Quantum Spintronics Design
(focusing on NV centers in diamond)

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2018.02.28

CMD Spintronics Design Course

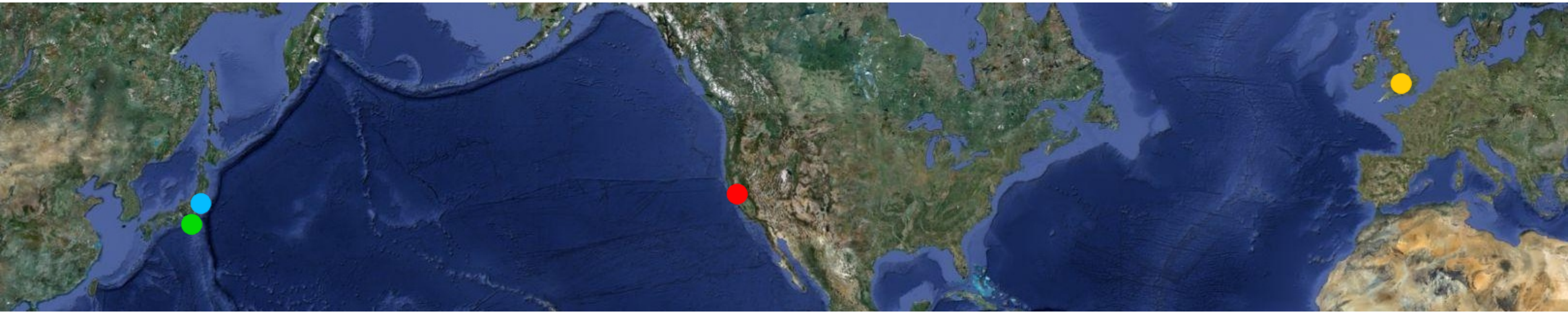
@Osaka University

Keio University

1858

CALAMVS GLADIO FORTIOR

Short CV



- **2001.4 – 2006.3 (Keio U)**
  - ESR and NMR in silicon
- **2006.4 – 2009.12 (ISSP, U Tokyo)**
  - Quantum transport with nanostructures (GaAs QDs, Josephson)
- **2010.1 – 2011.6 (Oxford U)**
  - ESR in silicon, spin-ensemble–cavity coupling
- **2011.7 – 2015.3 (Stanford U/RIKEN)**
  - Quantum optics with self-assembled InAs QDs
- **2015.4 – Present (Keio U)**
  - Magnetometry with NV centers in diamond

Outline

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

- **AC magnetometry**
  - Basics
  - Correlation spectroscopy and detection of nuclear spins
  - Ultrahigh resolution sensing

Outline

- **Basics of NV centers in diamond**
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Diamond envy

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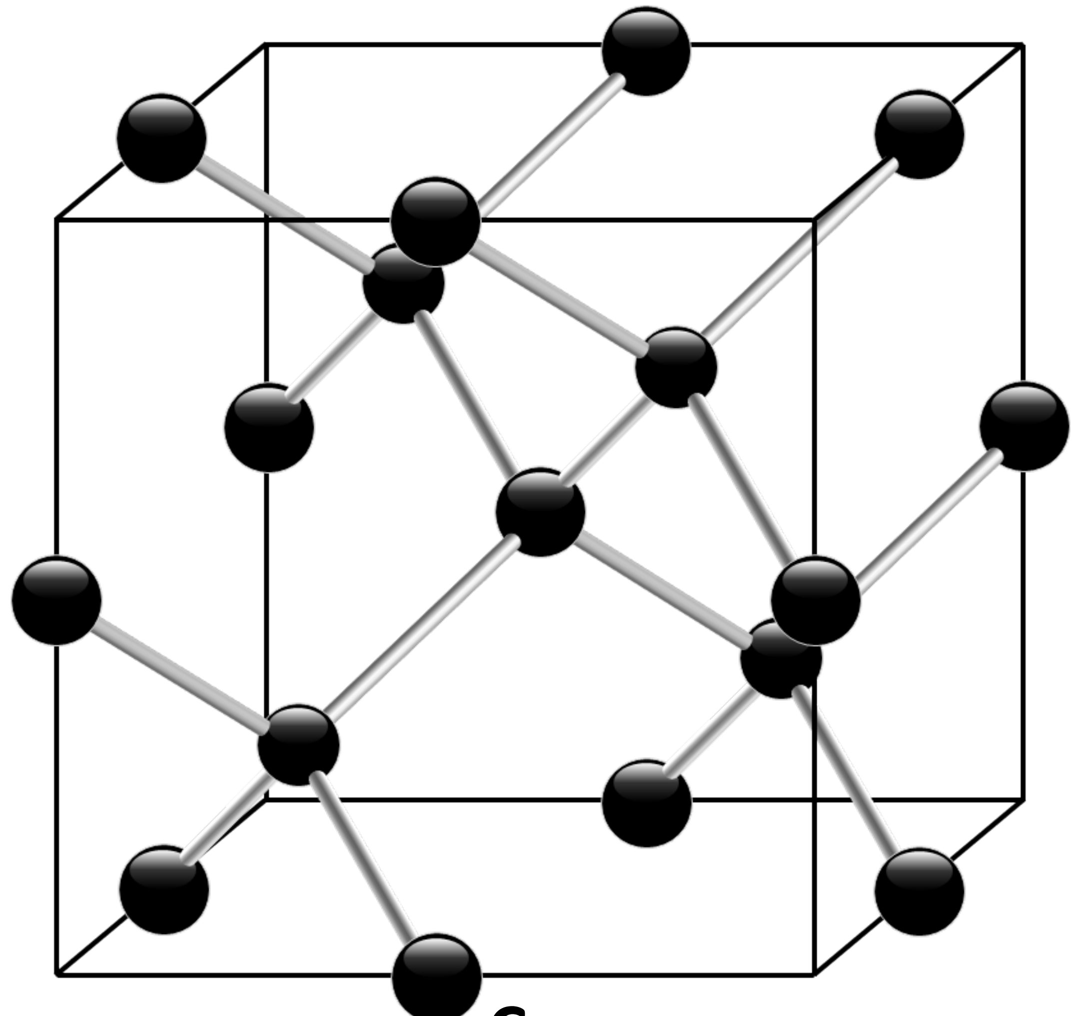
1109 carats, \$70M

ρ_N = 1.77 x 10^{23} cm^{-3}



C

Diamond NV

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1109 carats, \$70M

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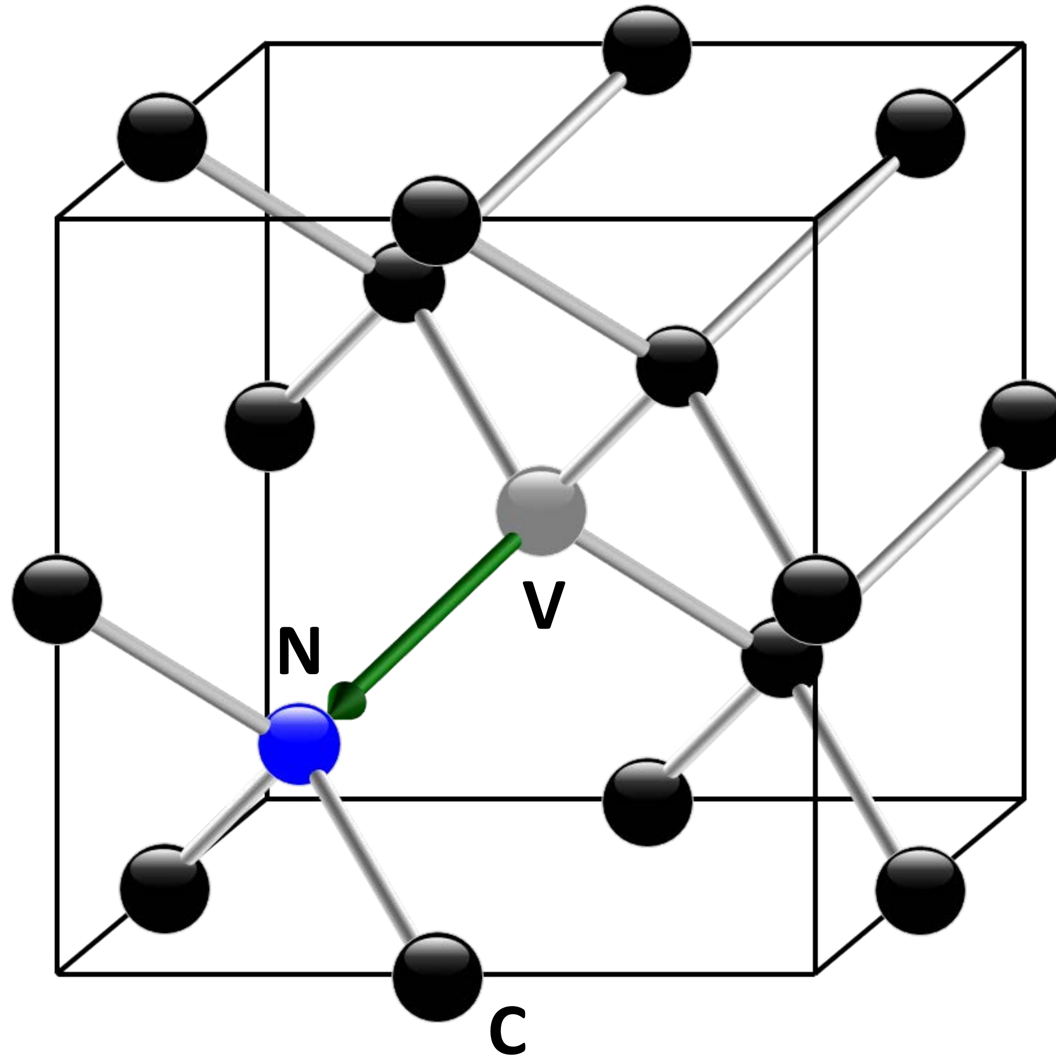
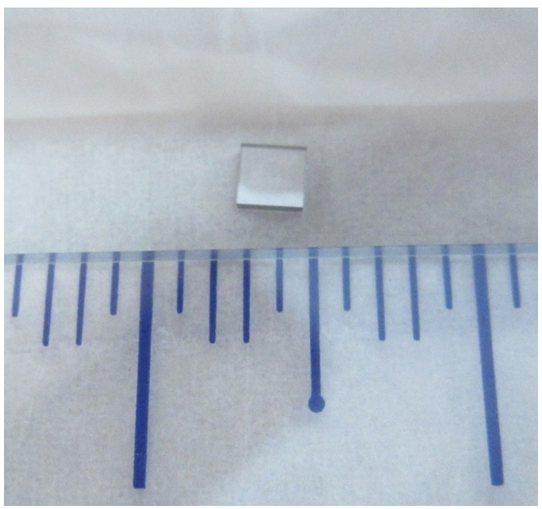
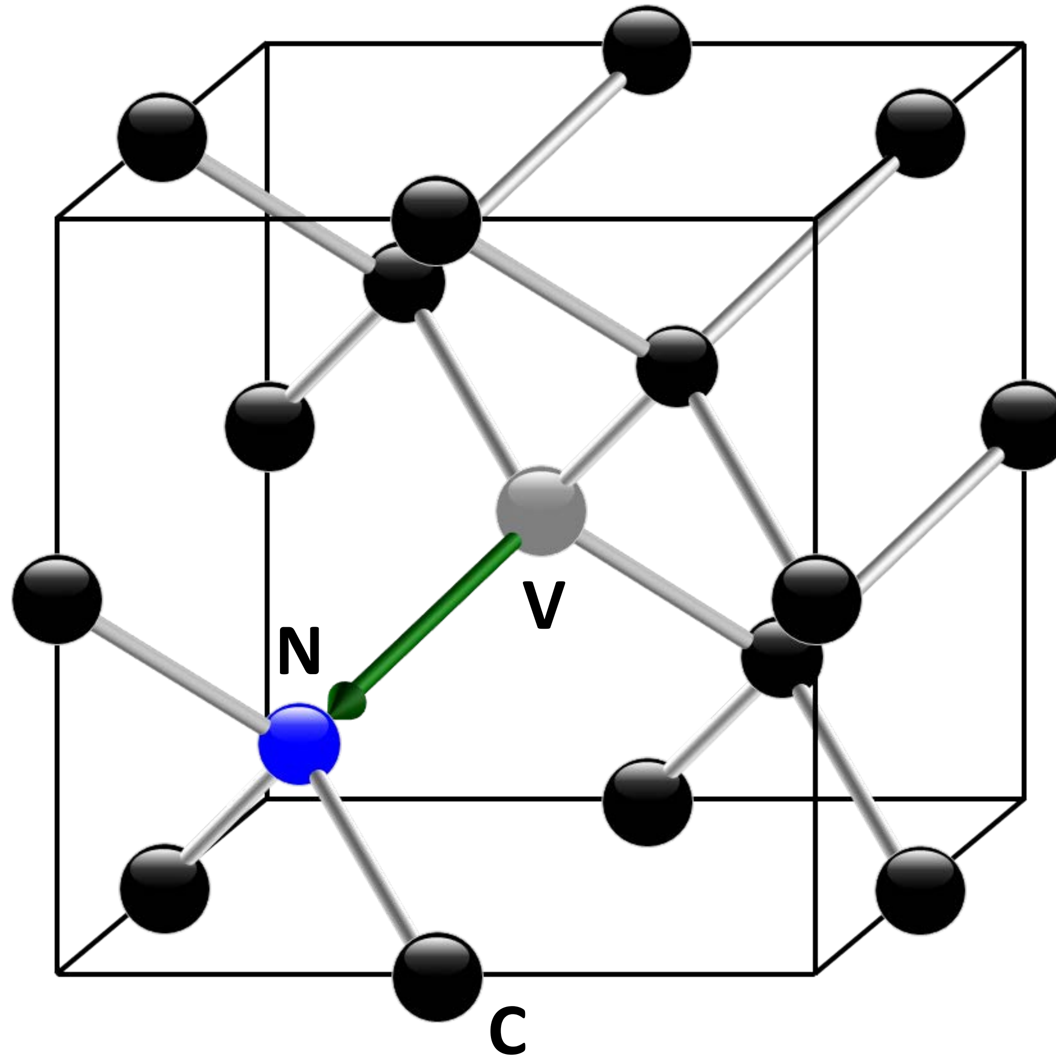


Diamond NV



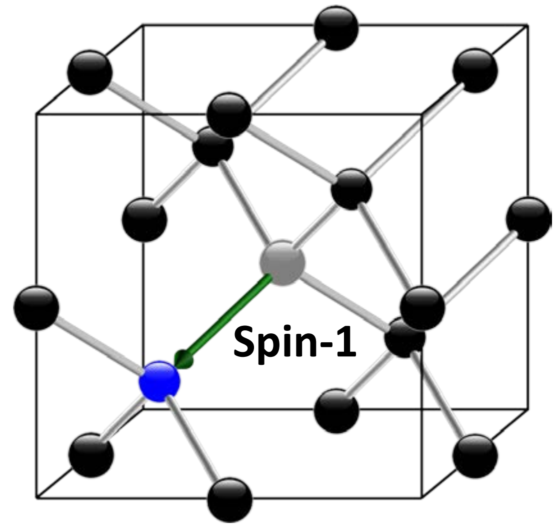
2^2 x 0.5 mm^3, $700 (E6)
[N] < 5 ppb, [NV] < 0.03 ppb

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



NV spin as a qubit/sensor

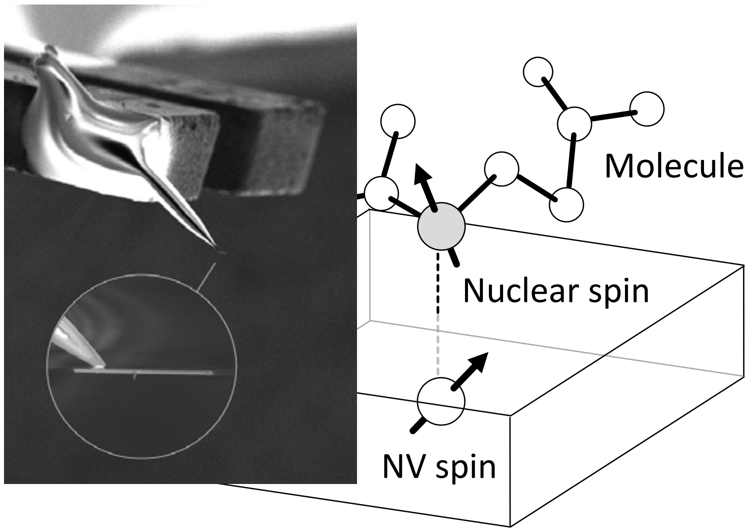
- **Quantum information**
  - Quantum network
  - Quantum computing

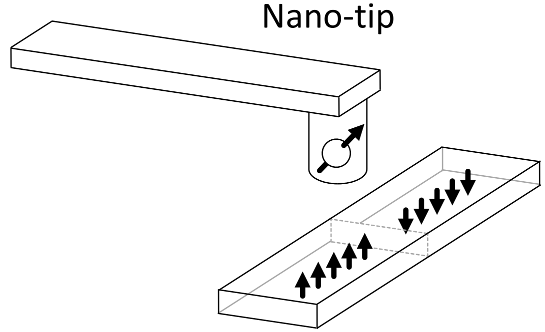


- **Quantum sensing**
  - *B*-field, *E*-field, *T*…
  - Nanoscale MRI
  - Probe for condensed matter physics
  - Biology, medicine

Quantum sensing

©Qnami





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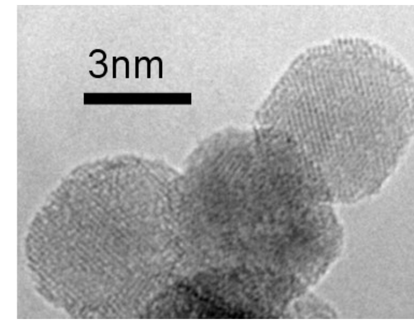
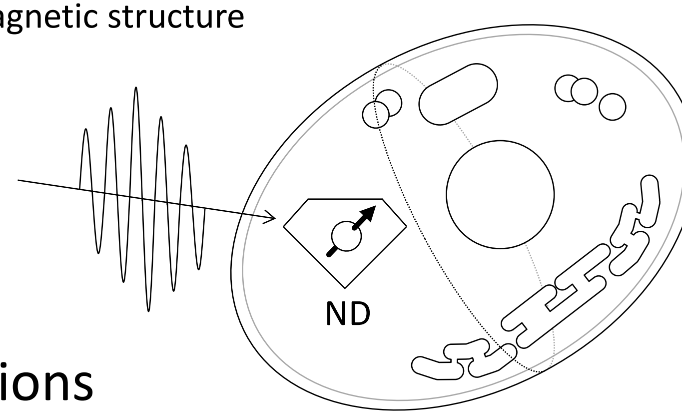
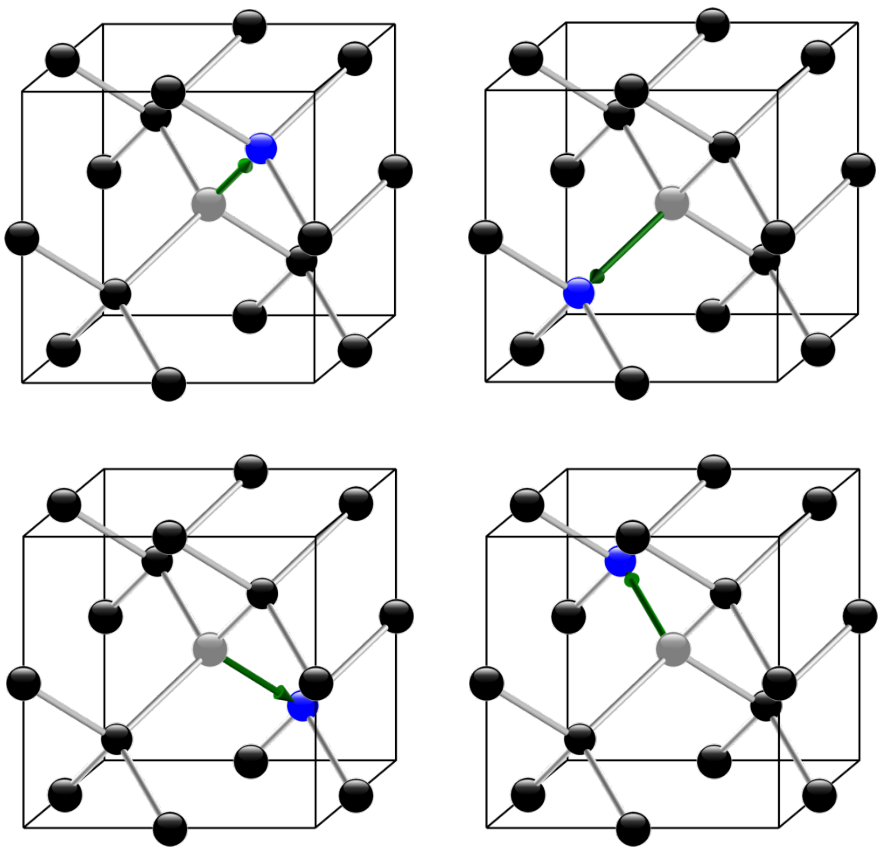




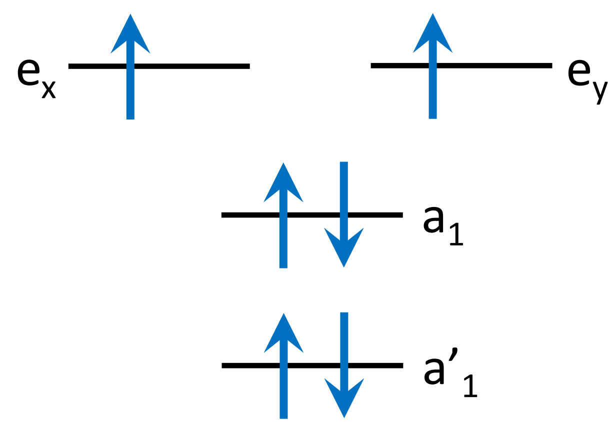
- Room temperature, ambient conditions
- High spatial resolution
- Non-destructive, non-invasive, non-toxic
- Various modalities

Crystal & energy level structures

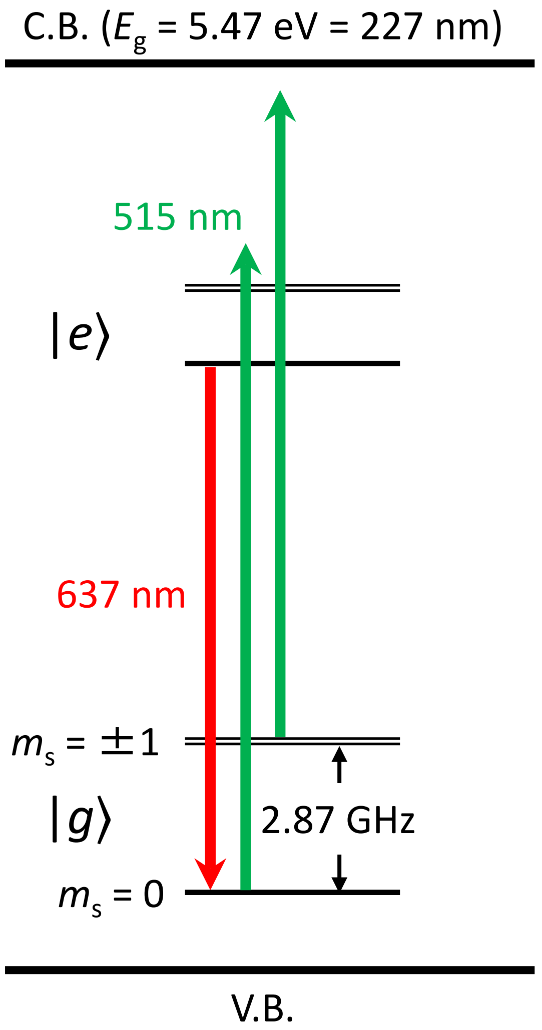
- Negatively-charged (NV^-)
- 4 sp^3 orbitals, 6 e^- (5 from the defect, 1 captured)
- C_{3v} (symmetry axis = quantization axis)

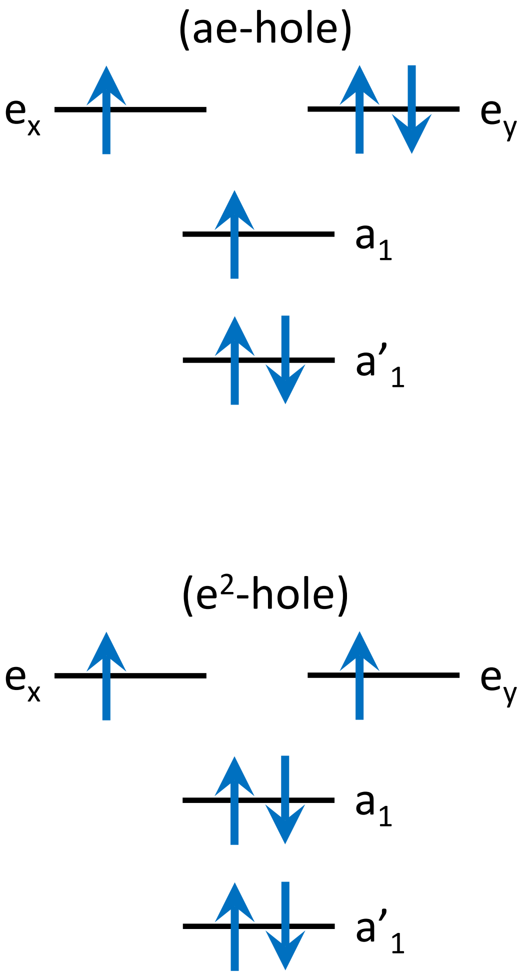


Effective spin-1 system
(e^2-hole spin-triplet)

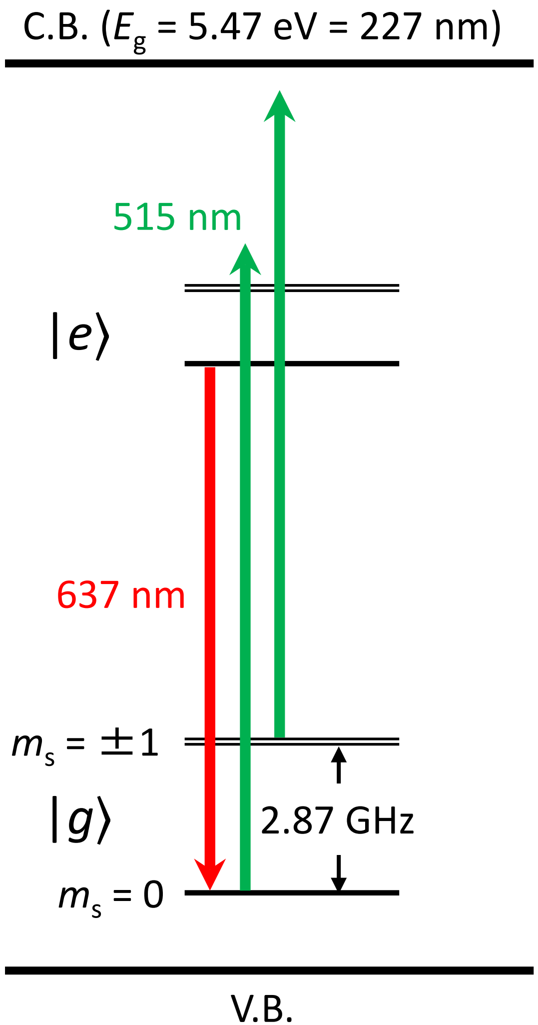


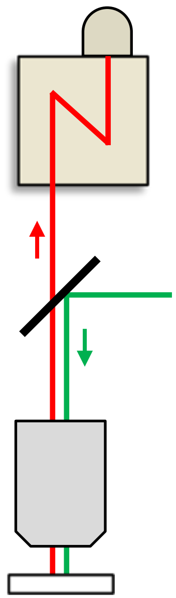
Optical transitions



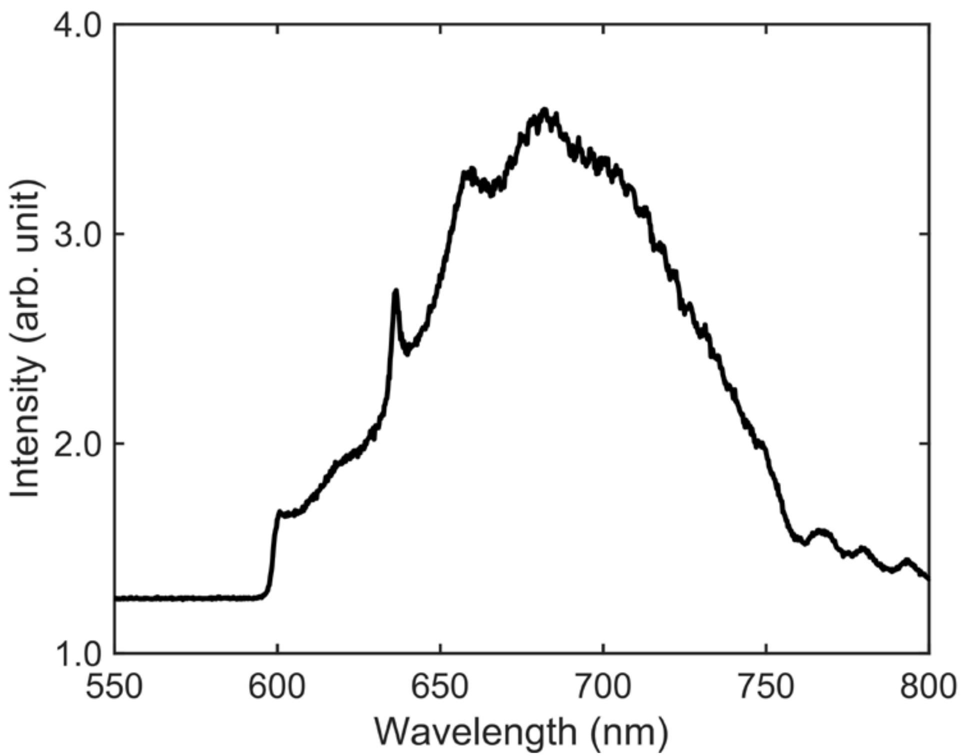


PL spectroscopy

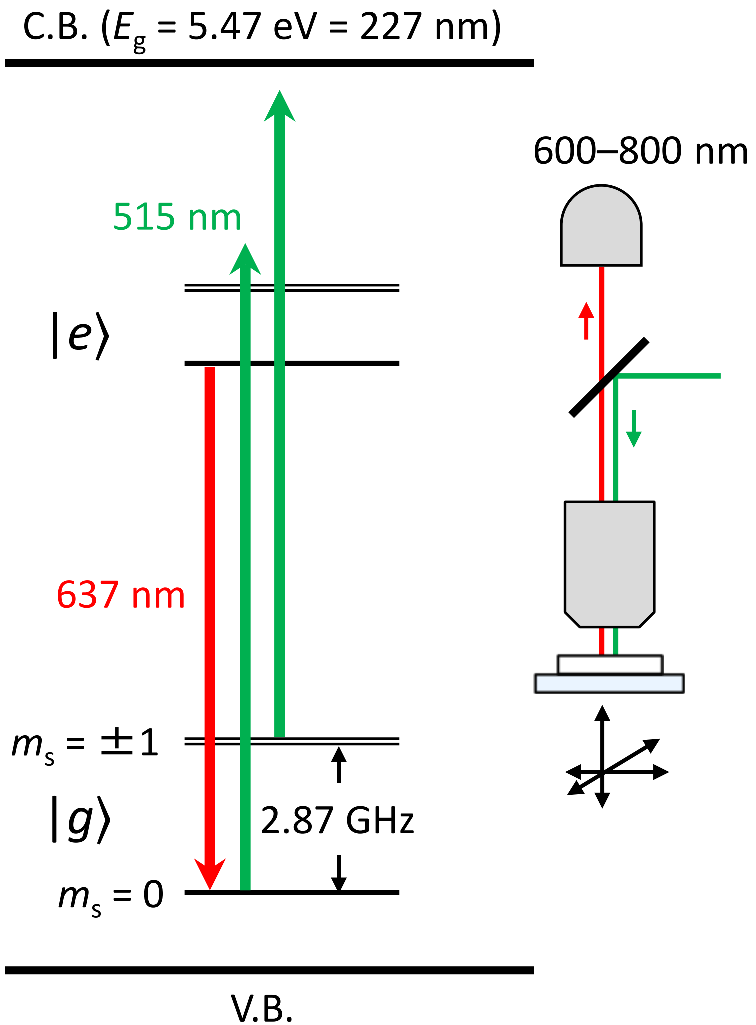




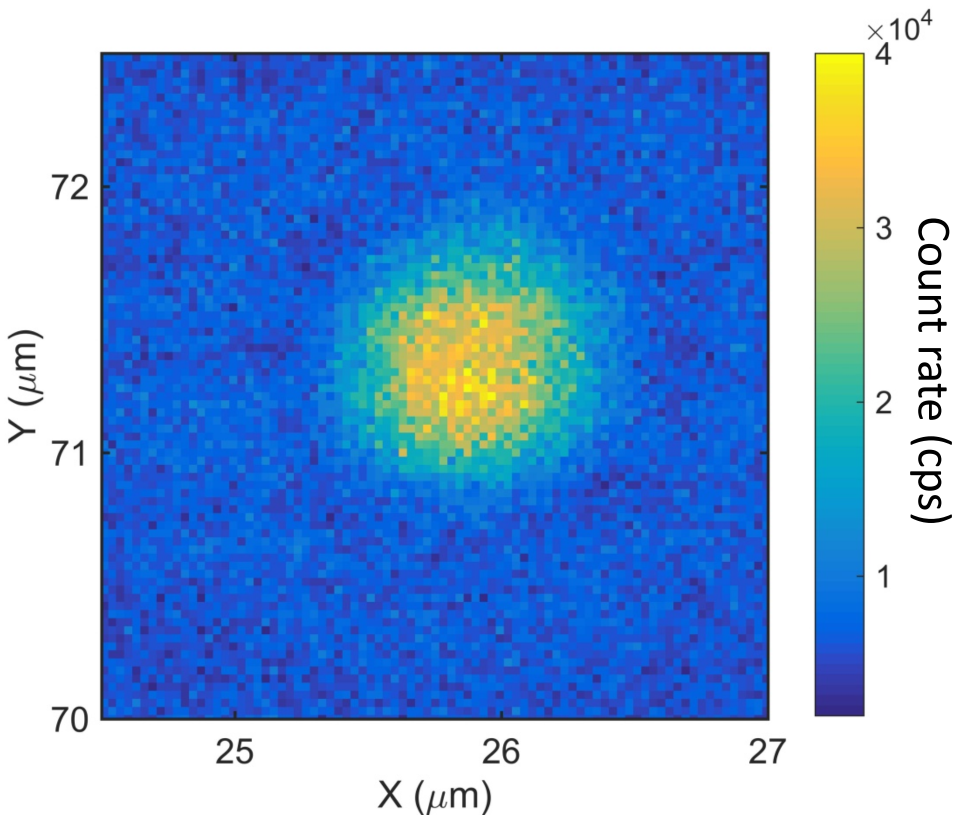
ZPL and PSB



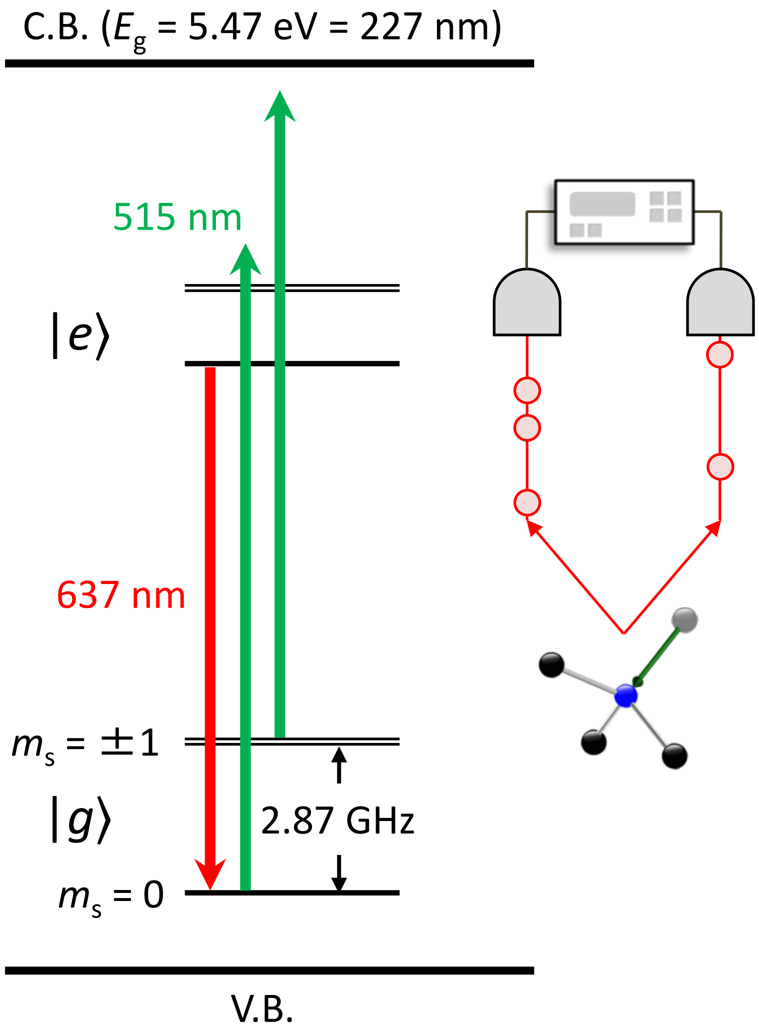
PL imaging



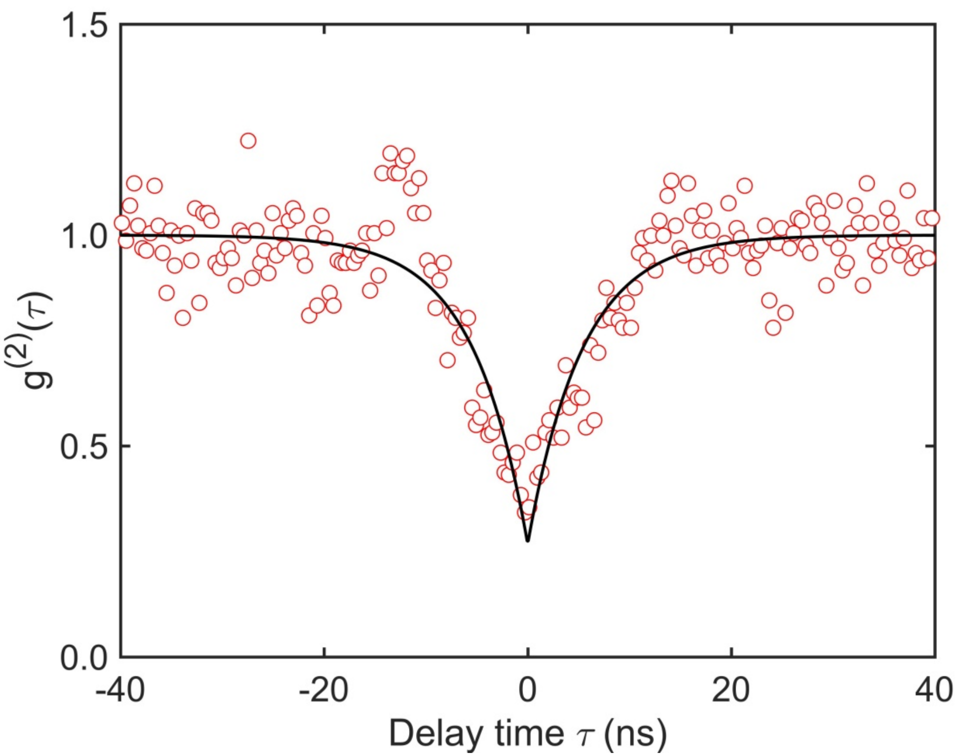
Bright spot... single NV?



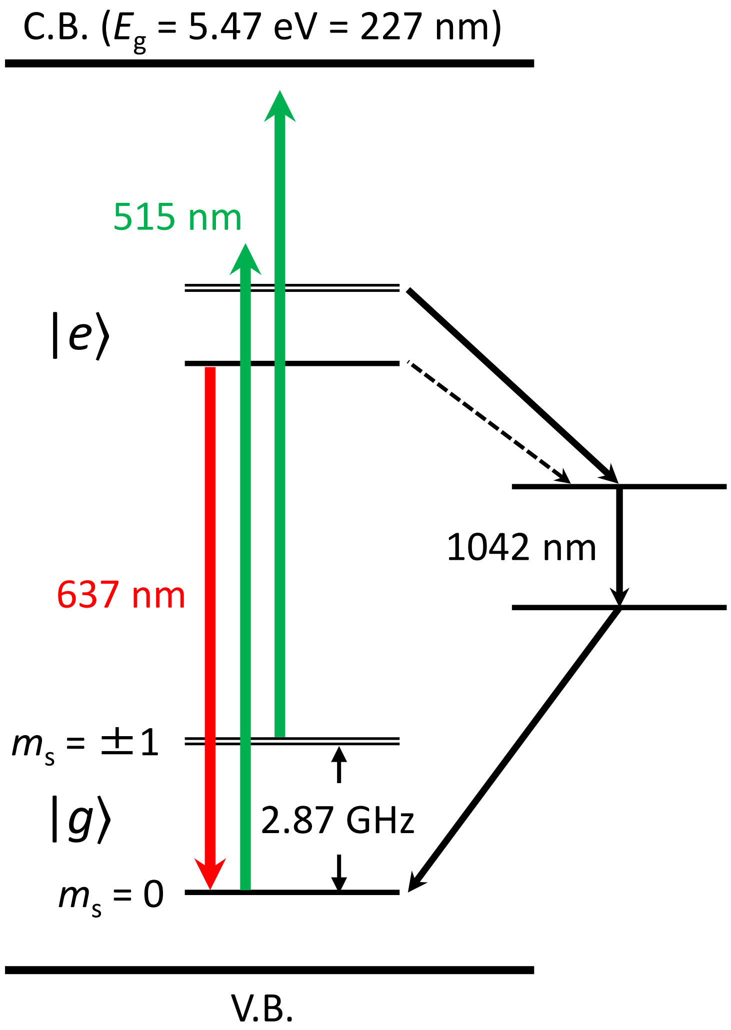
Photon statistics



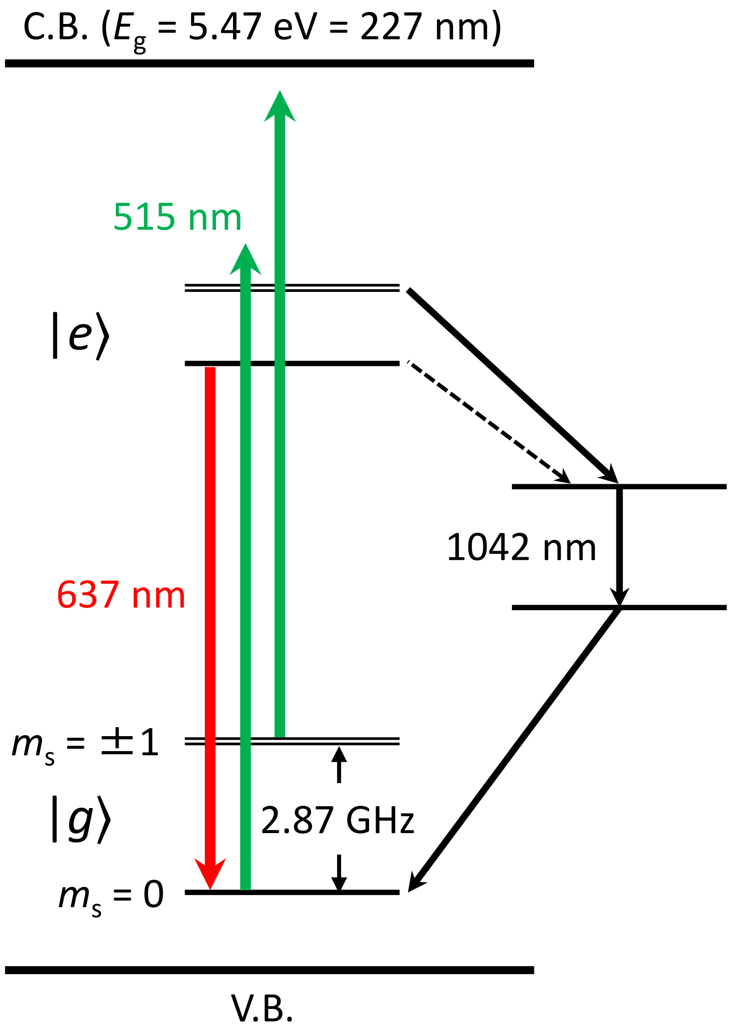
One photon at a time



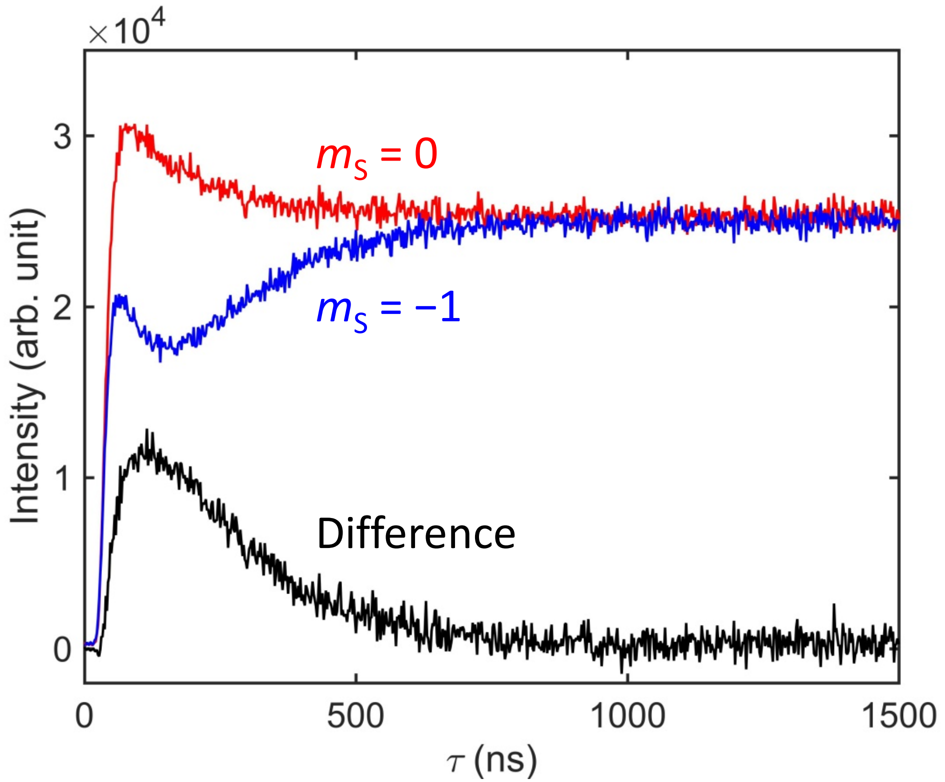
Non-radiative path



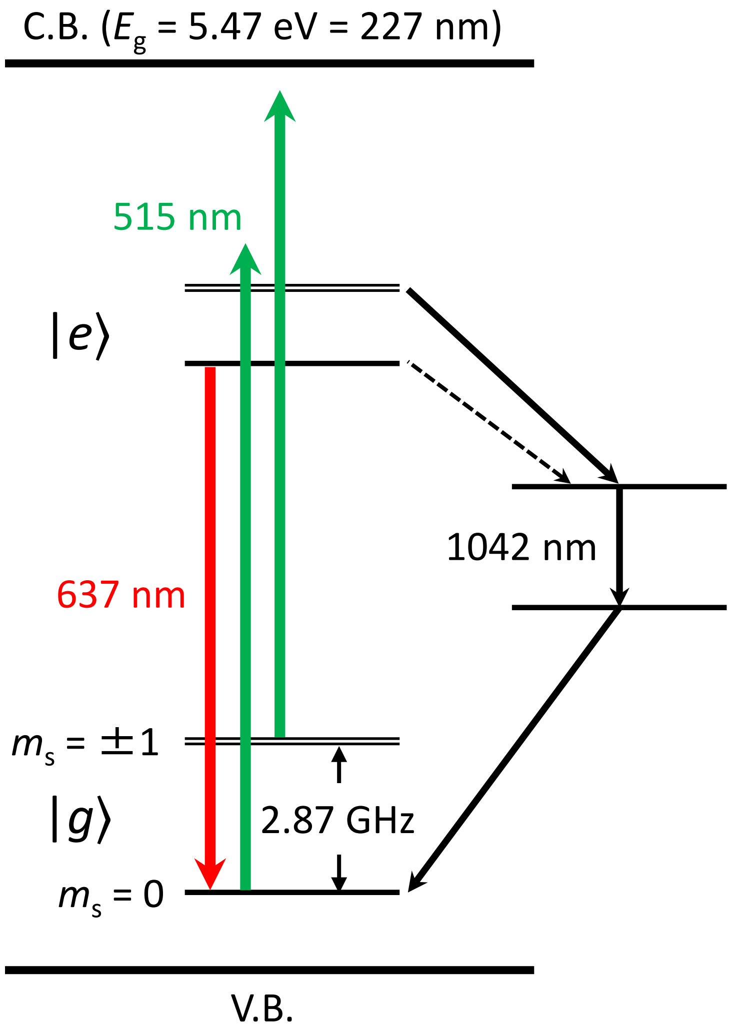
Time-resolved fluorescence

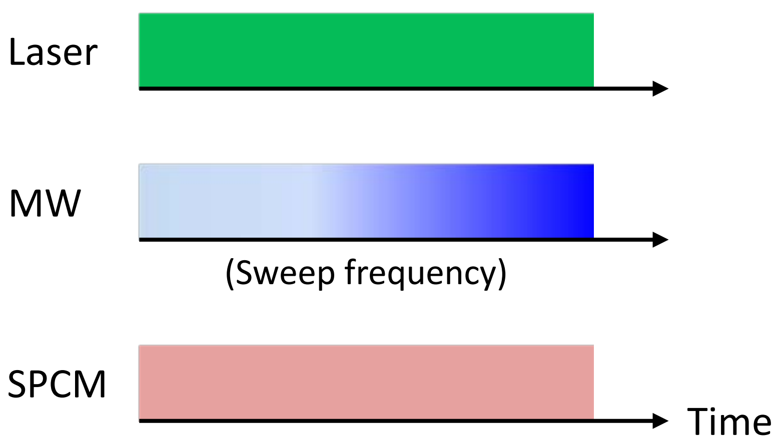


The NR channel provides a means to **read out** and **initialize** the NV spin

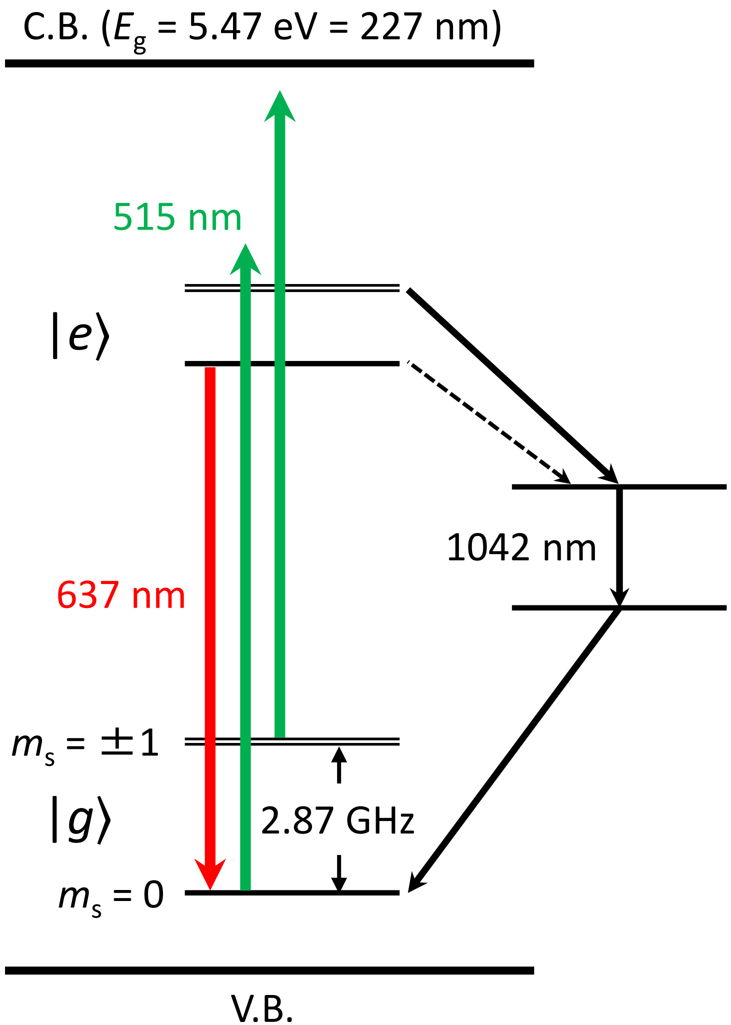


CW ODMR


C.B. (E_g = 5.47 eV = 227 nm)
515 nm
|e⟩
1042 nm
637 nm
m_s = ±1
|g⟩
2.87 GHz
m_s = 0
V.B.

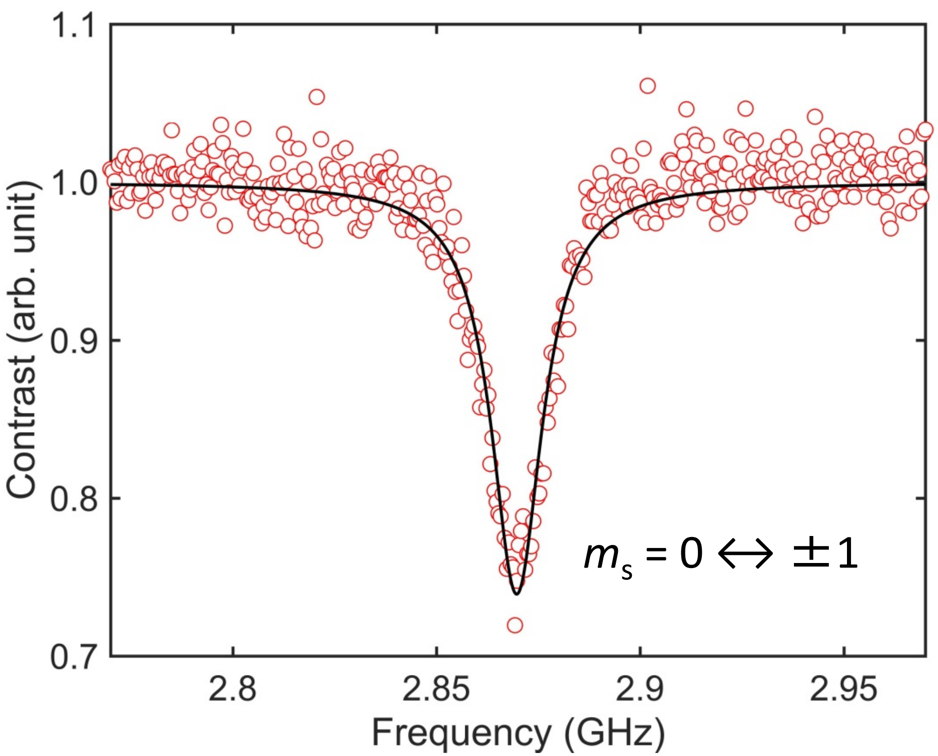

Laser
MW
(Sweep frequency)
SPCM
Time

CW ODMR at $B_0 = 0$

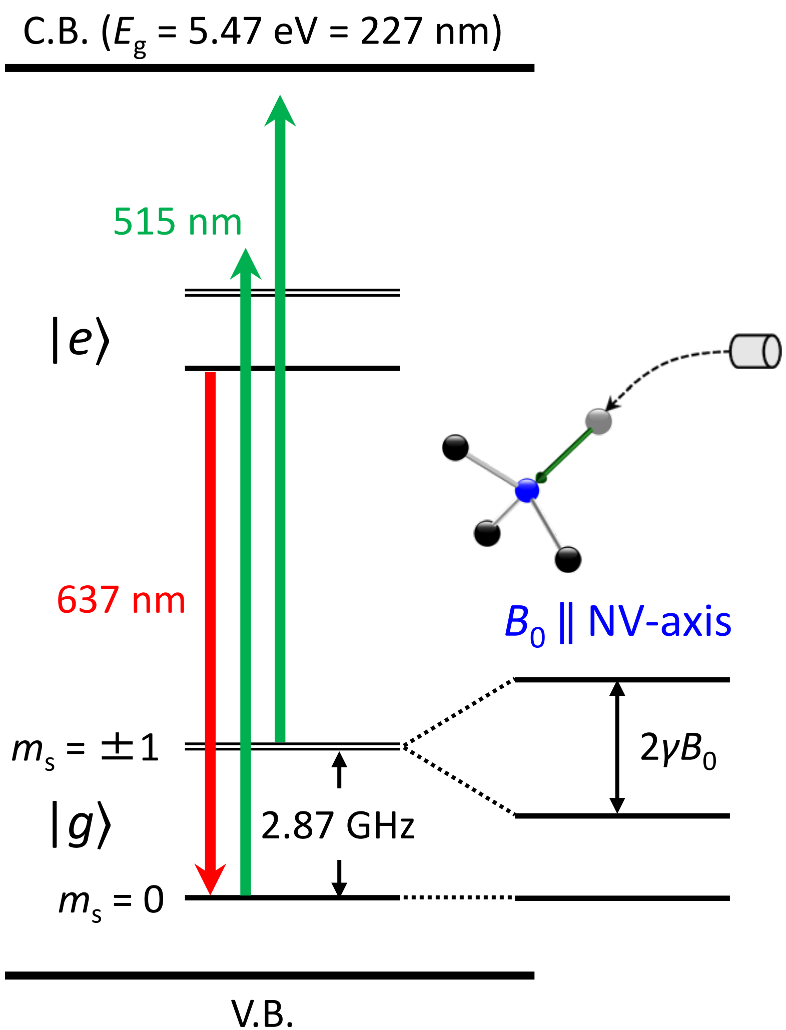


Zero-field splitting $H = DS_z^2$

$D/2\pi$ = 2.87 GHz

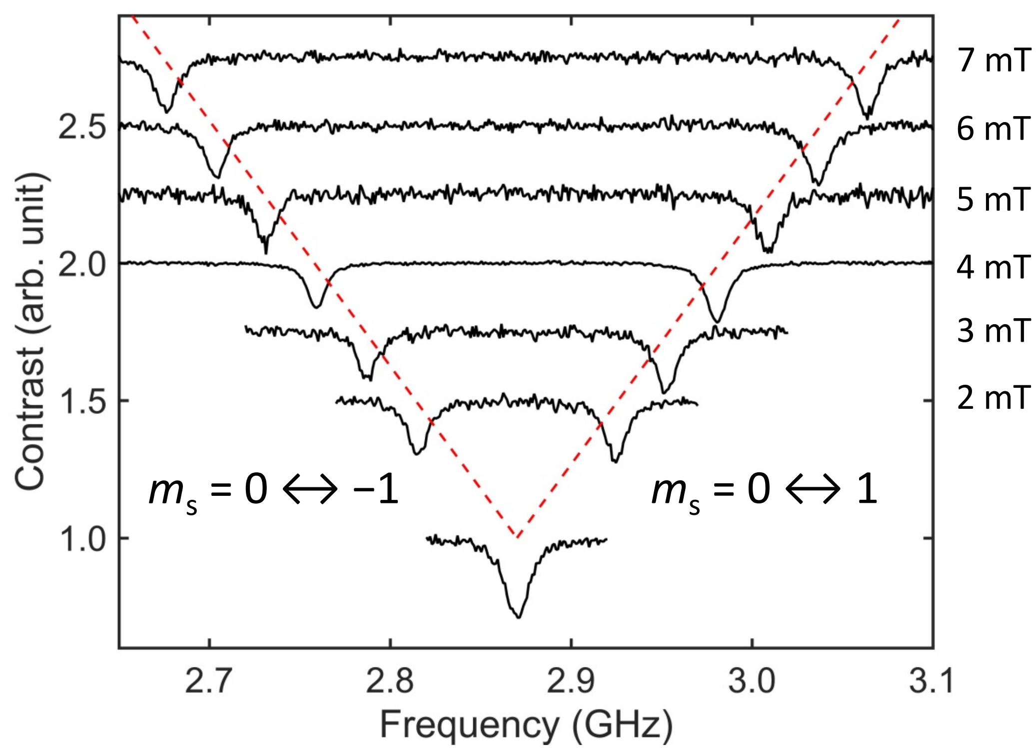


CW ODMR at $B_0 \geq 0$

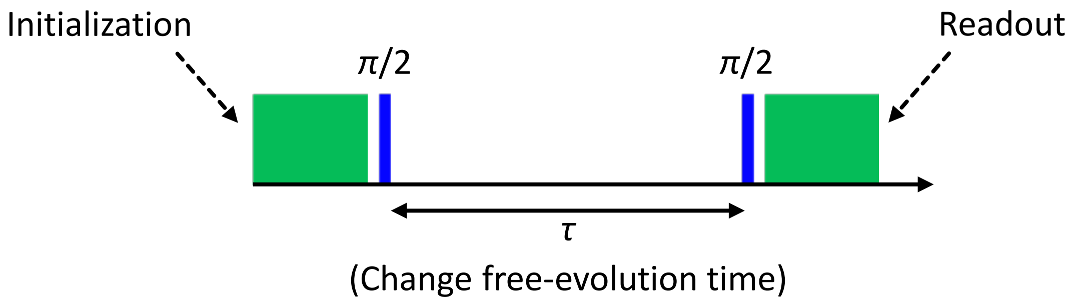


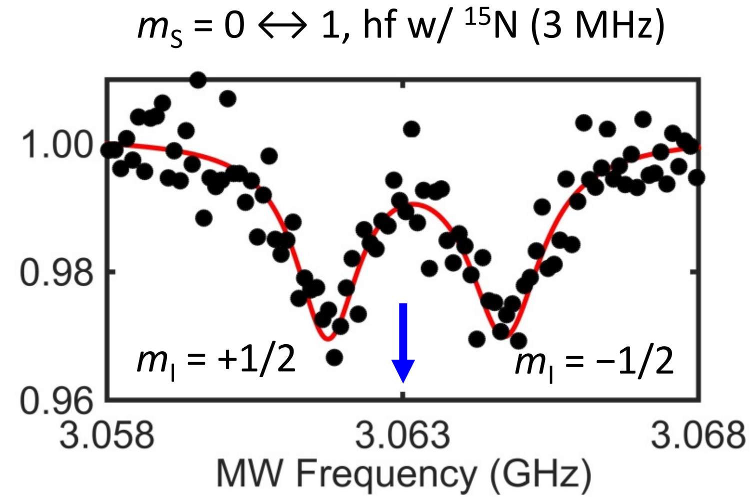
Zeeman $H = DS_z^2 + \gamma B_0 S_z$

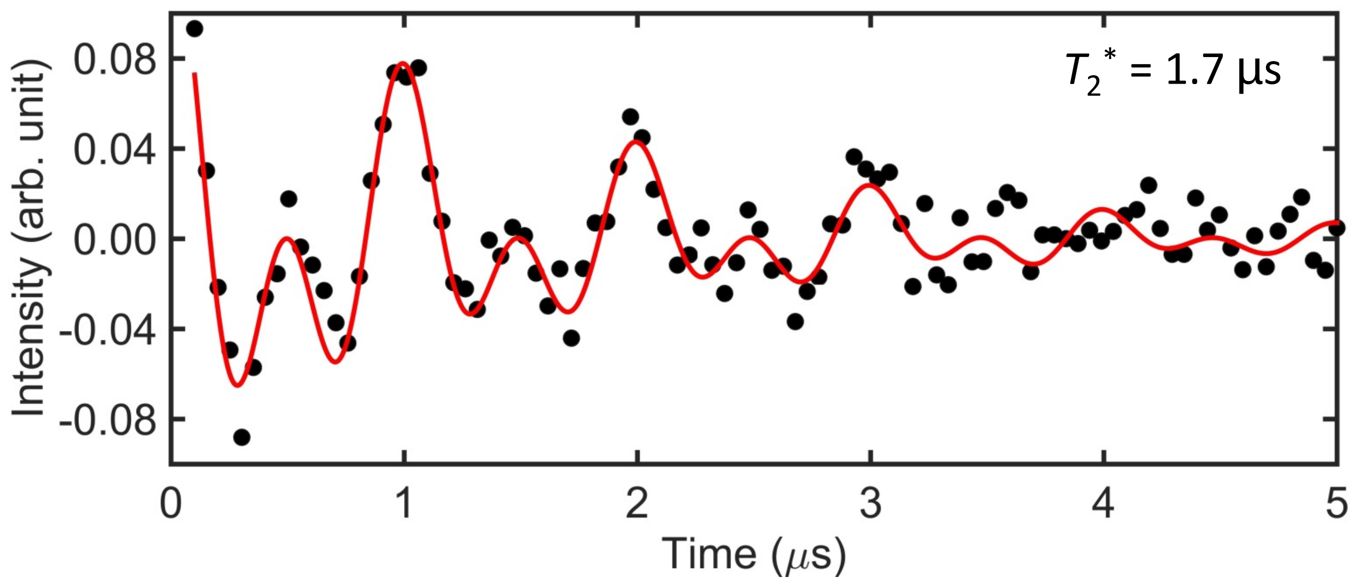
$\gamma/2\pi$ = 28 MHz/mT

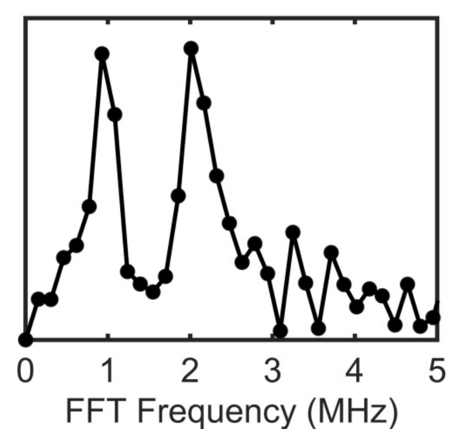


Ramsey interferometry

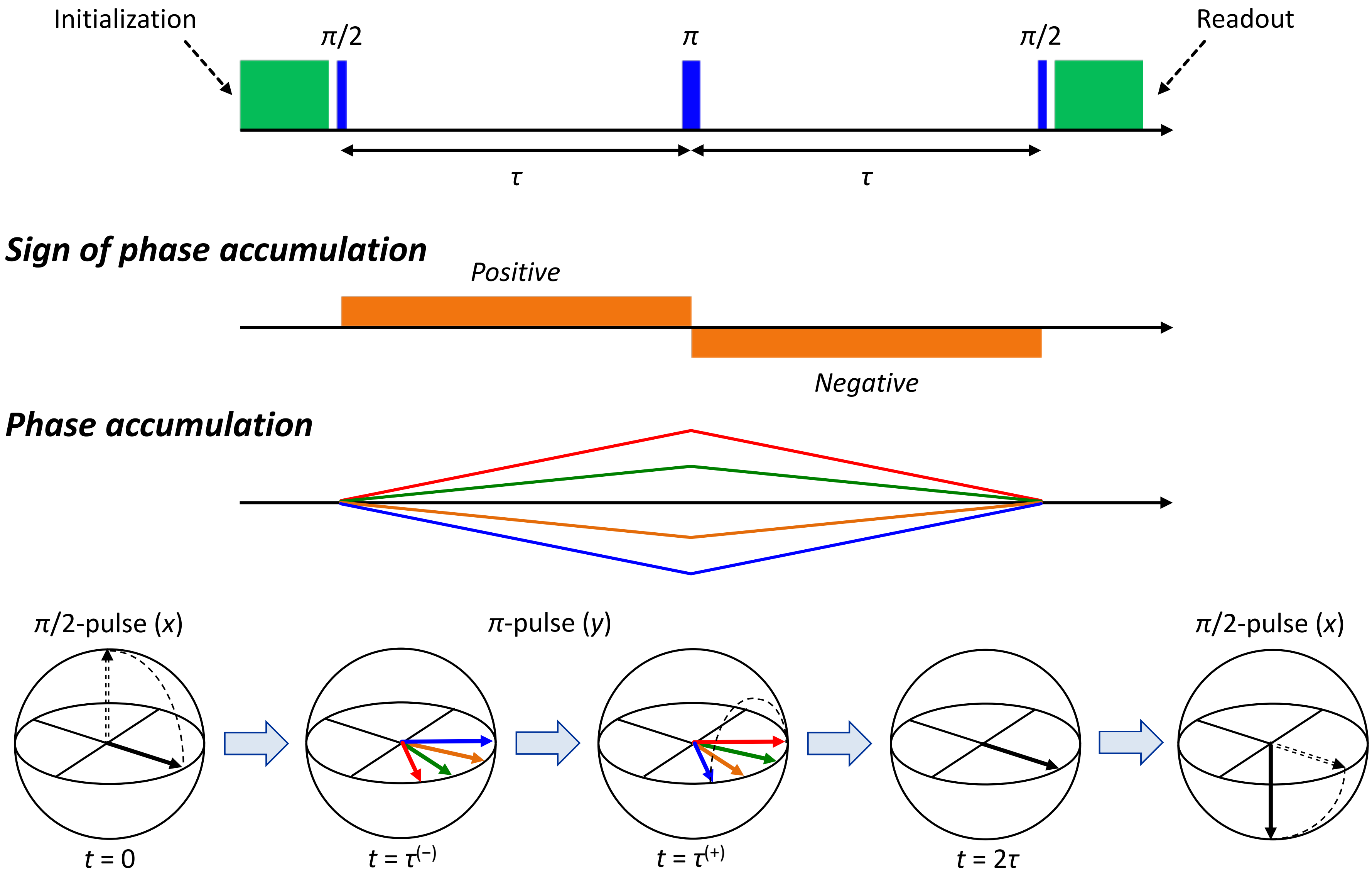




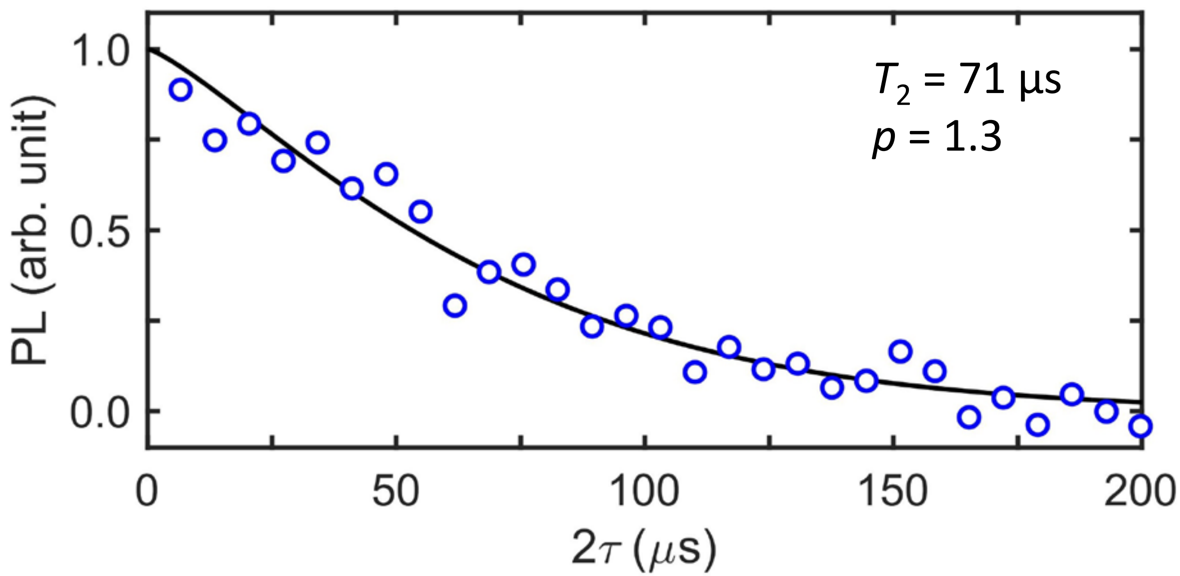




Hahn echo


Initialization
π/2
π
π/2
Readout
τ
τ
Sign of phase accumulation
Positive
Negative
Phase accumulation
π/2-pulse (x)
π-pulse (y)
π/2-pulse (x)
t = 0
t = τ(−)
t = τ(+)
t = 2τ

Coherence time



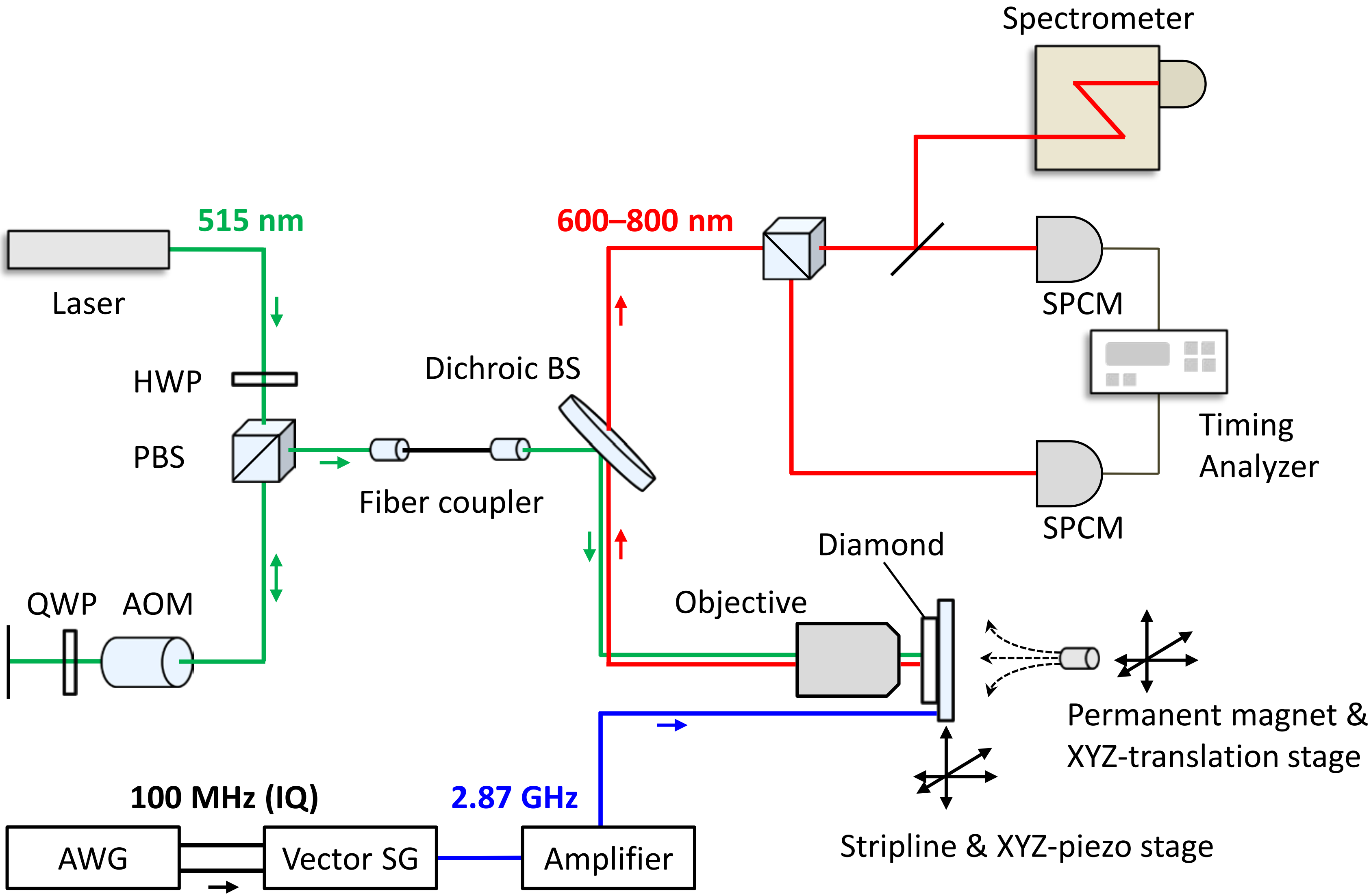
Stretched exponential decay

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

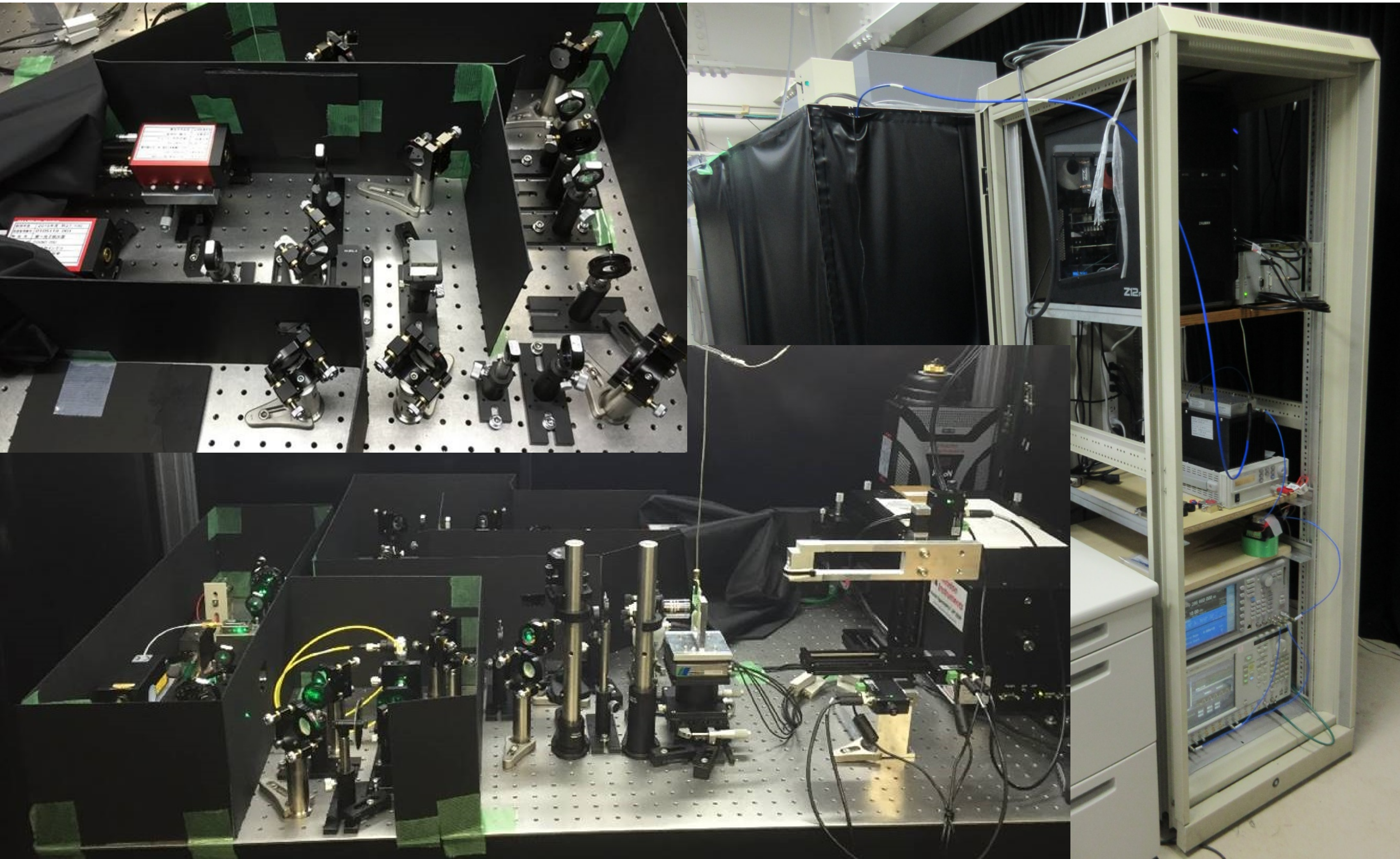
CVD growth of shallow single NV centers

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

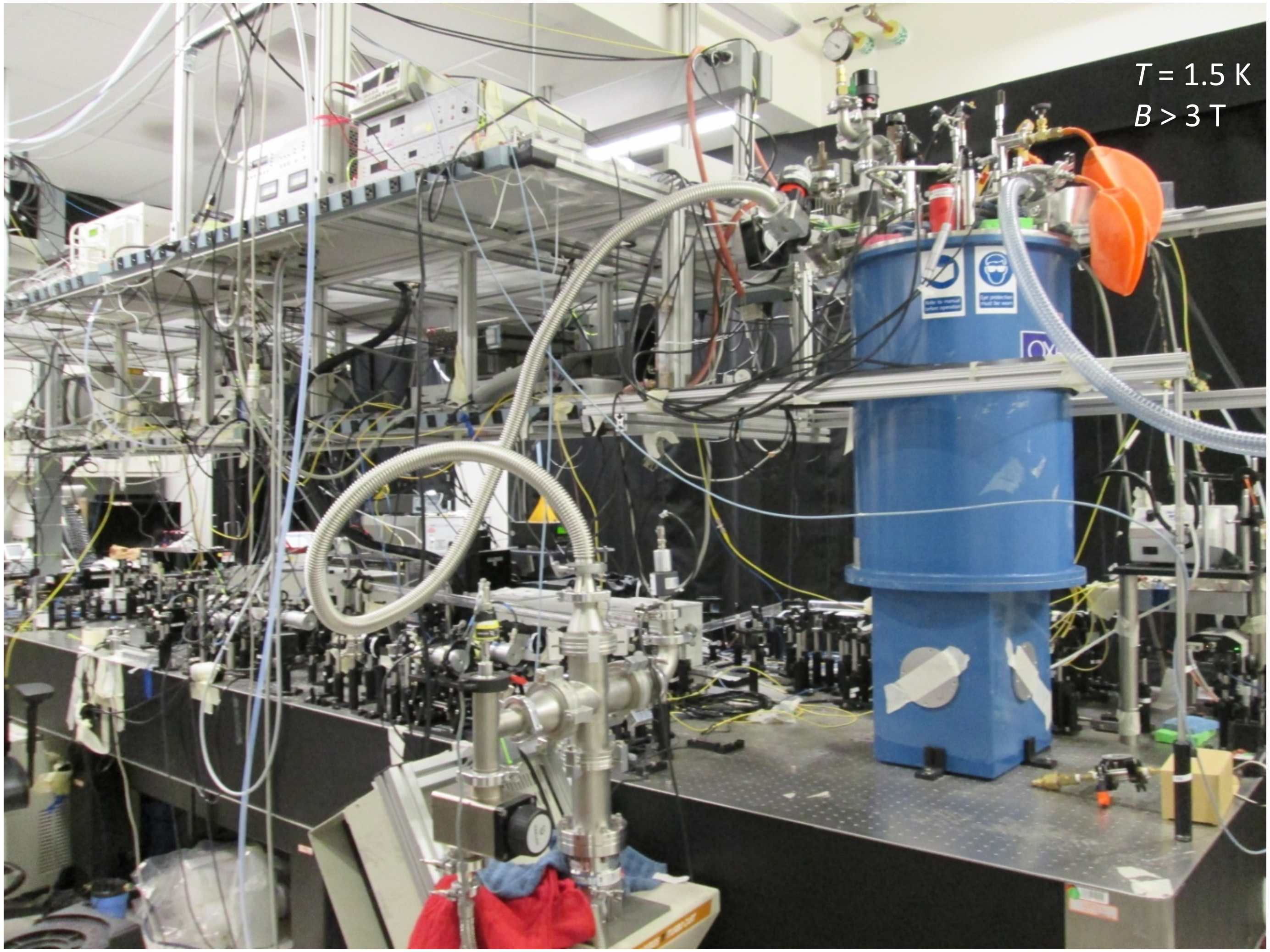
Experimental setup



Experimental setup



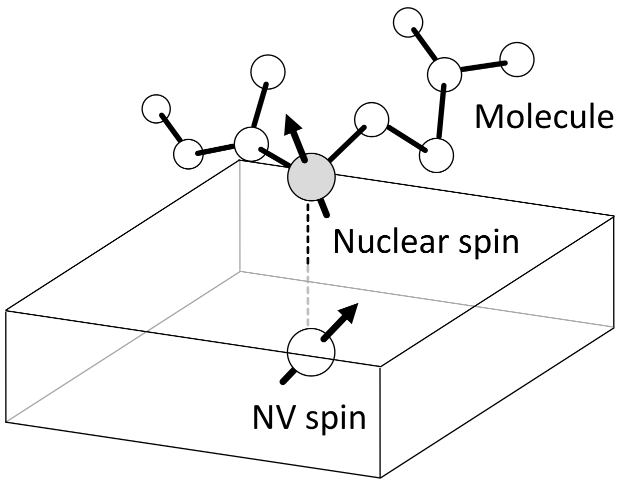
cf. a case of QDs @Stanford

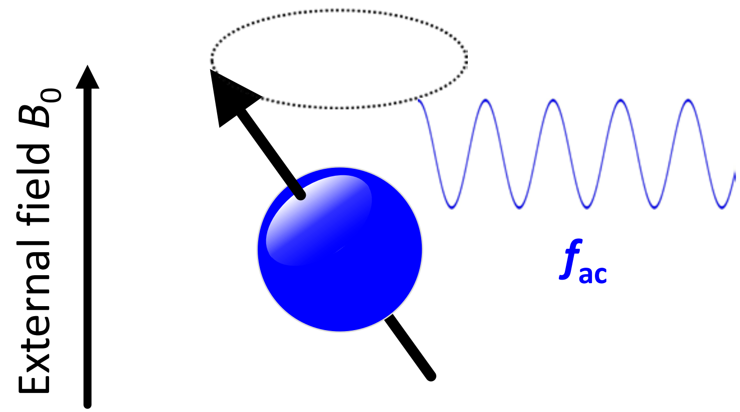


Outline

- **Basics of NV centers in diamond**
  - Structure
  - Optical properties
  - Spin properties
- **AC magnetometry**
  - Basics
  - Correlation spectroscopy and detection of nuclear spins
  - Ultrahigh resolution sensing

Quantum sensing





Nuclear spins precess at a few kHz–MHz under B_0

⇨ **Weak AC magnetic fields** on an NV spin (11 nT for d_{NV} = 5 nm)

⇨ Detect them using **quantum coherence**

AC magnetometry

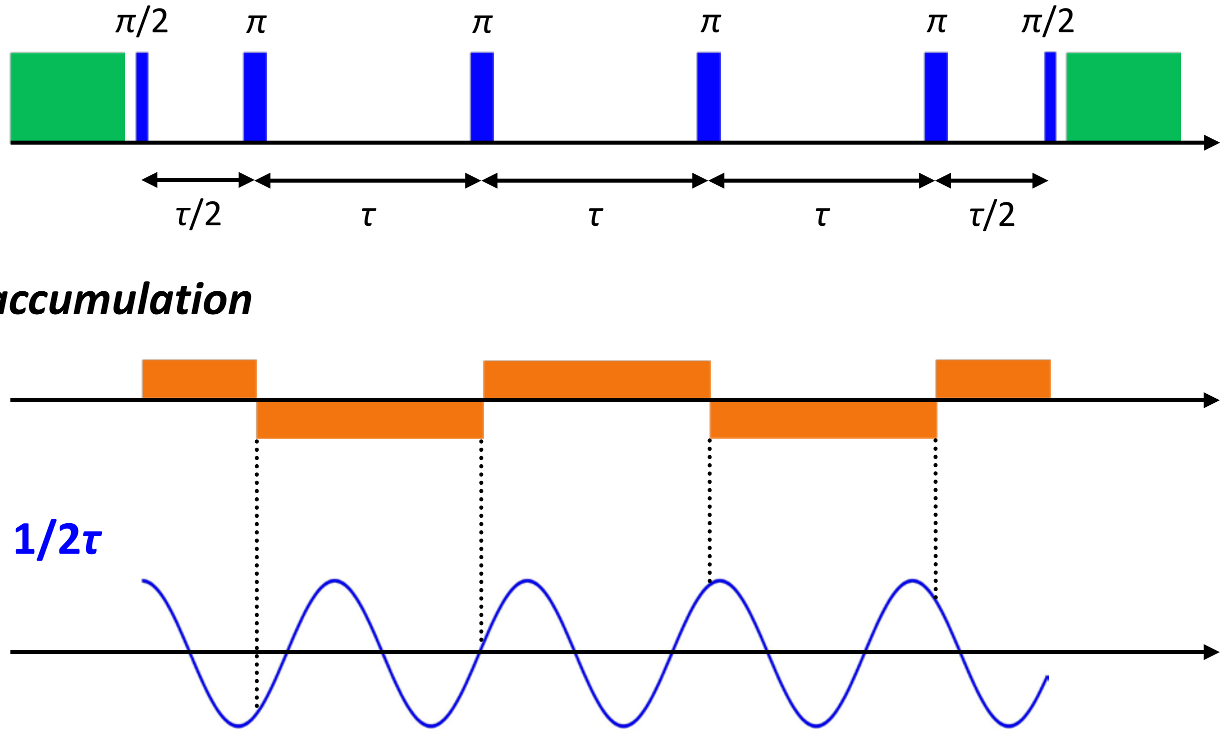
- **Spin echoes** cancel the phase accumulation due to **DC magnetic fields**
- How about **AC magnetic fields**? → In many case, **YES**
- However, **for specific AC frequencies, and the phase is accumulated** constructively → AC magnetometry

AC magnetometry

CP (N = 4)

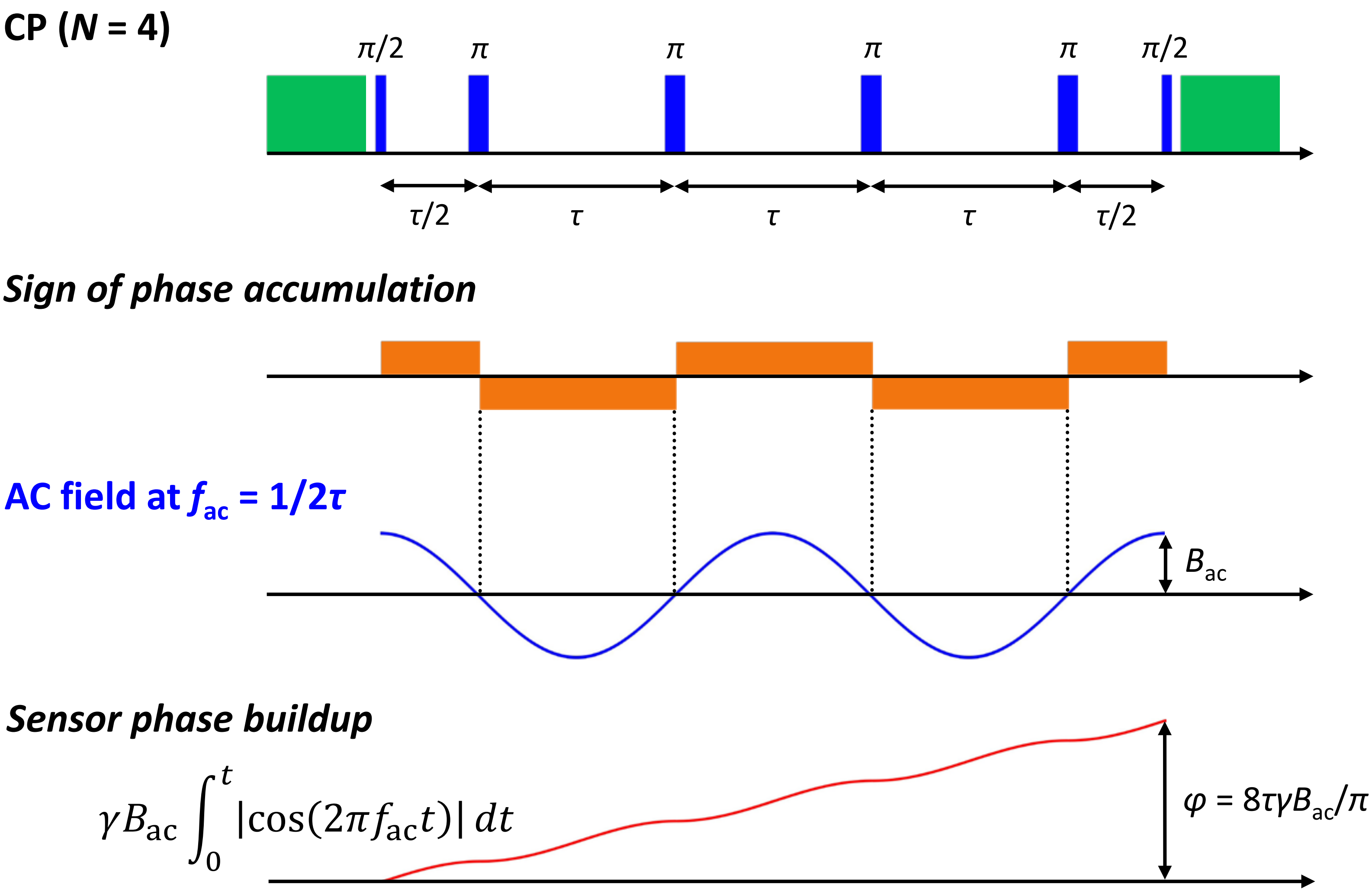
Sign of phase accumulation

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



- If we have multiple oscillations between π-pulses, the sensor phase averages out

AC magnetometry

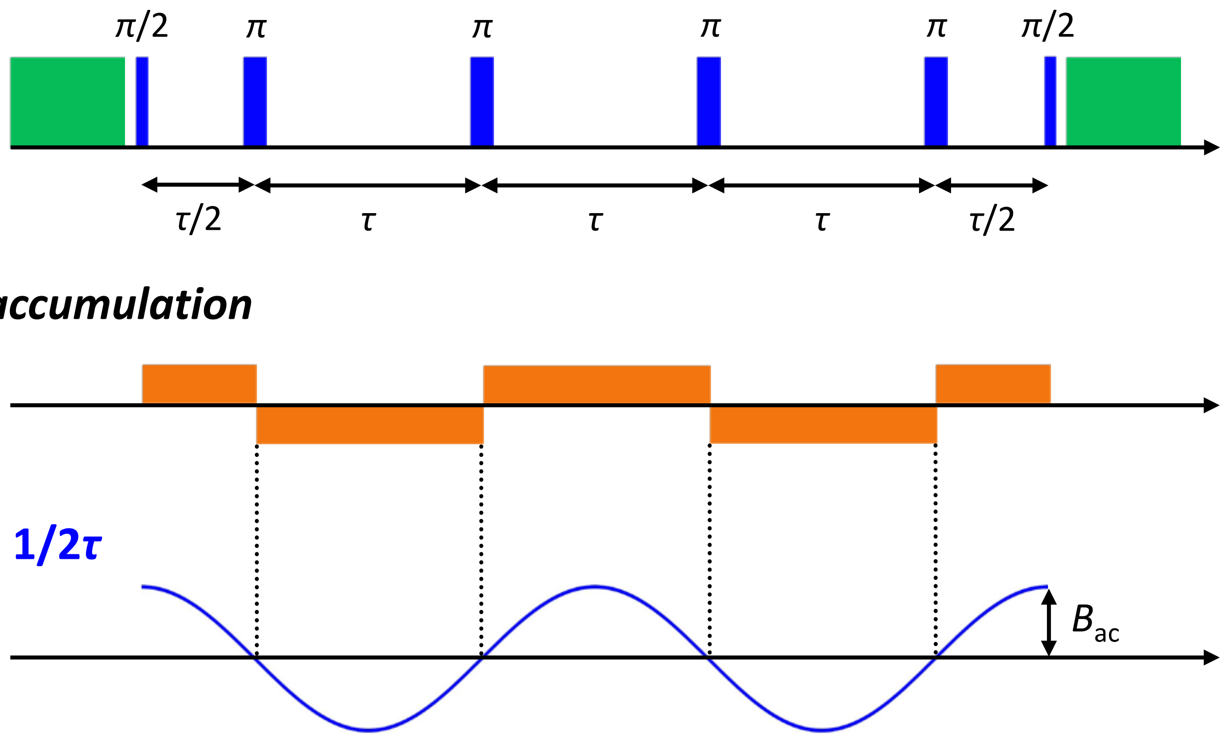


AC magnetometry

CP (N = 4)

Sign of phase accumulation

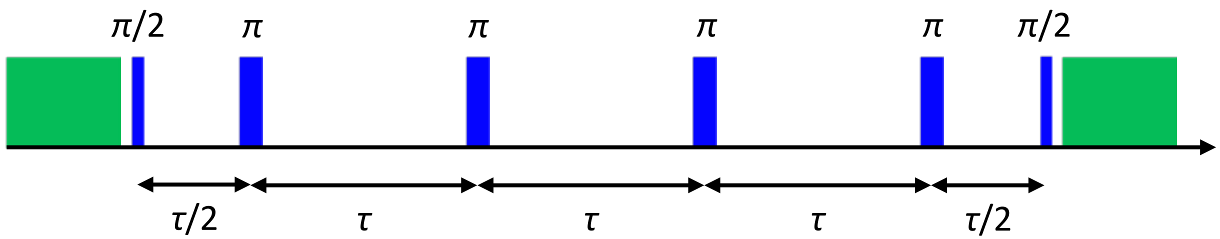
AC field at $f_{ac} = 1/2\tau$



- π-pulses cancel the sensor phase except $f_{ac} \approx 1/2\tau$ (& odd-harmonics)
- To obtain a spectrum, sweep τ and repeat
- Resolution $\propto 1/T_2$

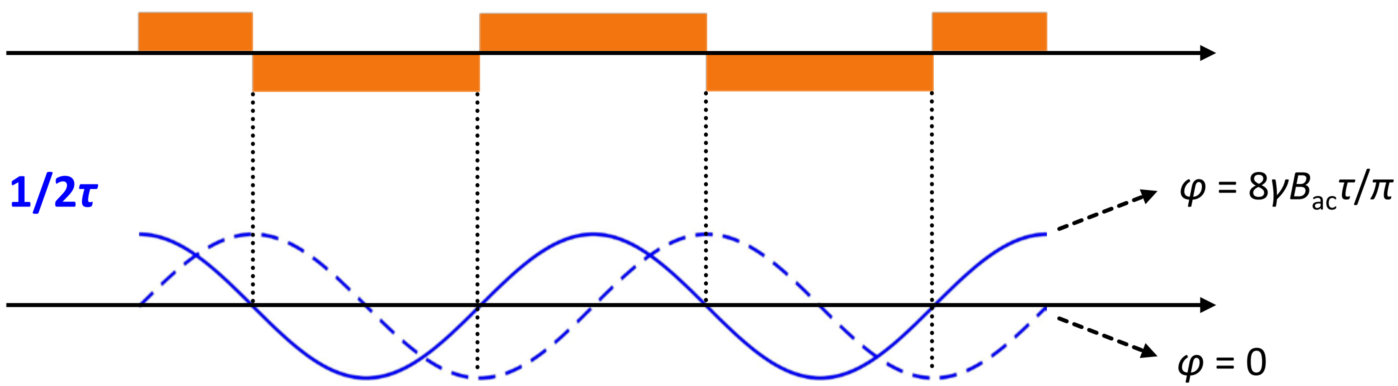
AC magnetometry

CP (N = 4)



Sign of phase accumulation

AC field at f_{ac} = 1/2τ



- Even if $f_{ac} = 1/2\tau$, the accumulated phase φ depends on the **initial phase α of the AC field**
- In many cases, we do not know α

AC magnetometry

AC signal

$$B_{\mathrm{ac}}(t) = B_{\mathrm{ac}} \cos(2\pi f_{\mathrm{ac}} t + \alpha)$$

Modulation function

$$h(t) = \begin{cases} 1 \\ -1 \end{cases} = \frac{4}{\pi} \sum_{n=\mathrm{odd}} \frac{\cos(\pi t/\tau)}{n}$$

Accumulated phase

$$\varphi(t) = \gamma B_{\mathrm{ac}} \int_0^t h(t) \cos(2\pi f_{\mathrm{ac}} t + \alpha)\, dt = \gamma B_{\mathrm{ac}} t W(f_{\mathrm{ac}}, \alpha)$$

Weighting (filter) function

Present case: $t = 4\tau = t_s$, $f_{ac} = 1/2\tau$

$$\varphi = \frac{2\gamma B_{\mathrm{ac}} t_{\mathrm{s}}}{\pi} \cos\alpha$$

⇒ Average over many possible α with the transition probability $p = \sin^2\varphi$

AC magnetometry

$$W_{\mathrm{CP}}(f_{\mathrm{ac}}, \alpha) = \frac{\sin(\pi f_{\mathrm{ac}} n \tau)}{\pi f_{\mathrm{ac}} n \tau} [1 - \sec(\pi f_{\mathrm{ac}} \tau)] \cos(\pi f_{\mathrm{ac}} n \tau + \alpha)$$

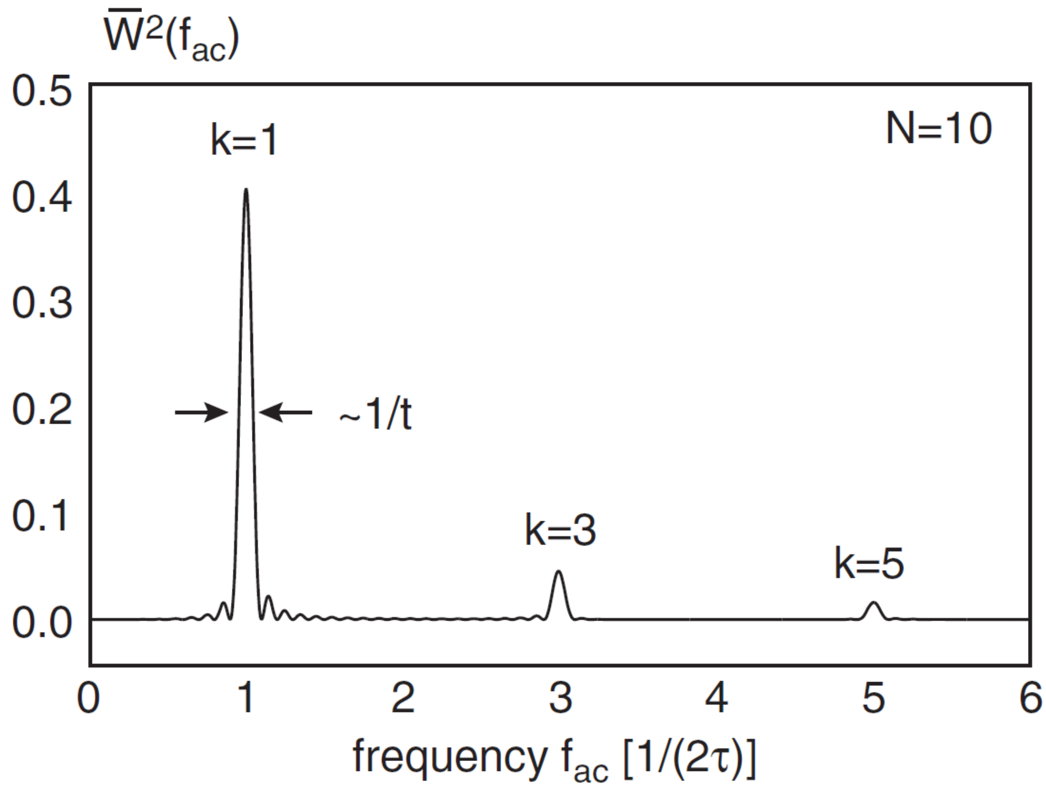
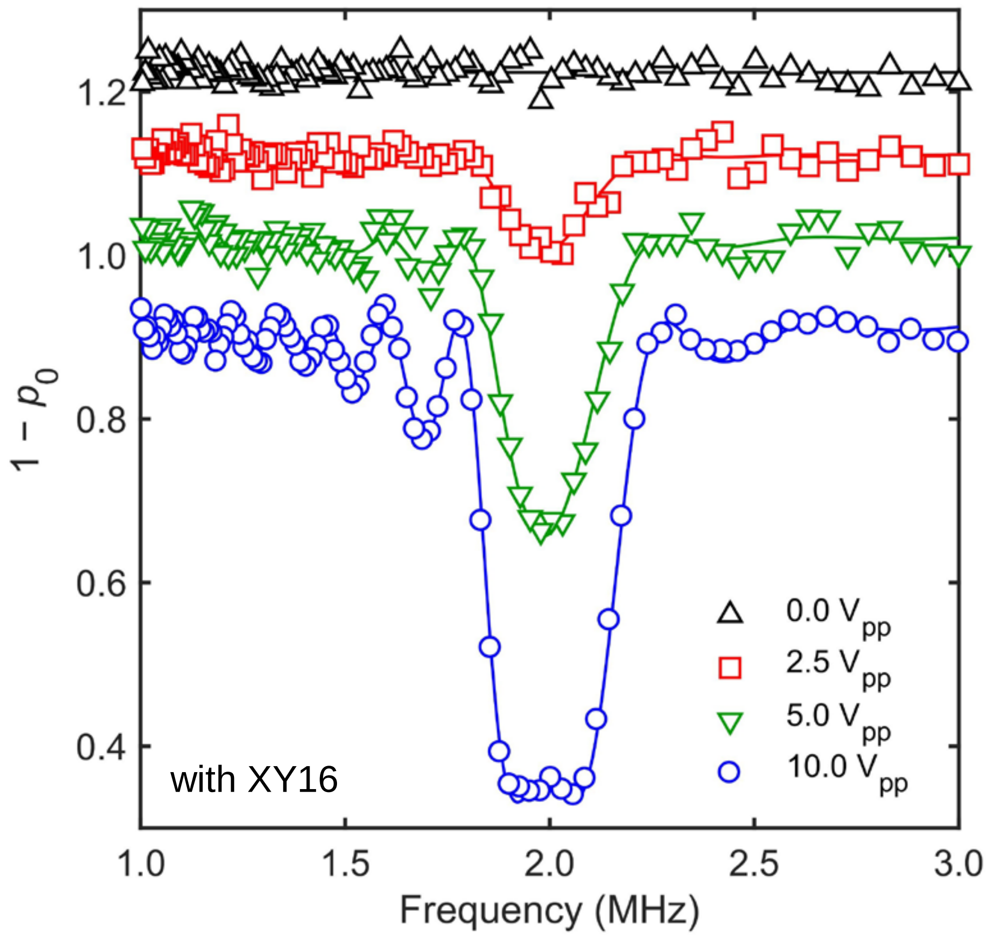
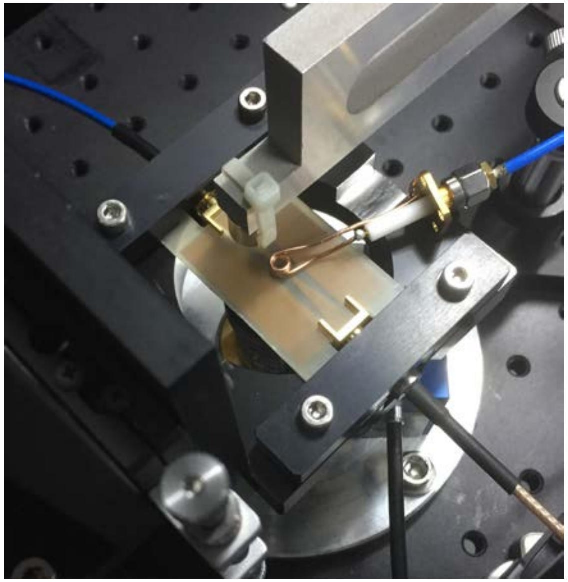


Figure: Rev. Mod. Phys. **89**, 035002 (2017) Degen *et al.*

AC magnetometry

AC signal at 2 MHz applied from a coil, detected by a single NV center





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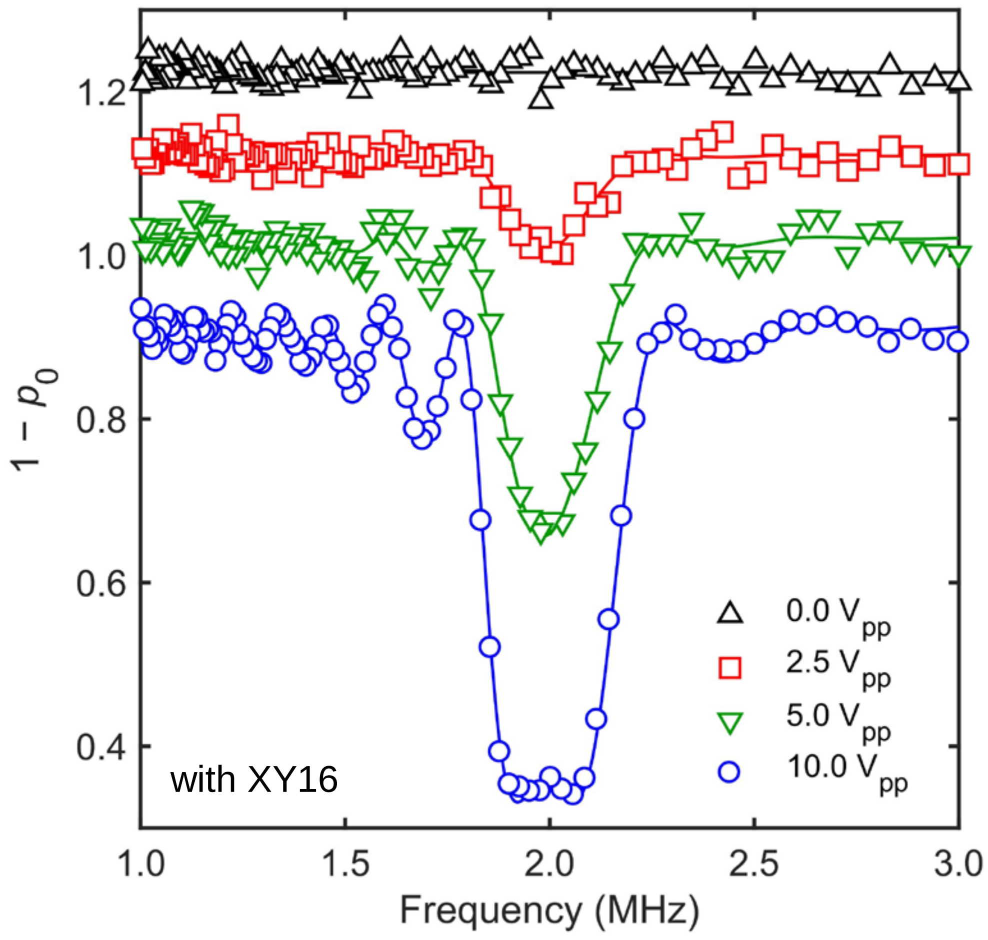
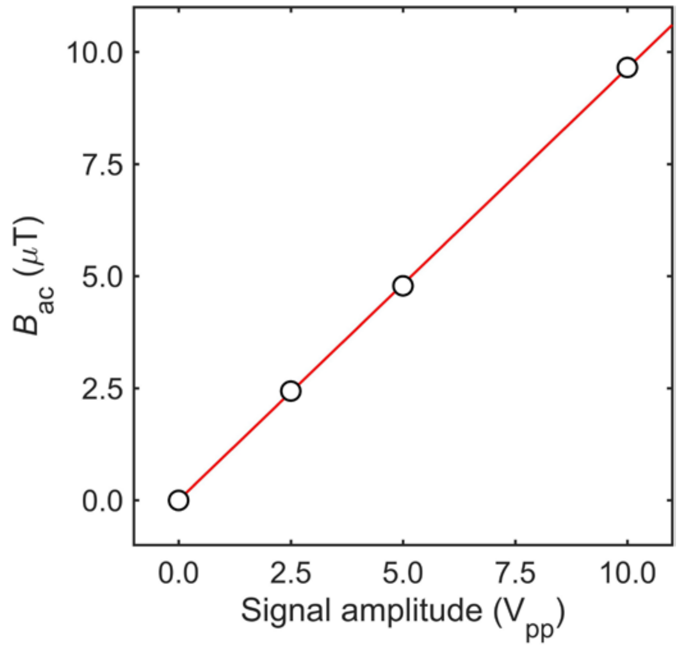




Nuclei in play

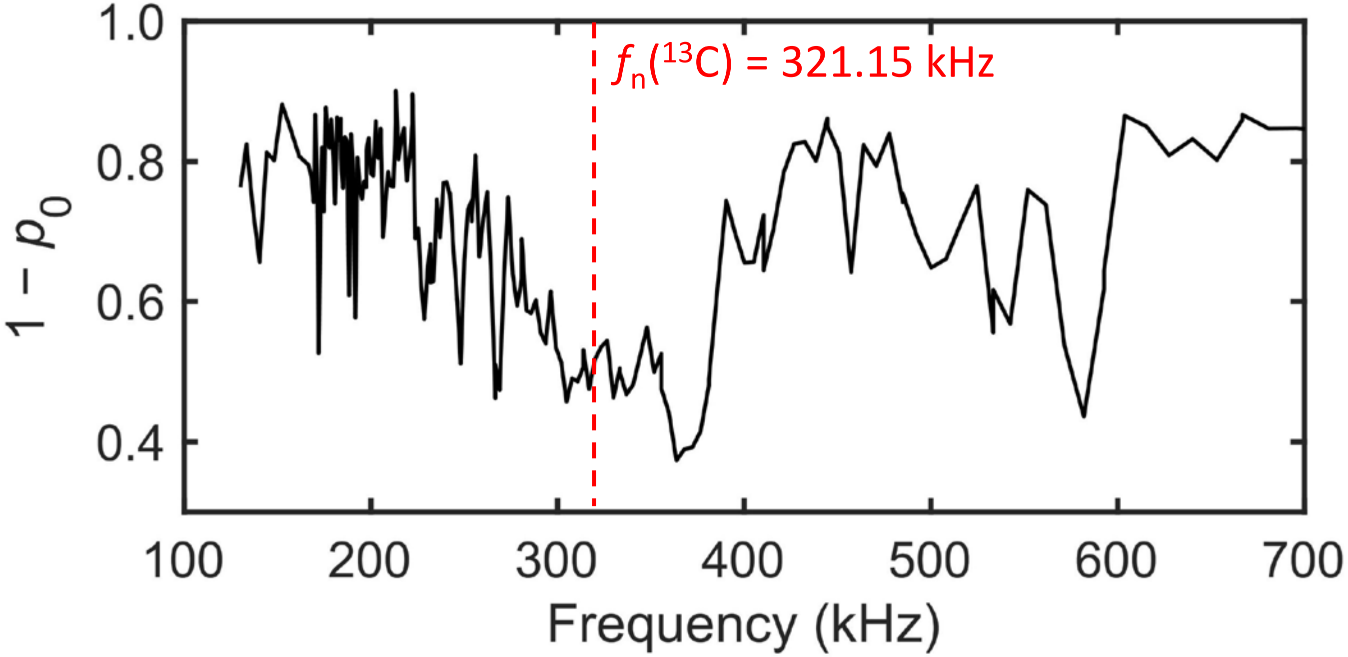
- **Hydrogen (^{1}H)**
  - Molecules on the diamond surface
  - $I = ½$, $\gamma_n/2\pi = 42.577$ kHz/mT

- **Carbon (^{13}C)**
  - Plenty in diamond itself (1.1%)
  - $I = ½$, $\gamma_n/2\pi = 10.705$ kHz/mT

- **Nitrogen (^{14}N)**
  - Contained in NV itself (99.6%)
  - $I = 1$, $\gamma_n/2\pi = 3.077$ kHz/mT

- **Nitrogen (^{15}N)**
  - Contained in NV itself (0.4%, often enriched)
  - $I = ½$, $\gamma_n/2\pi = -4.316$ kHz/mT

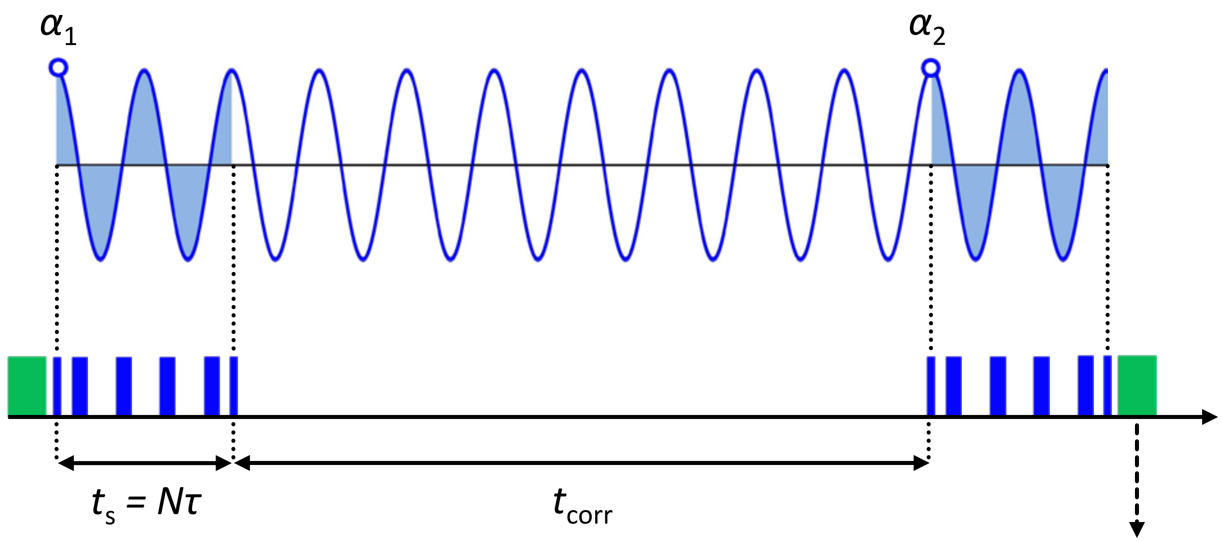
Nuclear spin sensing



- XY16 (N = 64)
- Increment: $\Delta\tau$ = 156 ns → $f = 1/2\tau$
- B_0 = 30 mT, $\gamma_n(^{13}C)/2\pi$ = 10.705 kHz/mT
- Measurement time = 1 day

Correlation spectroscopy

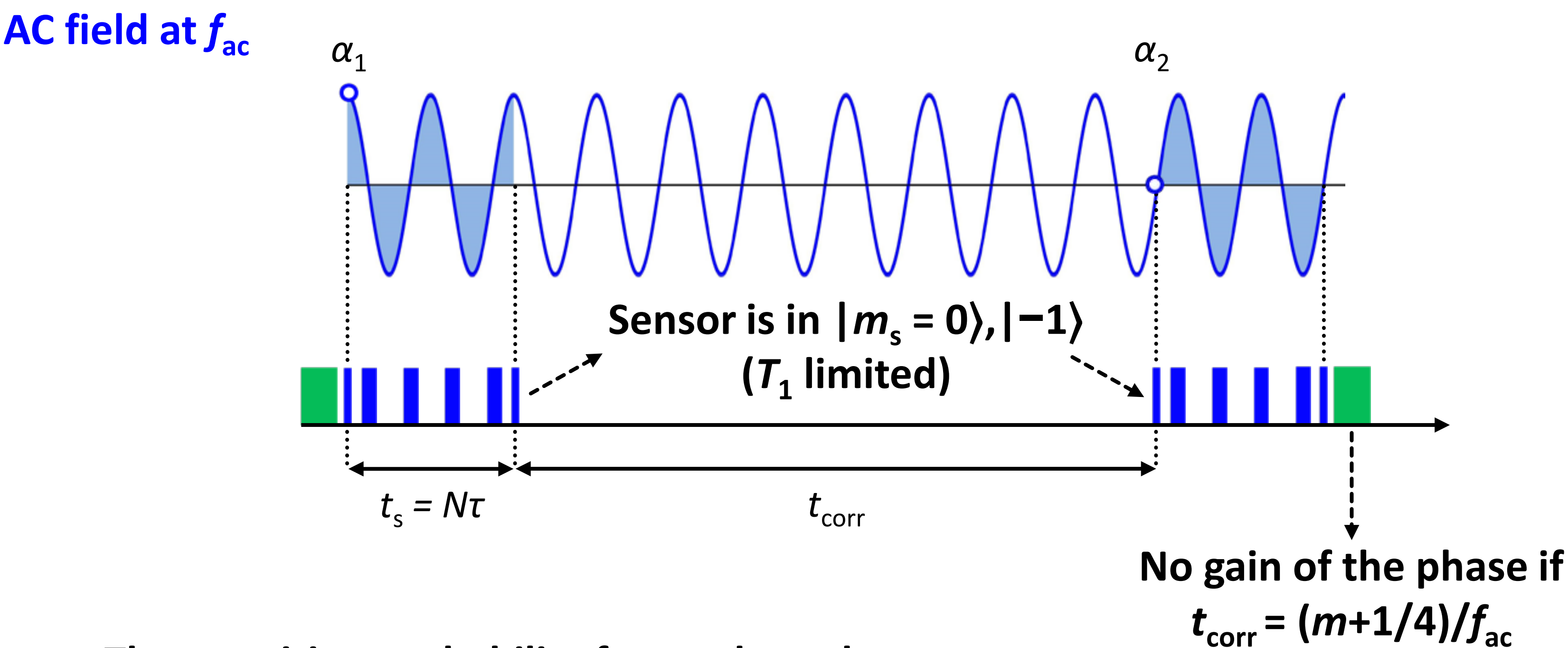
AC field at f_{ac}



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

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

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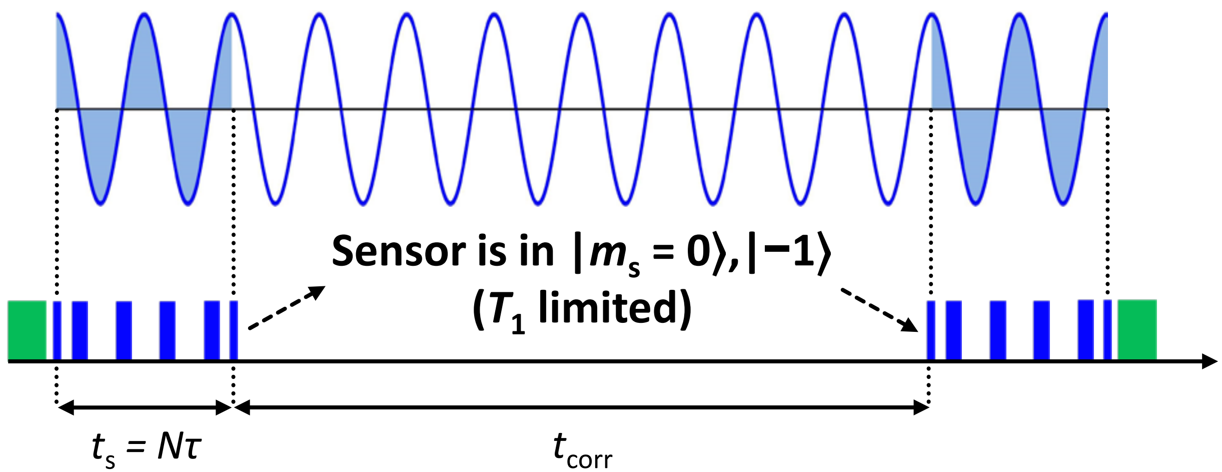
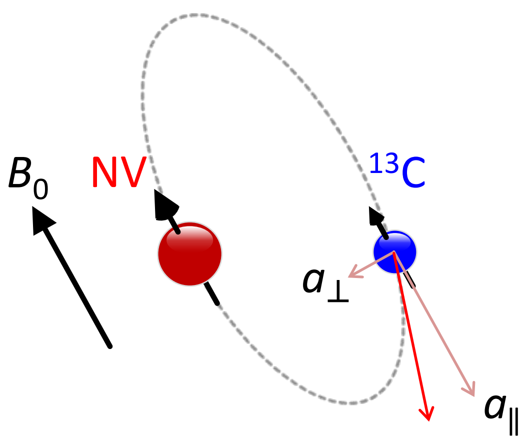
Phys. Rev. Appl. **4**, 024004 (2015) Kong *et al.*
Nature Commun. **6**, 8527 (2015) Staudacher *et al.*
Phys. Rev. Lett. **116**, 197601 (2016) Boss *et al.*

Correlation spectroscopy of nuclei

Nuclear spin precession at f_n





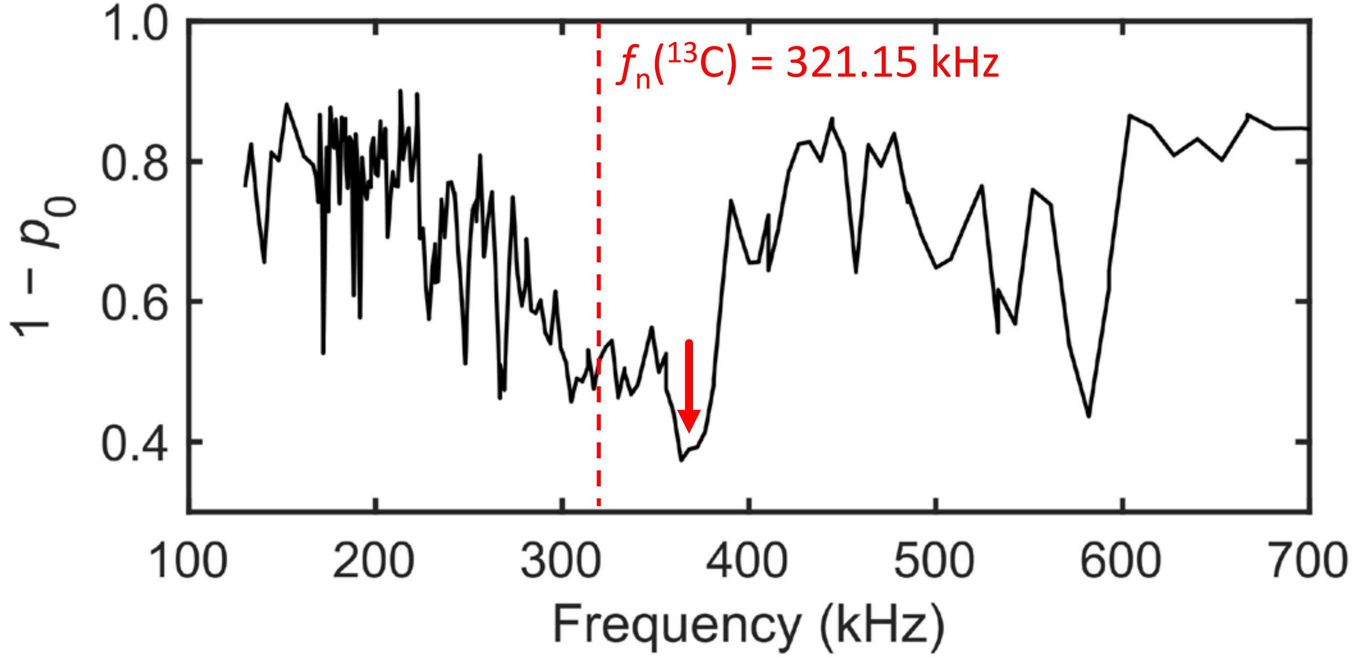
Hamiltonian of NV-^{13}C coupled system

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

→ $|m_s = 0\rangle$ does not feel hyperfine fields from ^{13}C

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.*

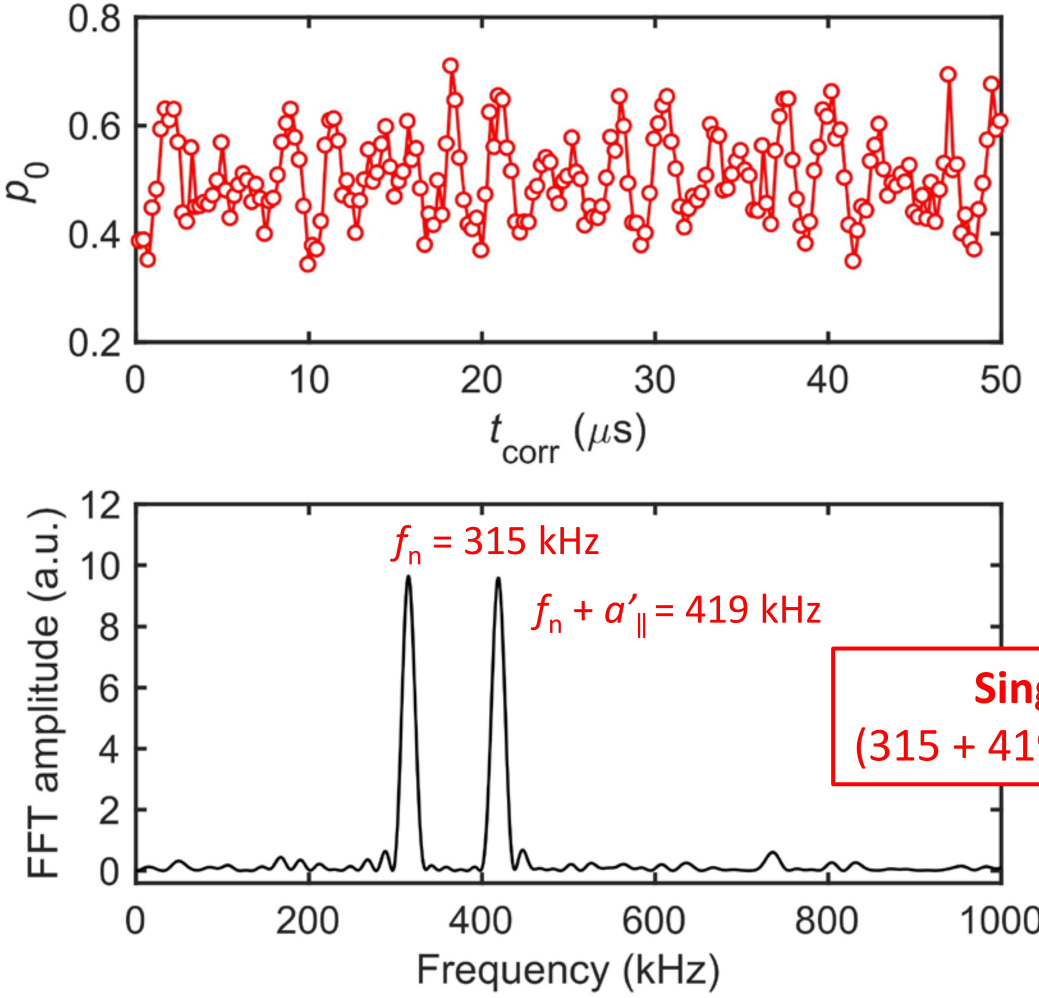
Correlation spectroscopy of nuclei



Choose where to look at

- XY8 (N = 8)
- τ = 1.311 μs
- $f = 1/2\tau$ = 381.3 kHz

Correlation spectroscopy of nuclei

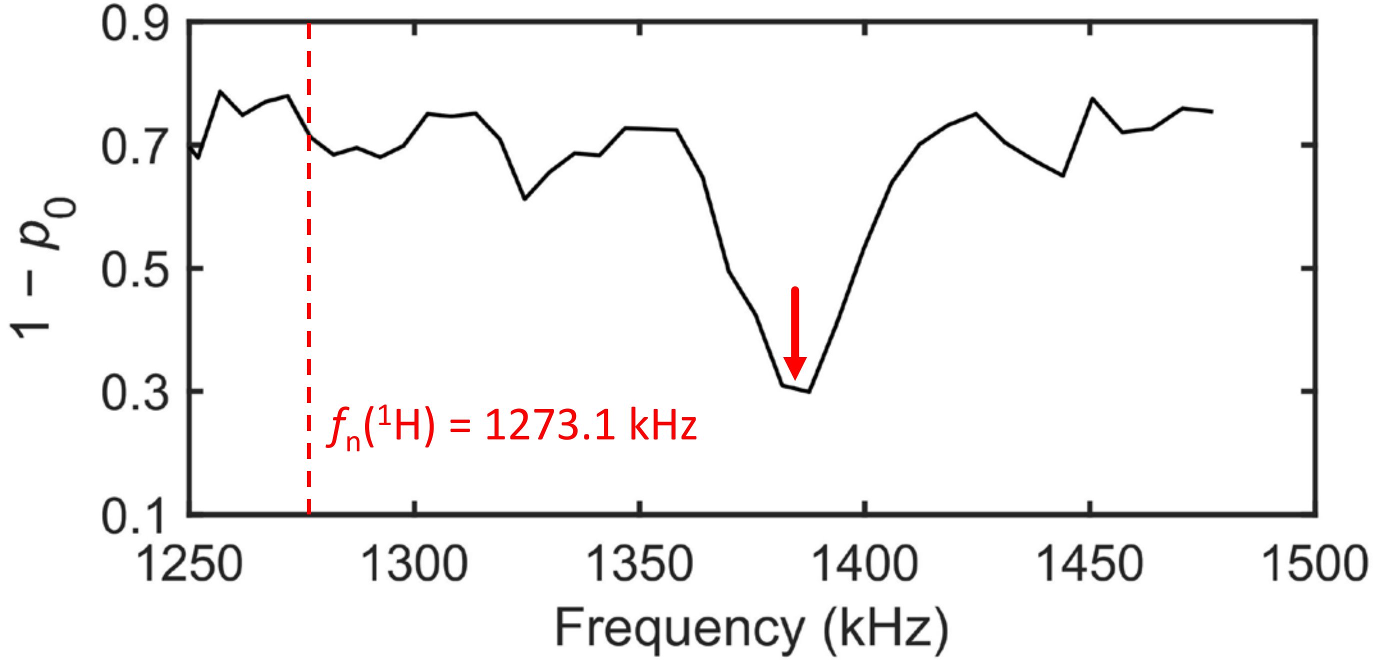


No decay up to 50 μs

Single ^{13}C nucleus

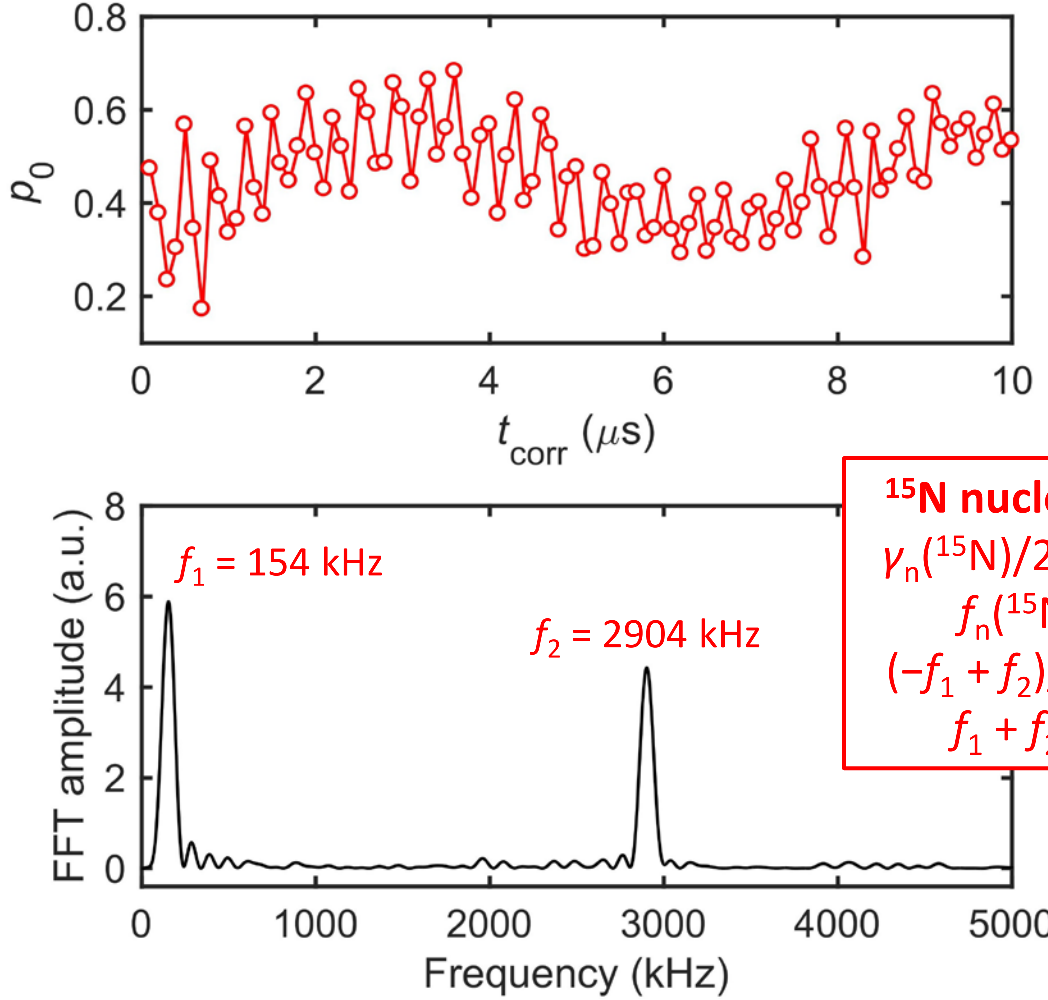
(315 + 419)/2 = 367 kHz → dip

Nuclear spin sensing



- XY16 (N = 64)
- B_0 = 29.9 mT, $\gamma_n(^1H)/2\pi$ = 42.577 kHz/mT
- Measurement time = 30 min

Correlation spectroscopy of nuclei



^{15}N nucleus of the NV itself

$\gamma_n(^{15}N)/2\pi = -4.316$ kHz/mT

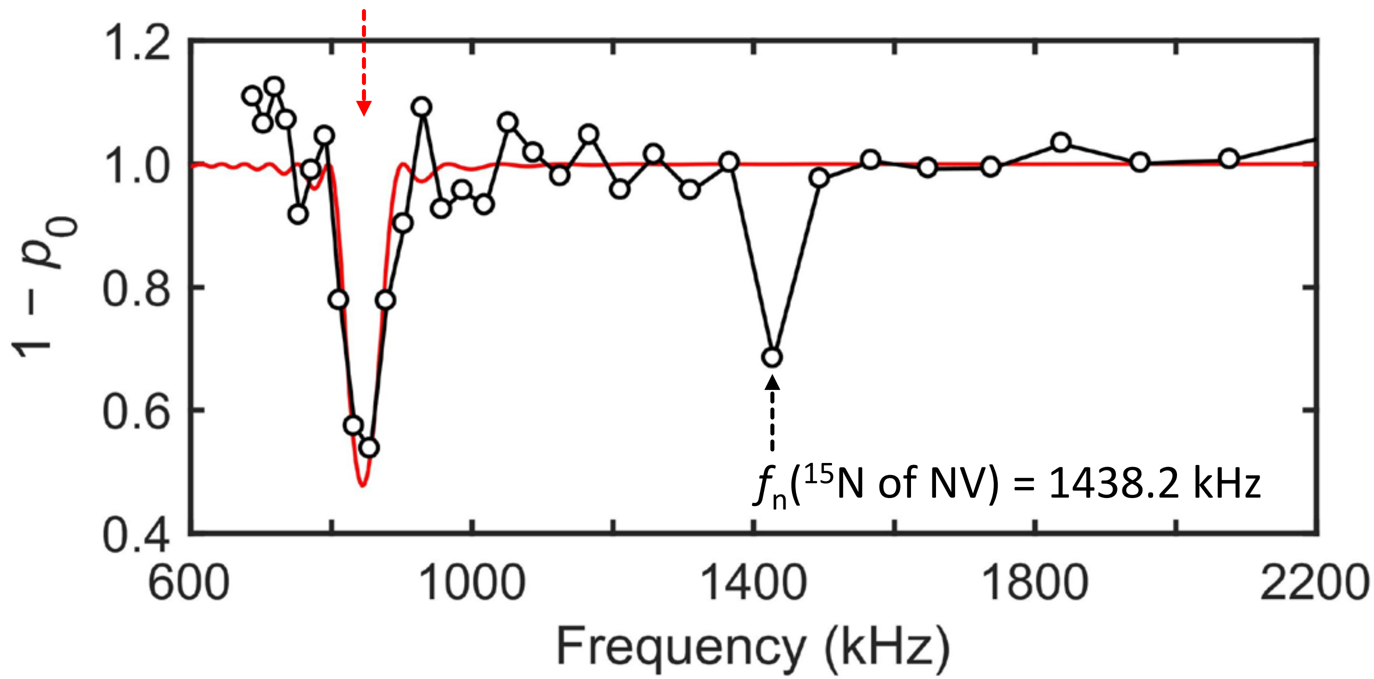
$f_n(^{15}N) = -129.05$ kHz

$(-f_1 + f_2)/2 = 1375$ kHz → dip

$f_1 + f_2 = 3.05$ MHz $= a_\parallel$

Nuclear spin sensing

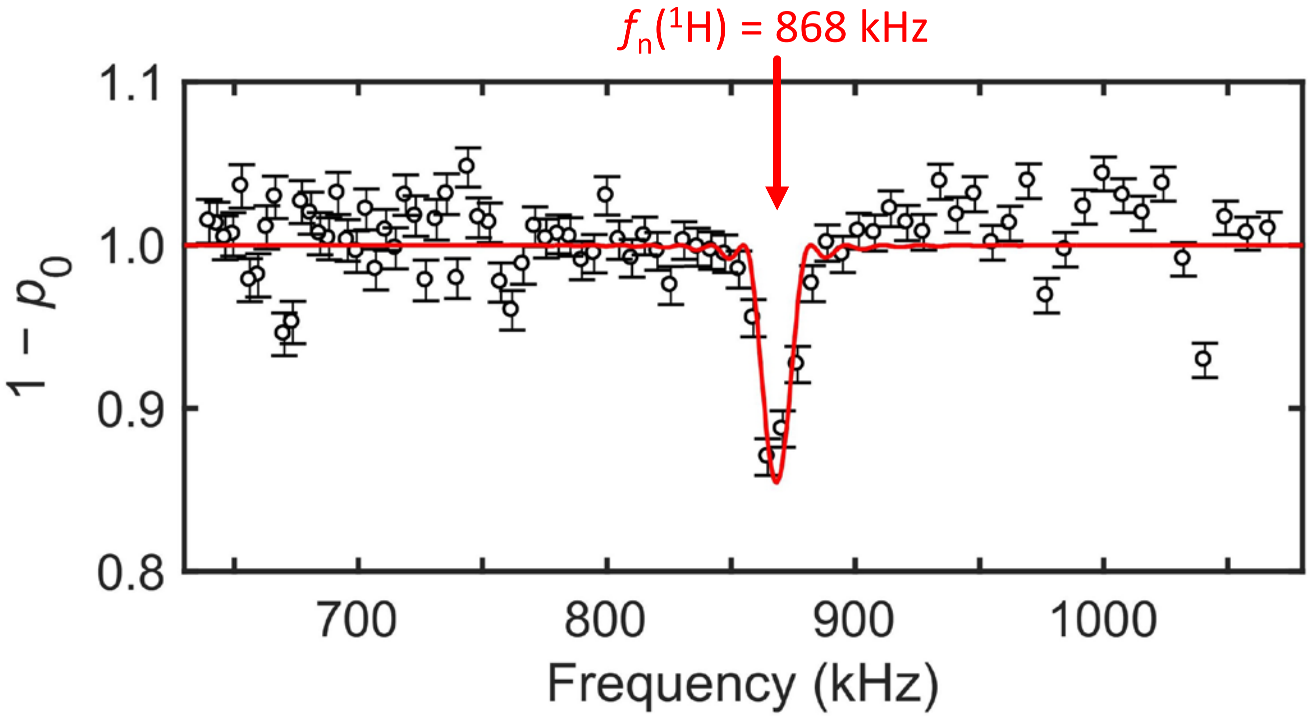
$f_n(^1H)$ = 855.80 kHz ↔ $f_n(^{13}C)$ **x 4** = 860.68 kHz (Spurious signal*)



- XY16 (N = 32), B_0 = 20.1 mT
- d_{NV} = 6.2 nm (Proton ensemble in oil)
- $f_n(^1H)/f_n(^{13}C)$ = 42.577/10.705 = 3.98

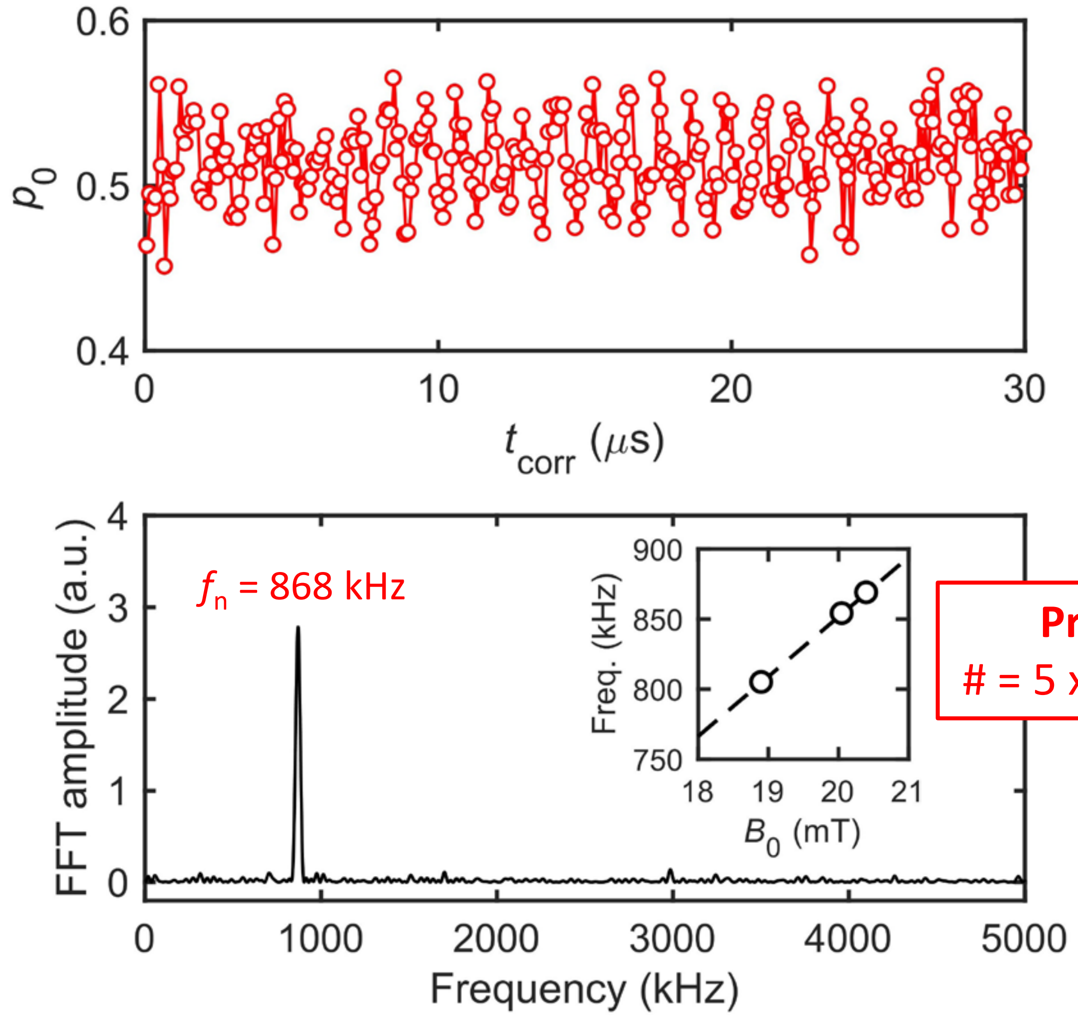
* Phys. Rev. X **5**, 021009 (2015) Loretz *et al.*

Nuclear spin sensing



- XY16 (N = 128), B_0 = 20.4 mT
- Measurement time = 0.5 day
- d_{NV} = 18 nm (Proton ensemble in oil)

Correlation spectroscopy of nuclei



Proton ensemble

= 5 x 10^6, V = 10–100 zL

AC magnetometry

- **"Seeing is NOT believing", "Appearances are deceiving"**
  - Careful analysis of the obtained spectra is necessary (especially when you look at a single nucleus)

- **Moderate spectral resolution**
  - Improved by correlation spectroscopy (T_{1e}) and/or using ^{15}N nuclear spin ($T_{2n/1n}$) as a memory, but
  - T_2 becomes shorter for shallower NV centers
  - Resolution required for chemical analysis is on the order of Hz (ppm)

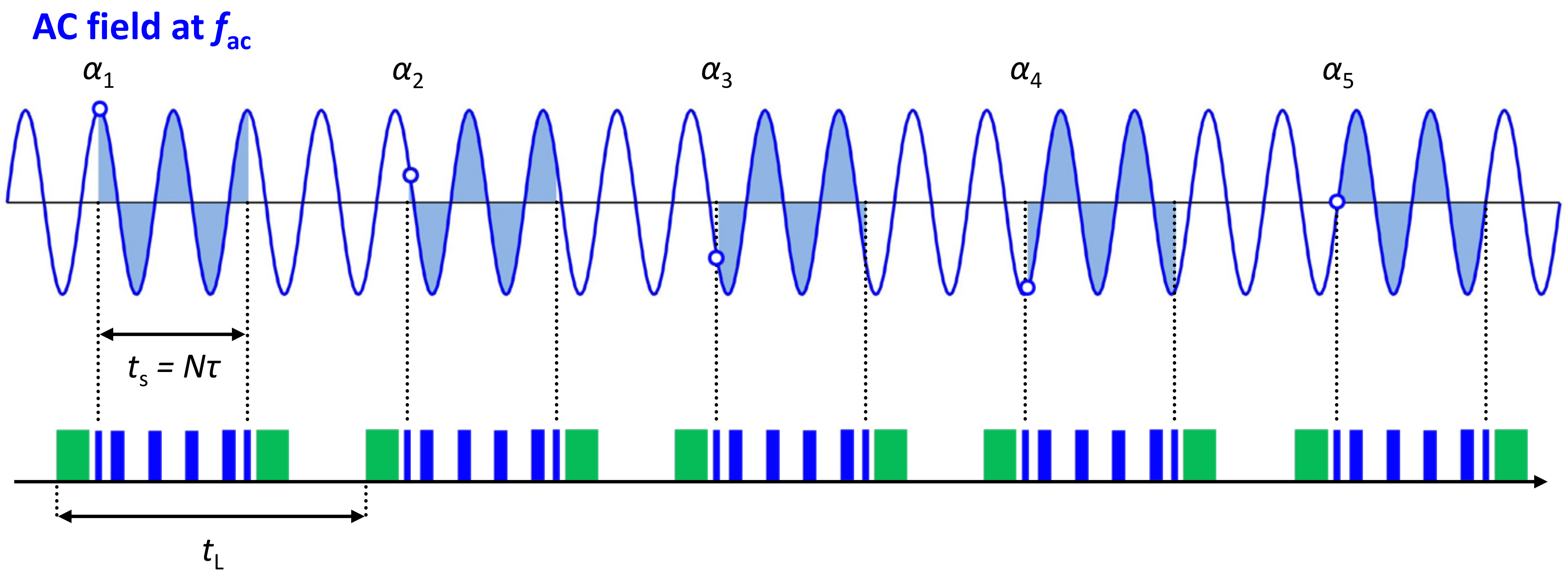
Ultrahigh resolution sensing

- **“Submillihertz magnetic spectroscopy performed with a nanoscale quantum sensor”**
  - Science **356**, 832 (2017) Schmitt *et al.* (Jelezko, Ulm)
  - → *Quantum heterodyne (Qdyne)*

- **“Quantum sensing with arbitrary frequency resolution”**
  - Science **356**, 837 (2017) Boss *et al.* (Degen, ETH)
  - → *Continuous sampling*

- **“High Resolution Magnetic Resonance Spectroscopy Using Solid-State Spins”**
  - arXiv:1705.08887 Bucher *et al.* (Walsworth, Harvard)
  - → *Synchronized readout*

Ultrahigh resolution sensing

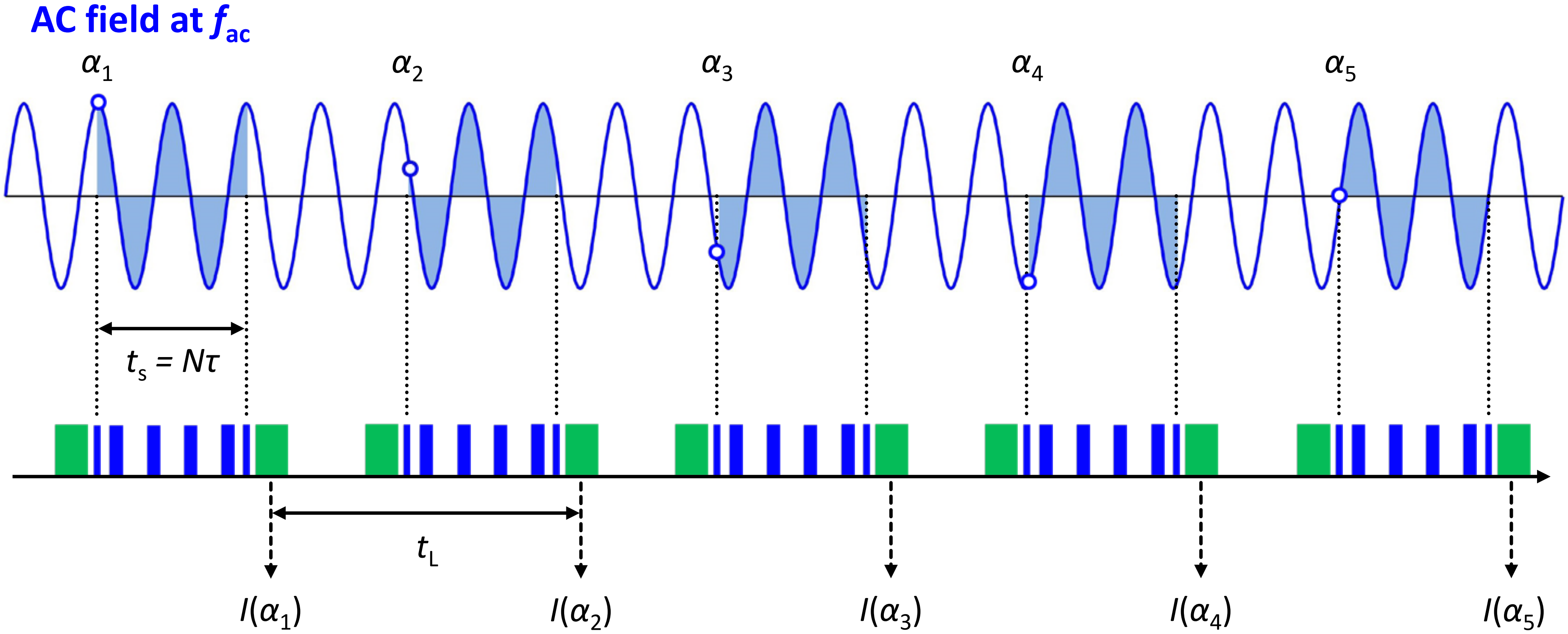


Sensing sequence ($\tau \approx 1/2f_{ac}$ & t_L-periodic)

$$\varphi_k = \frac{2\gamma B_{ac} t_s}{\pi} \cos \alpha_k \qquad \alpha_{k+1} = 2\pi f_{ac} t_L + \alpha_k$$

Science **356**, 832 (2017) Schmitt *et al.*
Science **356**, 837 (2017) Boss *et al.*
arXiv:1705.08887 Bucher *et al.*

Ultrahigh resolution sensing



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Science **356**, 832 (2017) Schmitt *et al.*
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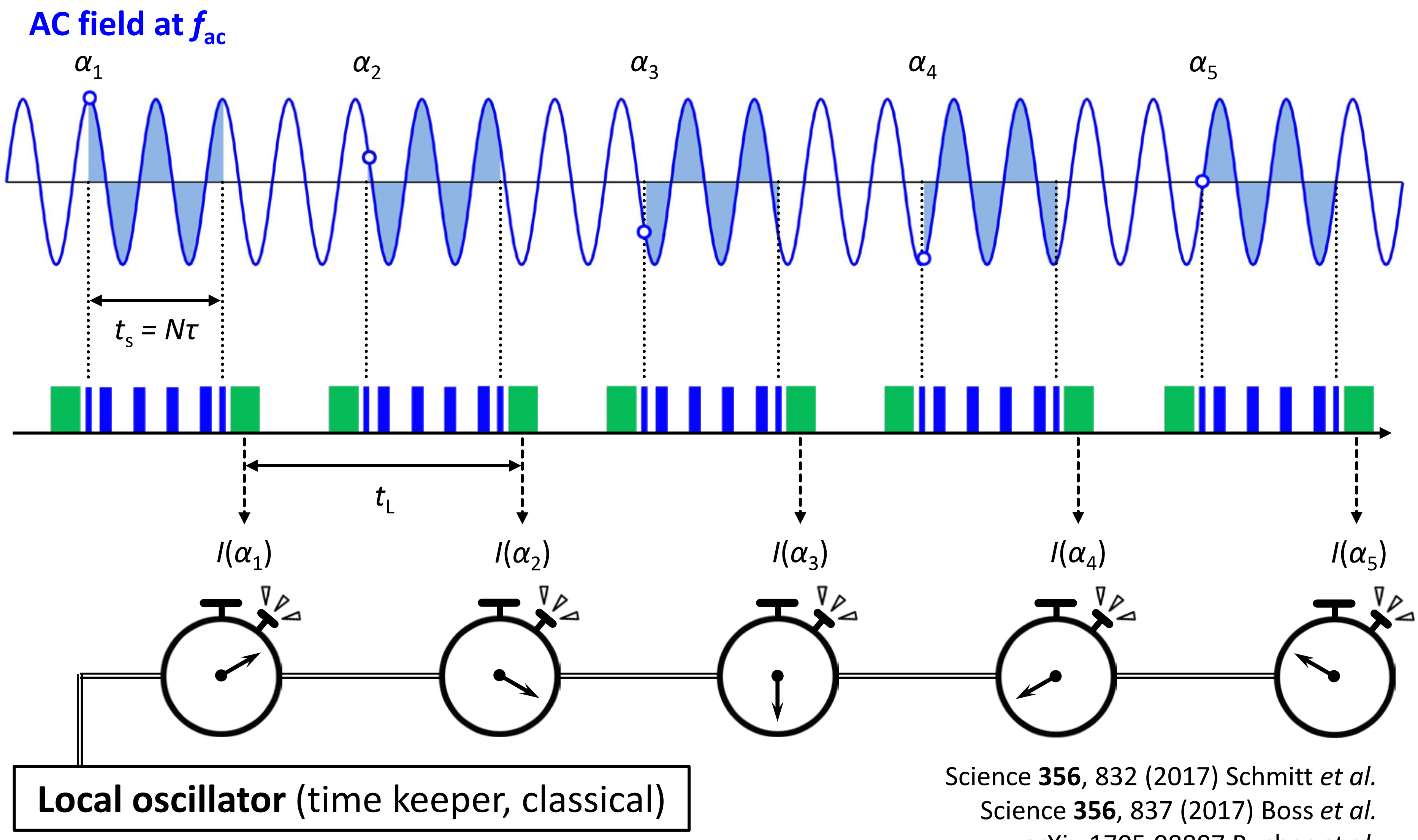
Ultrahigh resolution sensing



Science **356**, 832 (2017) Schmitt *et al.*
Science **356**, 837 (2017) Boss *et al.*
arXiv:1705.08887 Bucher *et al.*

Ultrahigh resolution sensing

Data obtained after many runs with time tagging

$$I \approx \sum_n \frac{B_{\mathrm{ac}} t_s}{\pi} \cos[2\pi(f_{\mathrm{ac}} - f_{\mathrm{LO}}) n t_L + \phi_0]$$

⇨ **FFT gives f_{ac} relative to f_{LO} (= e.g., 1/t_L)**

- The sensor works as a mixer for quantum & classical signals
  → *Quantum hetrodyne*

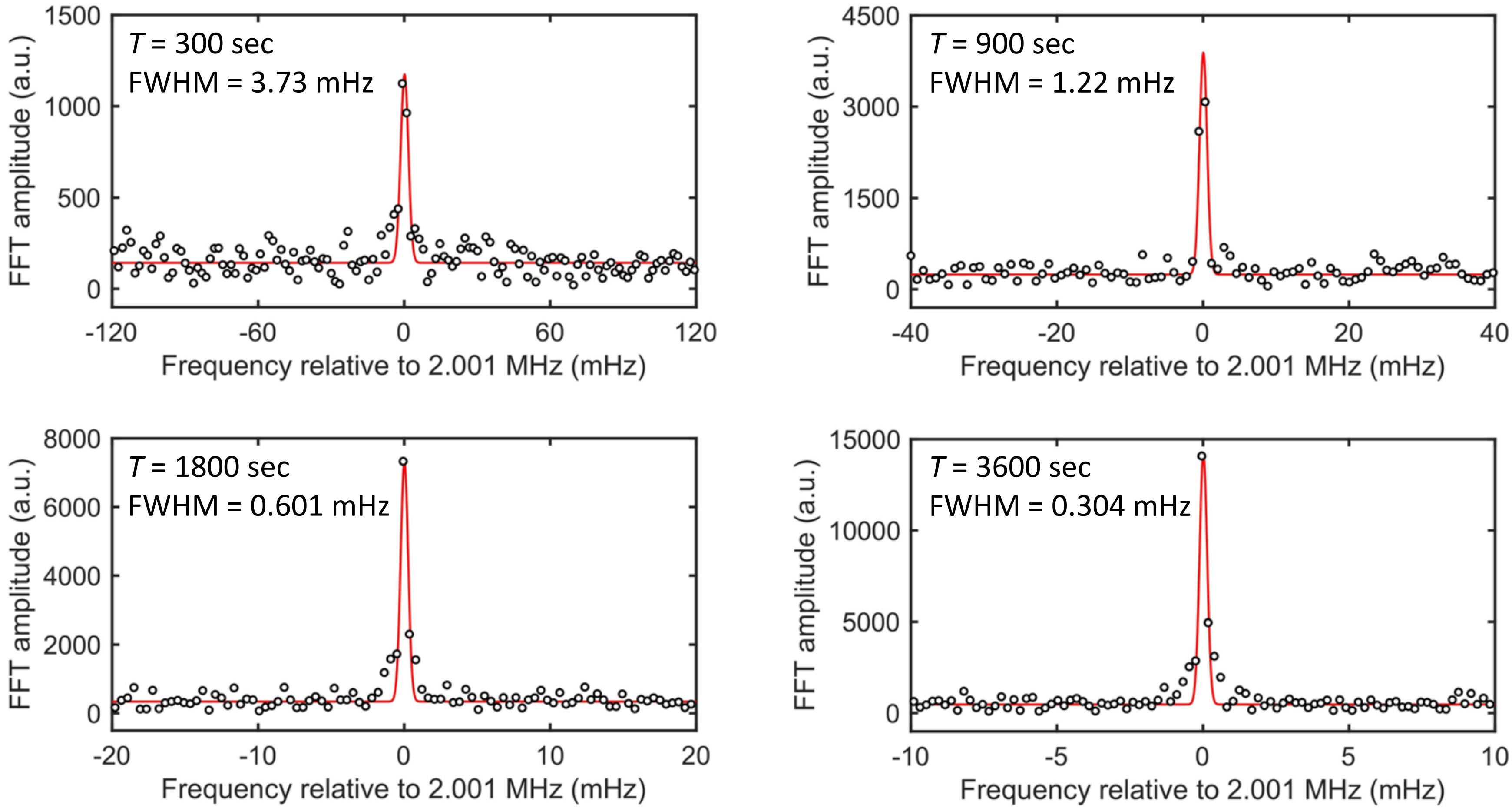
- The whole measurement can be regarded as a single measurement
  → *Continuous sampling*

- Readout outcomes are time-tagged
  → *Synchronized readout*

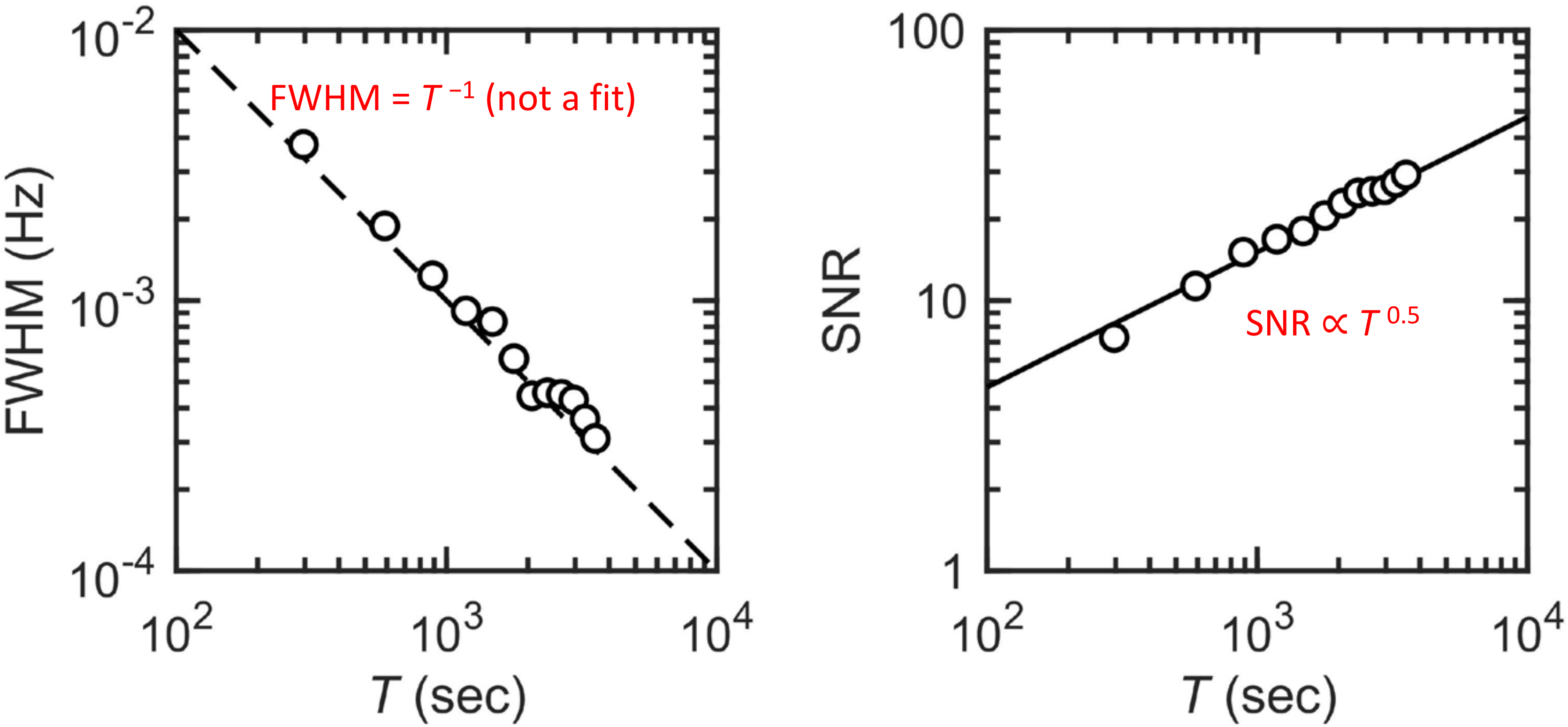
Science **356**, 832 (2017) Schmitt *et al.*
Science **356**, 837 (2017) Boss *et al.*
arXiv:1705.08887 Bucher *et al.*

Ultrahigh resolution sensing

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



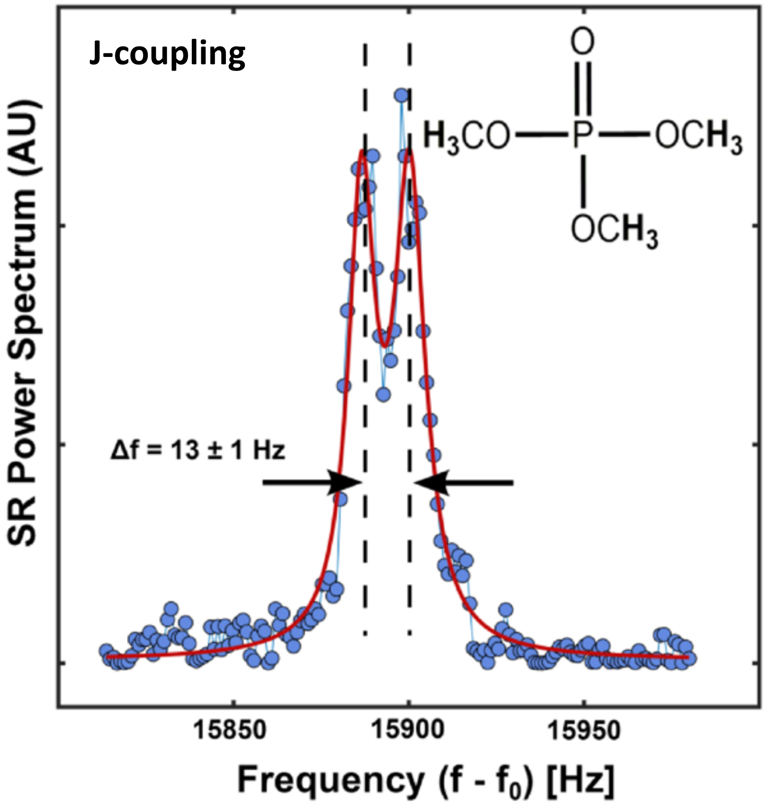
Ultrahigh resolution sensing

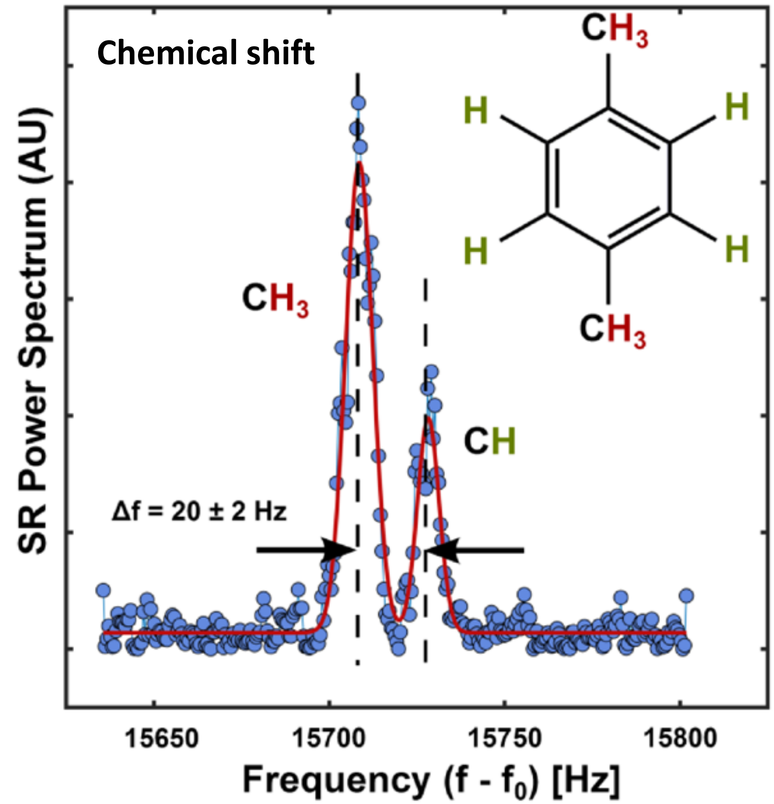


- Spectral resolution not limited by sensor/memory lifetimes ($T_{2e/n}$, $T_{1e/n}$)
- Only limited by the stability of LO (essentially infinite)
- Resolution = T^{-1} & SNR $\propto T^{0.5} \rightarrow$ Precision $\propto T^{-1.5}$

Ultrahigh resolution sensing

(Data from Harvard: arXiv:1705.08887 Bucher *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

- **NV centers in diamond**
  - The basic properties are well-understood, but there still remain many challenges in materials science such as how to create near-surface NV centers with high spin coherence, and how to control the direction of the NV axis out of possible four.

- **AC magnetometry**
  - We have now basic tools to achieve high AC magnetic field sensitivities and resolutions in the laboratory, and are moving toward the goal of bringing these technologies into real and practical applications (but of course, we anticipate many scientific surprises along the way).

Tutorial article to appear in ***J. Appl. Phys.***
arXiv.1802.07857 Abe *et al.*