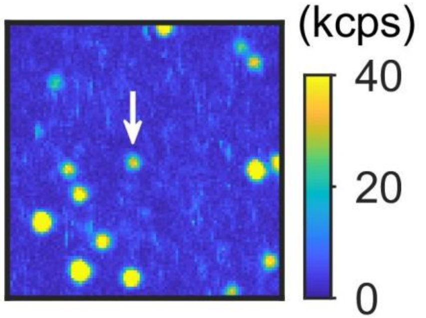
- **High spatial resolution**
  → Special about *single-nuclear-spin-level* NMR
  → Measure the positions of individual nuclear spins in a single molecule

- **High spectral resolution**
  → Routine in conventional ensemble NMR spectroscopy
  → Measure nuclear species ($^{1}H$, $^{13}C$, $^{19}F$…)
  → Measure *J*-couplings & chemical shifts with ppm accuracy



# Sensing of single *n*-spin



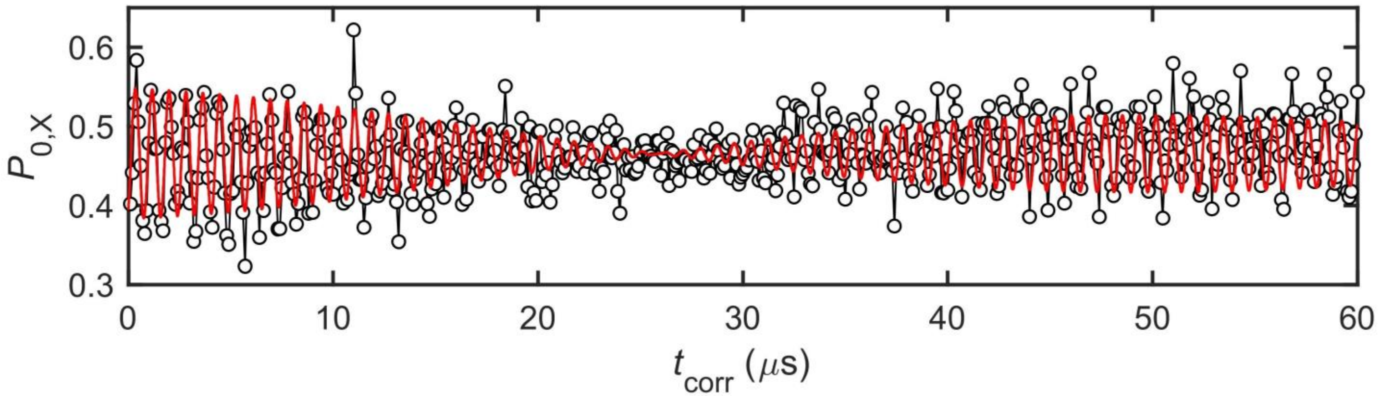



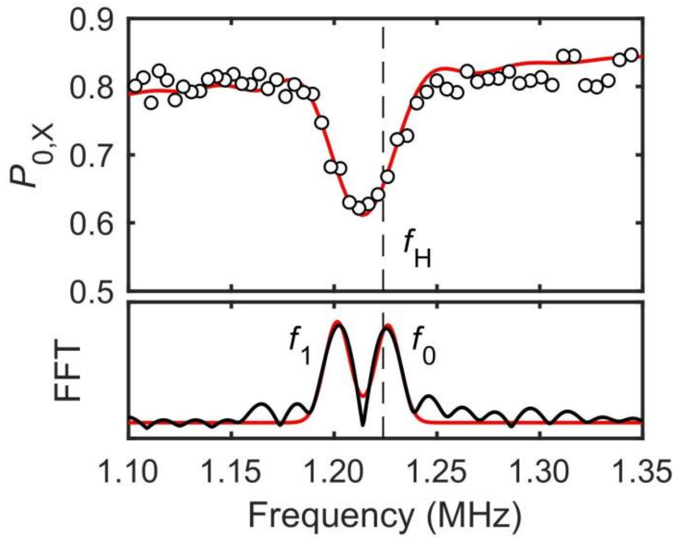

10 x 10 μm²

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

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

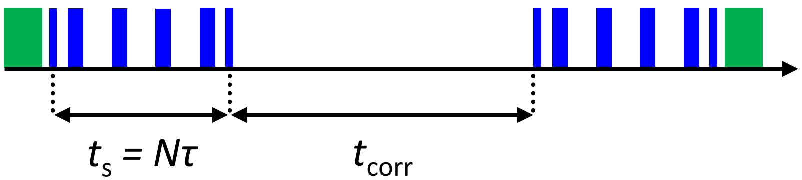
# Correlation spectroscopy of single *n*-spin



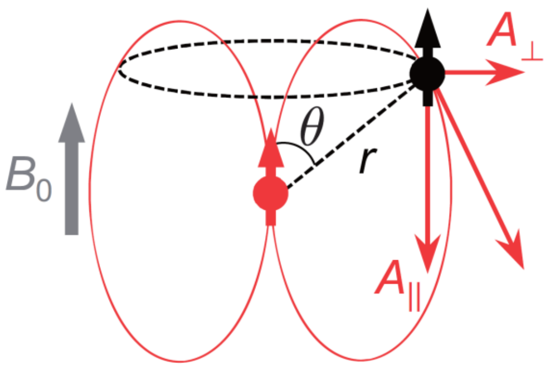

- $f_0$ = 1.2234 MHz
- $f_1$ = 1.2046 MHz

$T_1$-limited spectroscopy




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

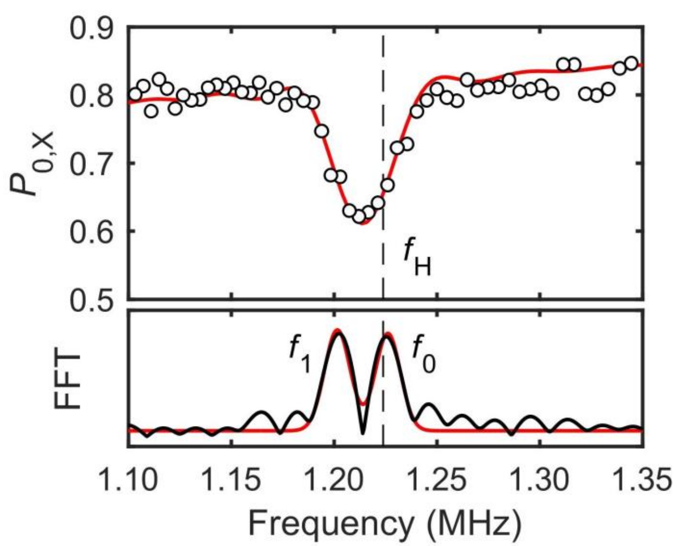
# Correlation spectroscopy of single *n*-spin




**Hamiltonian of [1]H *n*-spin coupled with NV *e*-spin**

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

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

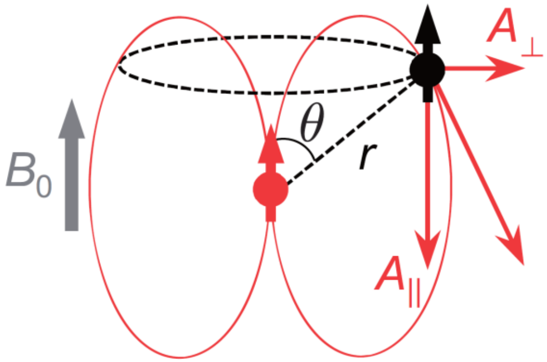



- $f_0$ = 1.2234 MHz = $f_H$ ($m_s$ = 0)
- $f_1$ = 1.2046 MHz = $f_H + A'_\parallel$ ($m_s$ = −1)

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

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

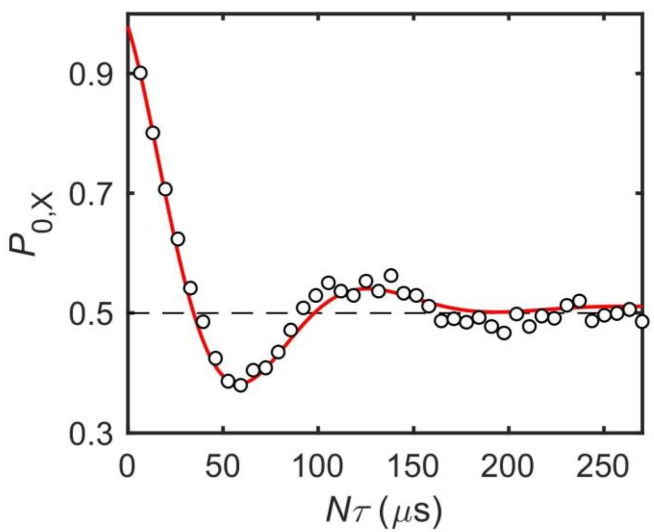
# Coherent control of single *n*-spin




**Hamiltonian of [1]H *n*-spin coupled with NV *e*-spin**

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

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




- $N$ → 656 ($\tau$ = 411.5 ns, fixed)
- $f_{osc}$ = 7.414 kHz = $A'_\perp/2$

$P_{0,X}$ < 0.5 (coherent rotation)
→ Single proton

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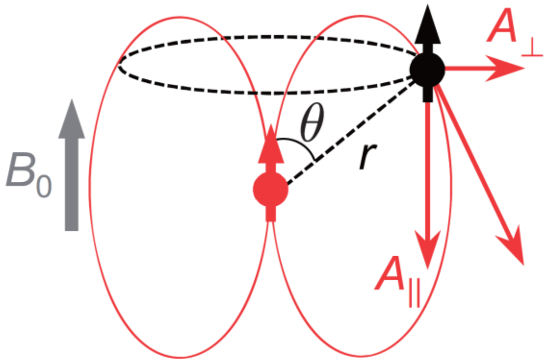
# Determination of hyperfine constants




**Magnetic dipole interaction**

$$A_\parallel = h\gamma_\mathrm{e}\gamma_\mathrm{H}\frac{3\cos^2\theta - 1}{r^3}$$

$$A_\perp = h\gamma_\mathrm{e}\gamma_\mathrm{H}\frac{3\cos\theta\sin\theta}{r^3}$$

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

⟺

$r = 1.44$ nm
$\theta = 72.3^\circ$

The position of the nucleus can be determined
→ Basis for single-molecular structure analysis

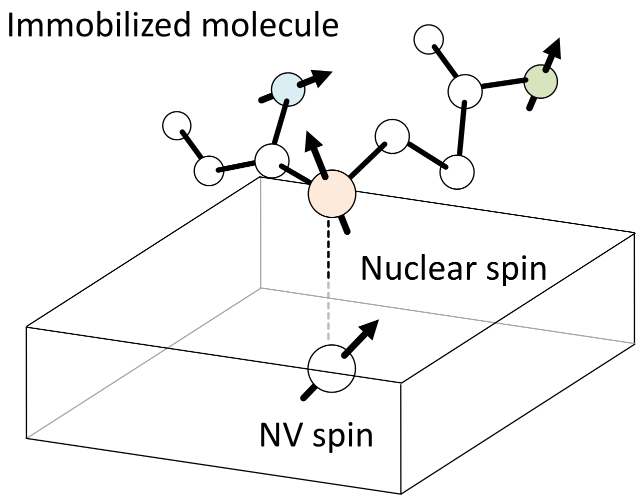
[Azimuthal angle $\phi$ can determined by RF control] Phys. Rev. B **98**, 121405 (2018) Sasaki *et al.*

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

# Toward single-molecular imaging

- **High spatial resolution**
  → Accurate measurement of *e*–*n* int. const's $(A_{\parallel}, A_{\perp}) \approx (r, \theta)$
  → $\phi$ can be determined by RF control

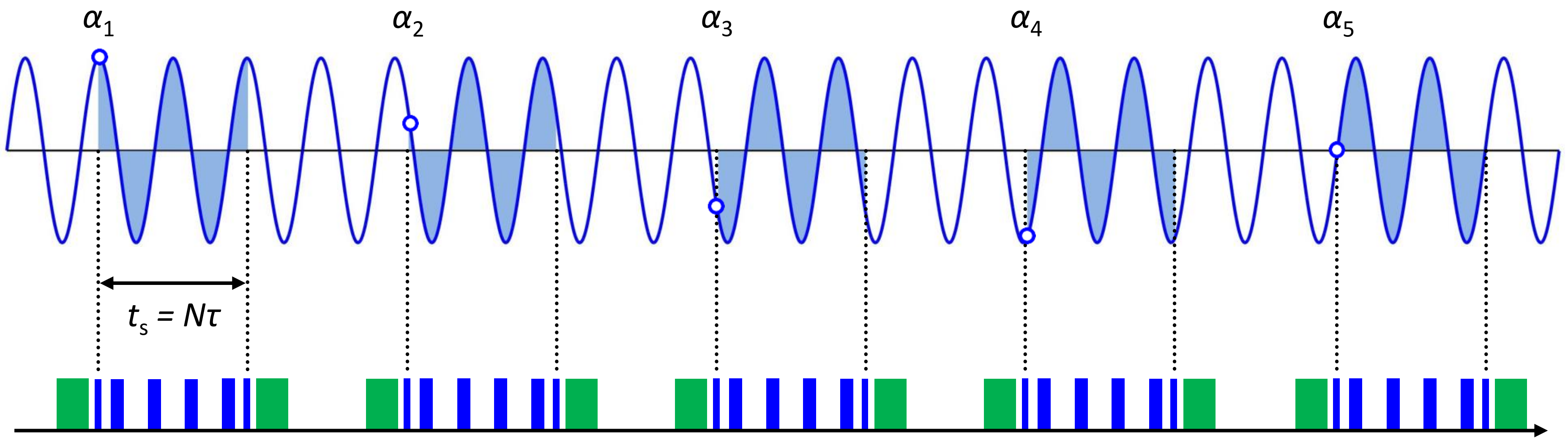
- **High spectral resolution**
  → Routine in conventional ensemble NMR spectroscopy
  → Measure nuclear species ($^{1}H$, $^{13}C$, $^{19}F$…)
  → Measure *J*-couplings & chemical shifts with ppm accuracy




*Not so easy with NV centers*
Limited by sensor/memory spin lifetimes ($T_{2e/n}$, $T_{1e/n}$)

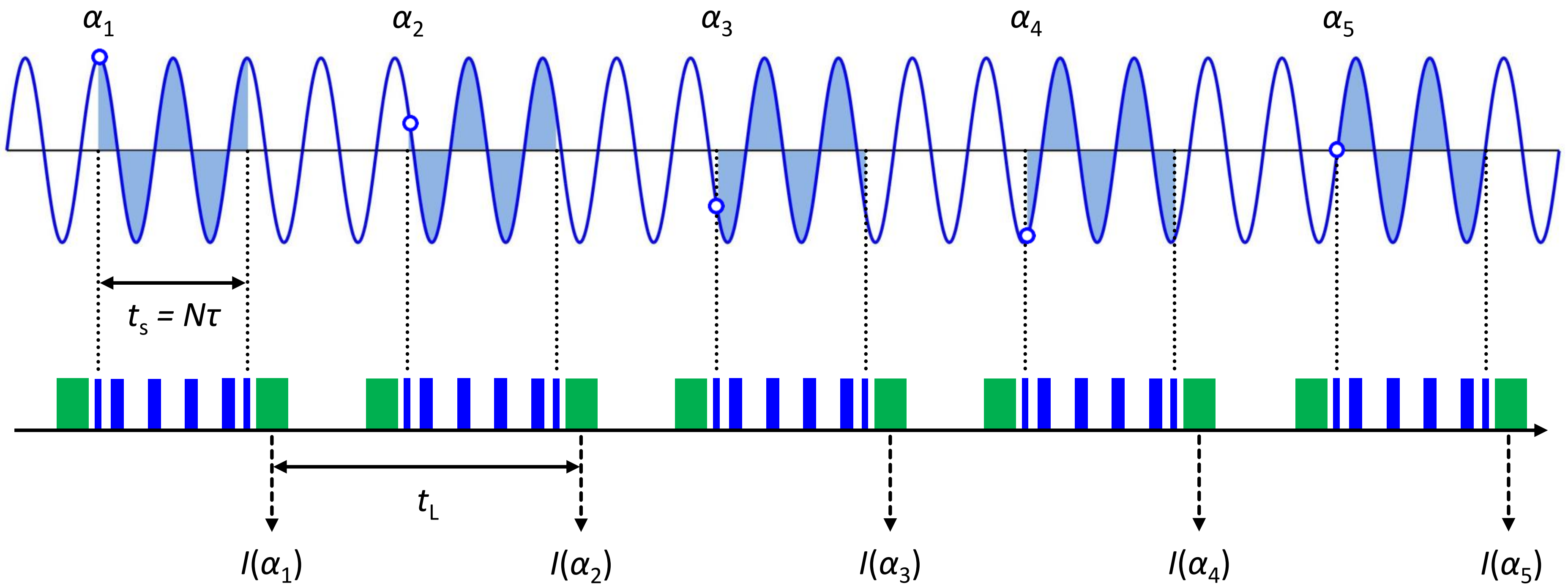
$T_{2e}$ tends to be shorter for near-surface NV centers

# AC magnetometry revisited



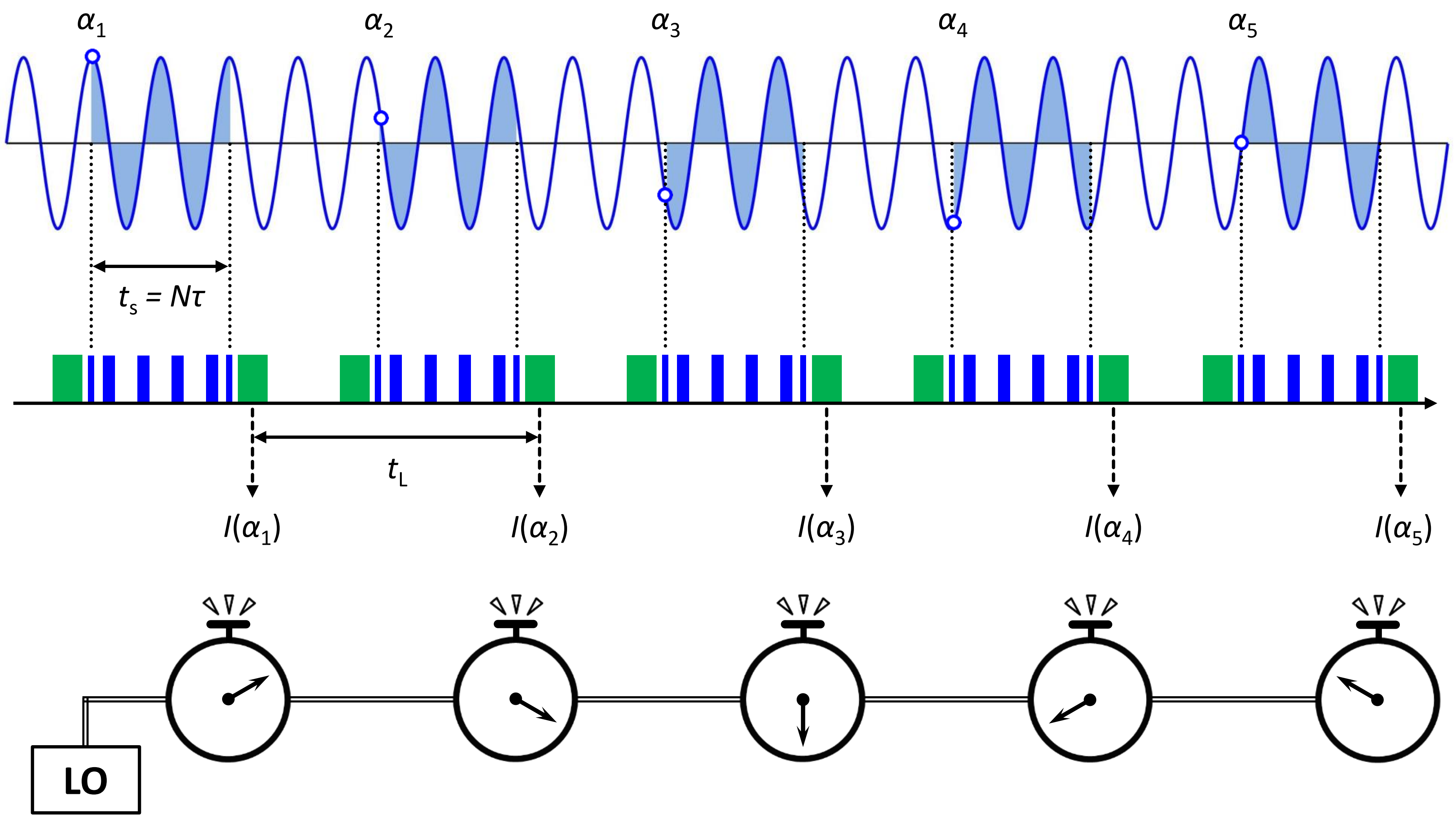

- $\varphi \propto \cos\alpha$
- Usually, we average over **random** $\boldsymbol{\alpha}$

# AC magnetometry revisited




- $\varphi \propto \cos \alpha$
- Usually, we average over **random** $\boldsymbol{\alpha}$
- **If the data acq. is periodic,** adjacent $\alpha$'s are related by $\alpha_{k+1} = 2\pi f_{ac} t_L + \alpha_k$

# Ultrahigh resolution sensing

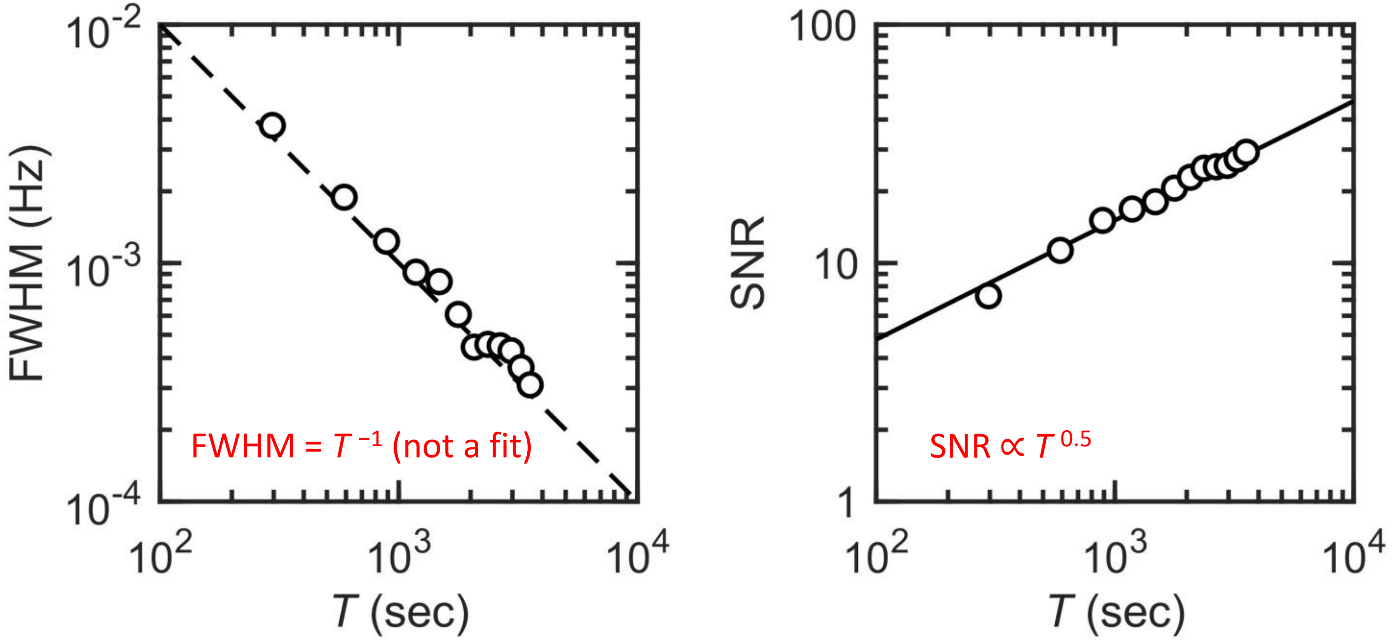


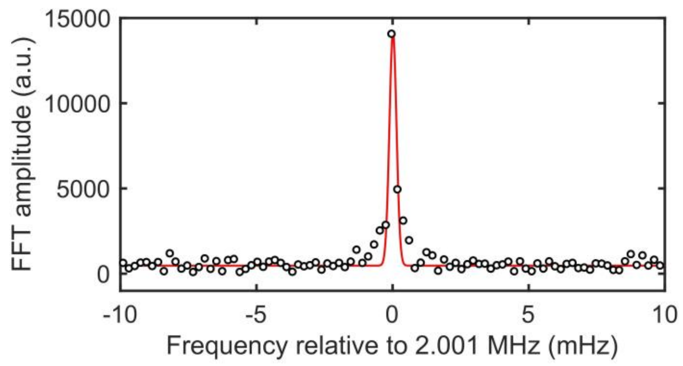

**Undersampled, sensor-lifetime-unlimited signal**

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



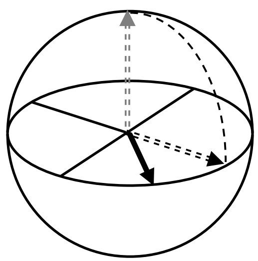



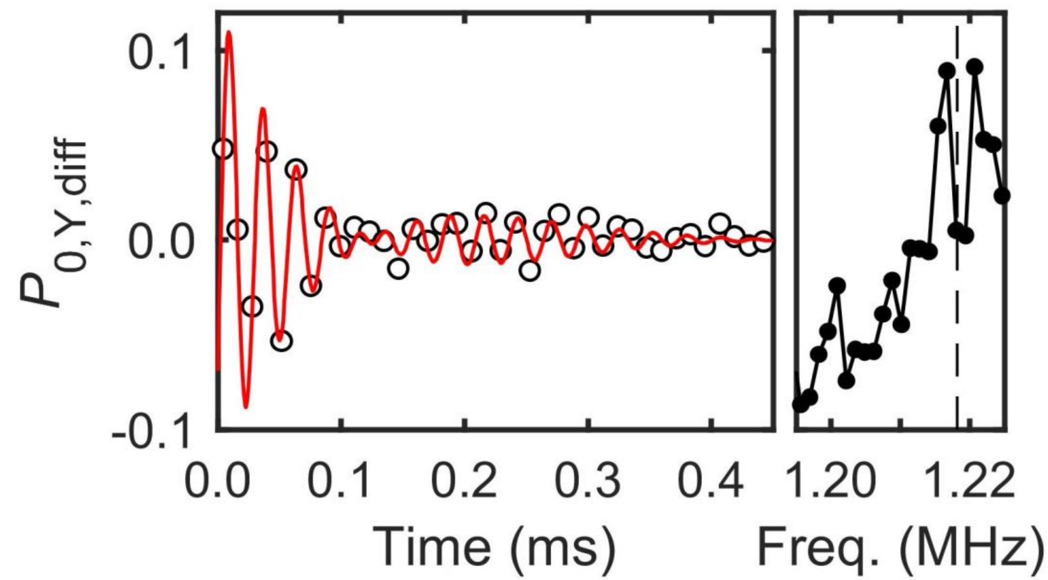

- $T$ = 3600 sec
- FWHM = 0.304 mHz

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

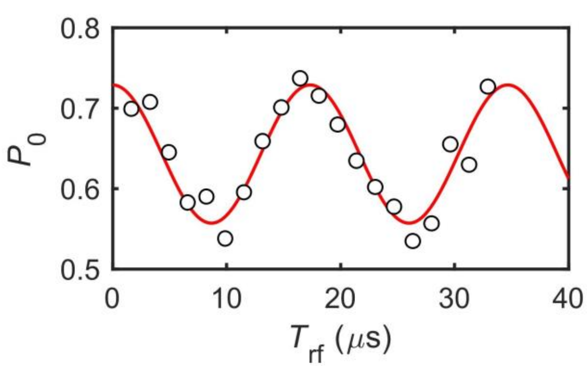
# Free induction decay of single *n*-spin

RF control & free precession of *n*-spin






**Nuclear Rabi oscillation**




- $T_{\mathrm{rf},\,\pi/2}$ = 4.115 μs
- [PulsePol]–$T_{\mathrm{rf},\,\pi/2}$–$[\mathrm{X/2}–(\mathrm{XY16})–\mathrm{Y/2}–\mathrm{L_{RO}}]^{50}$
- $f_{\mathrm{sample}} = 1/t_{\mathrm{L}}$ = 84.46 kHz
- $f_{\mathrm{p}} = (f_0+f_1)(t_{\mathrm{s}}/t_{\mathrm{L}})/2+f_0(t_{\mathrm{s}}-t_{\mathrm{L}})/t_{\mathrm{L}}$ = 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 positions of individual *n*-spins via RF control[7,8,9,10]
  → Detection and control of single proton spins[11,12]

- **Also useful for fundamental physics? I hope so.**


[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)
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