

Quantum Spintronics Design (NV centers in diamond)

Eisuke Abe

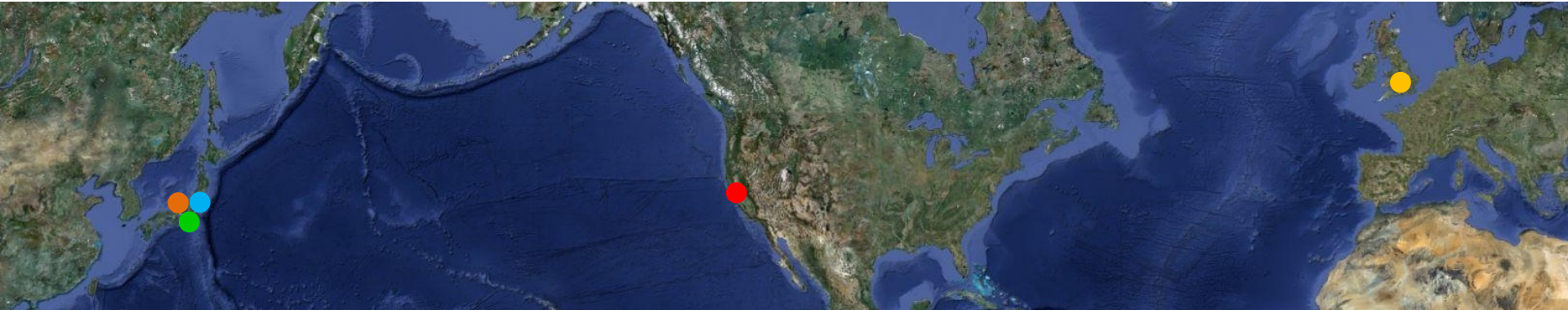
RIKEN Center for Emergent Matter Science

2020.02.19

CMD Spintronics Design Course
@Osaka University



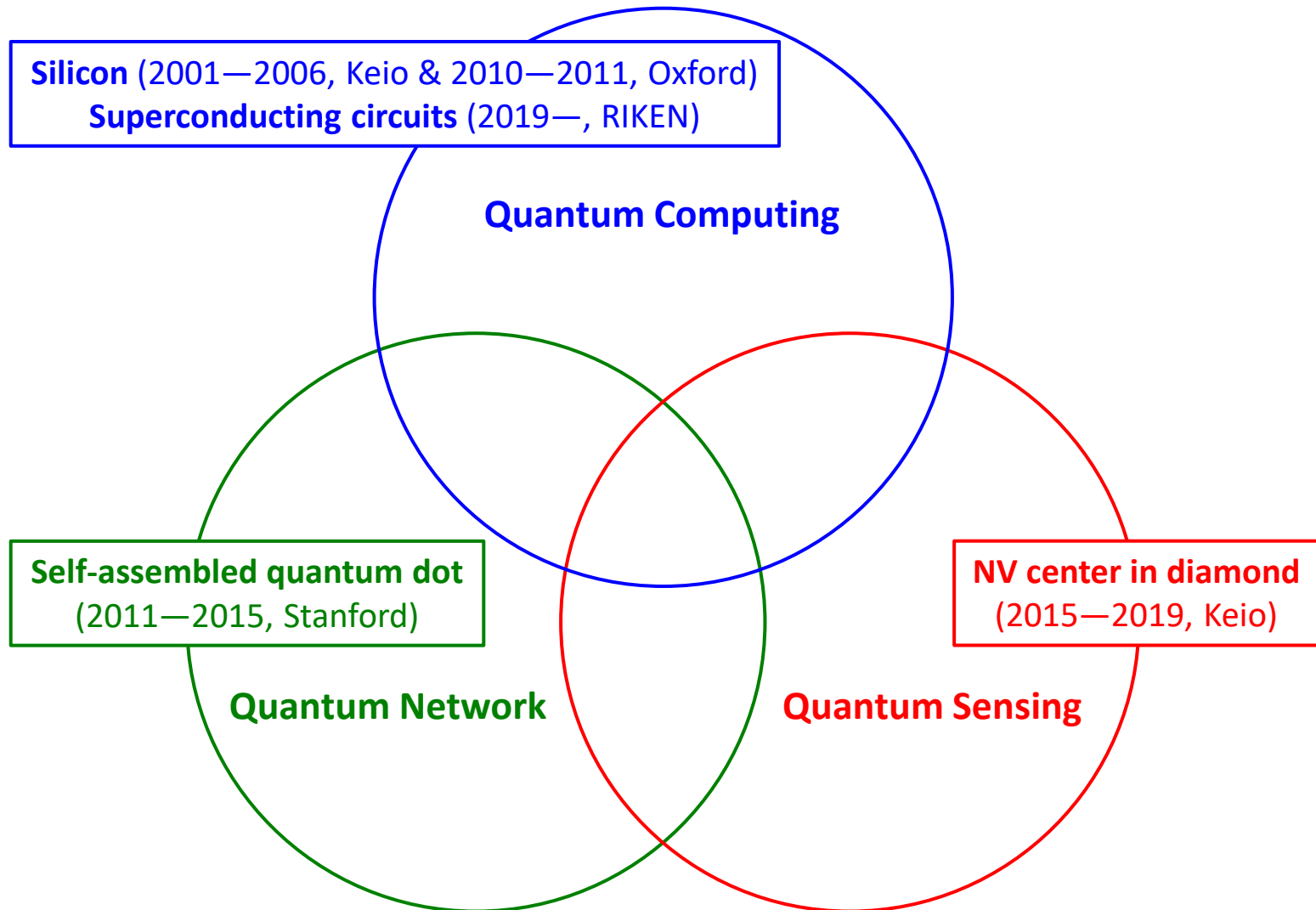
Short CV



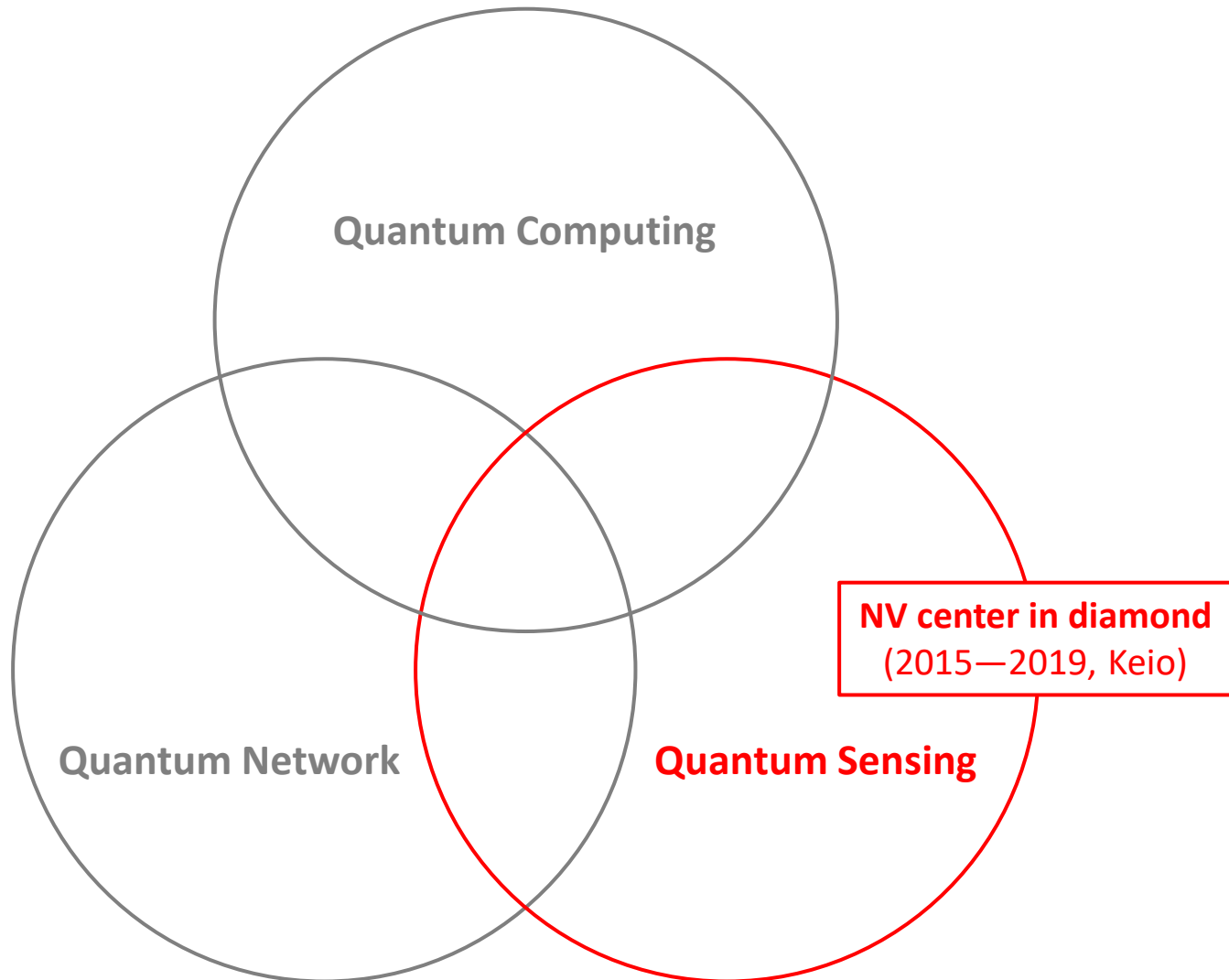
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- **2001.4 – 2006.3 (Keio)** → Quantum computing (silicon)
- **2006.4 – 2009.12 (ISSP, UT)** → Quantum transport (GaAs QDs, Josephson)
- **2010.1 – 2011.6 (Oxford)** → Hybrid system (spin–cavity coupling)
- **2011.7 – 2015.3 (Stanford/RIKEN)** → Quantum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

Quantum technologies



Quantum technologies



Outline

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

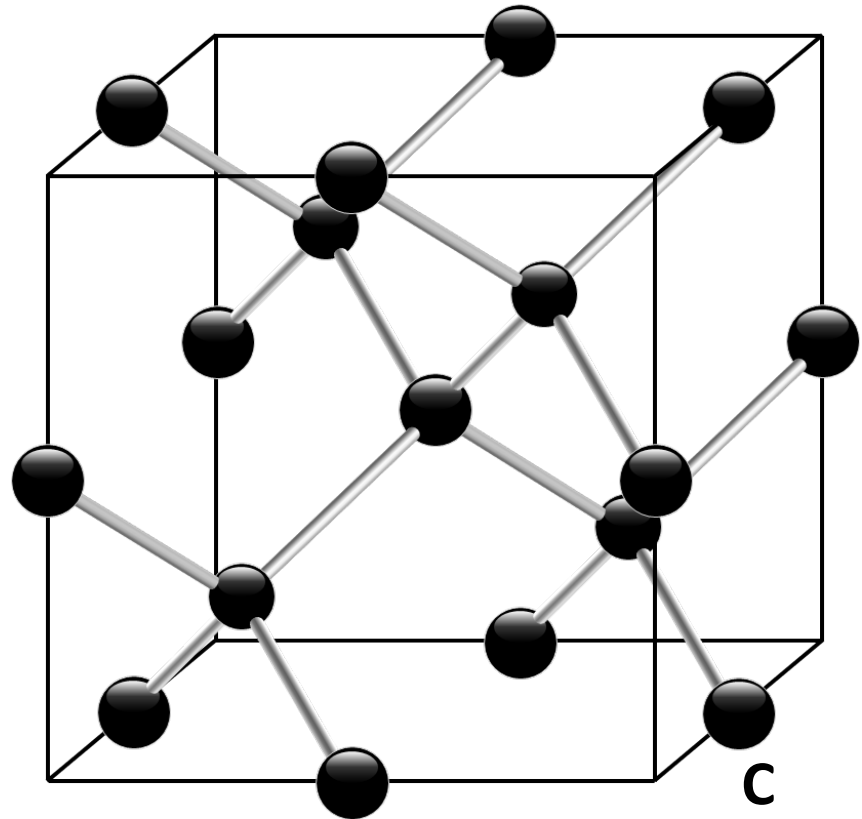
Outline

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Diamond envy



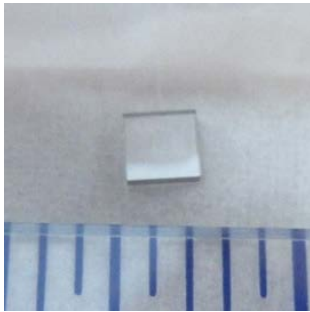
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$$\rho_N = 1.77 \times 10^{23} \text{ cm}^{-3}$$

Diamond NV

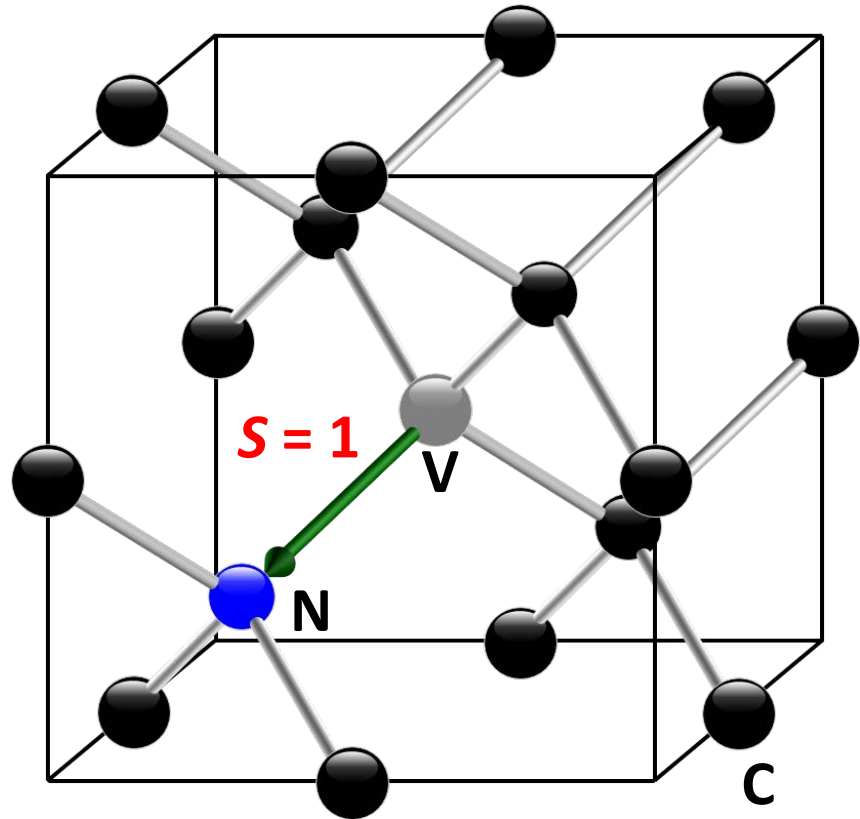
Synthetic (CVD) diamond
2² x 0.5 mm³, \$700 (E6)
[N] < 5 ppb, [NV] < 0.03 ppb



Not like...



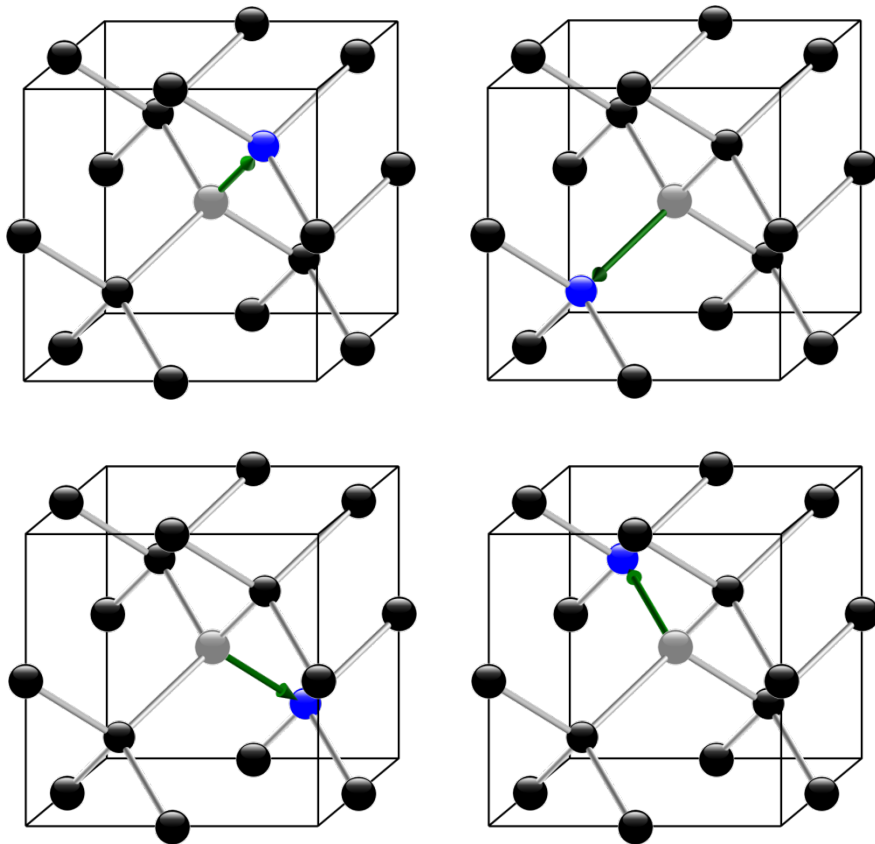
©GIA



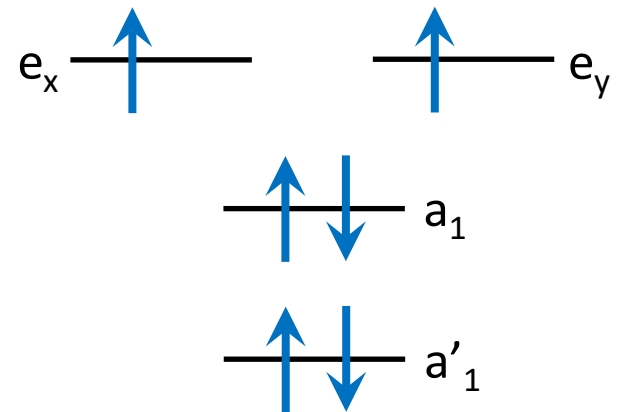
$$\rho_N = 1.77 \times 10^{23} \text{ cm}^{-3}$$

Crystal & energy level structures

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

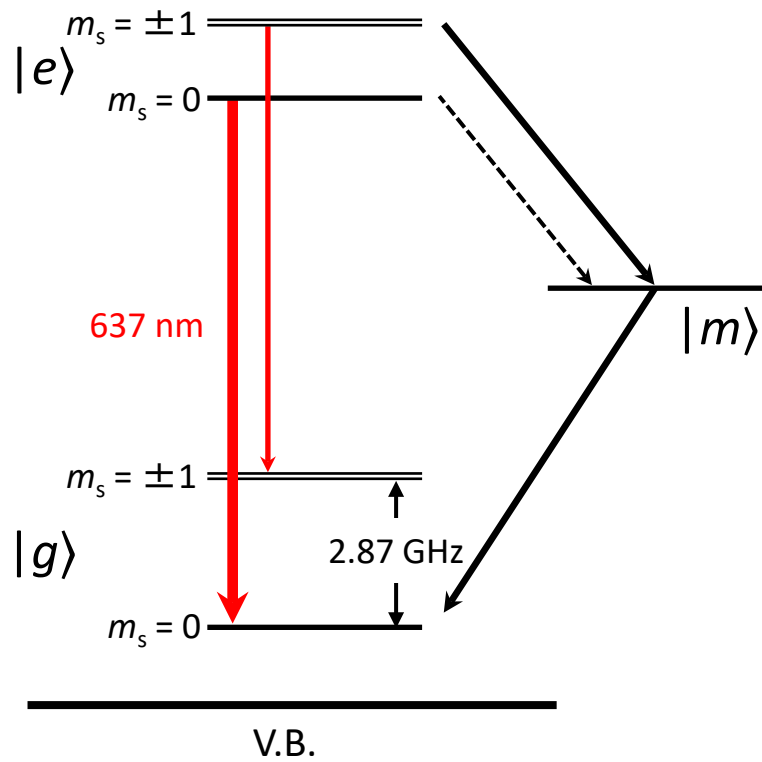


Effective spin-1 system
(e^2 -hole spin-triplet)

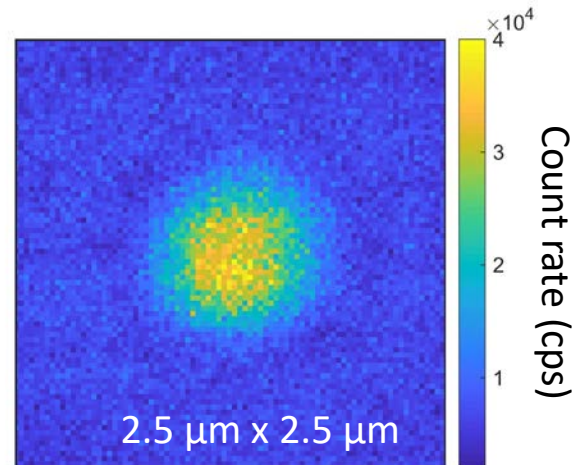
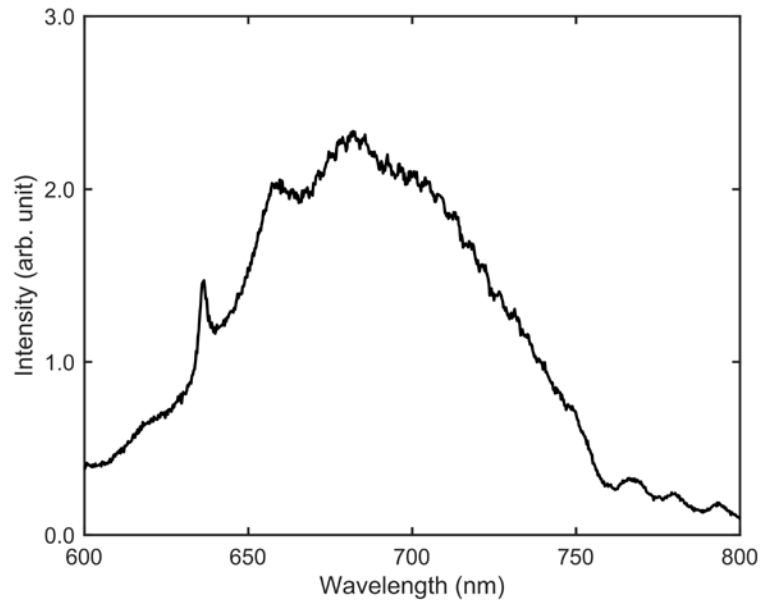
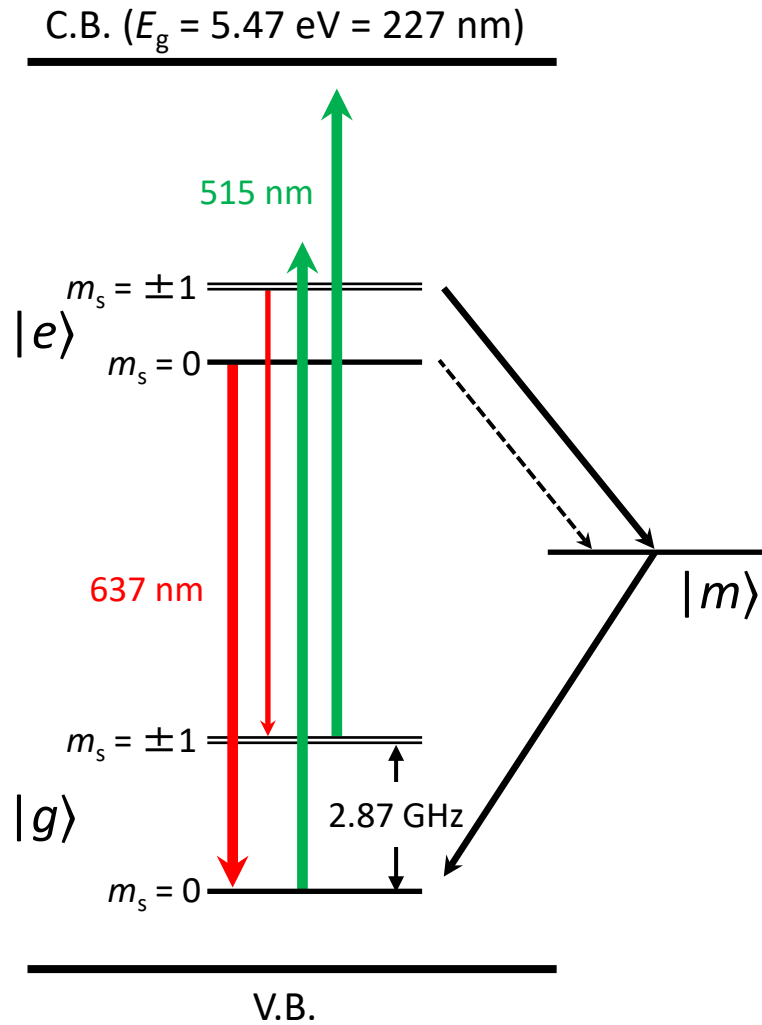


Energy levels

C.B. ($E_g = 5.47 \text{ eV} = 227 \text{ nm}$)

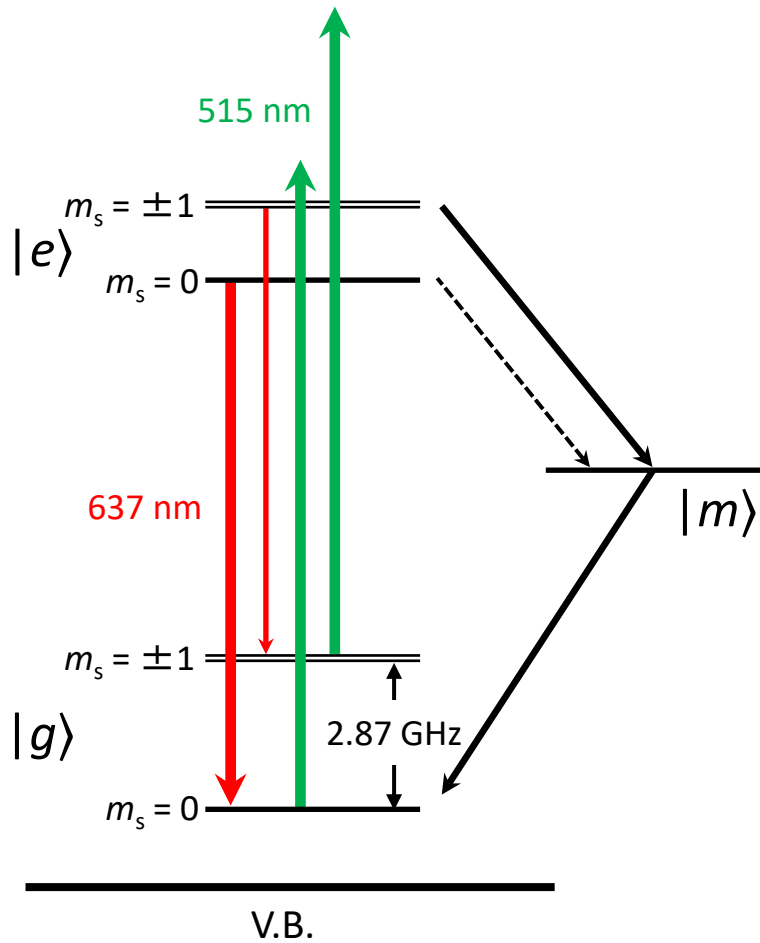


PL spectroscopy & imaging

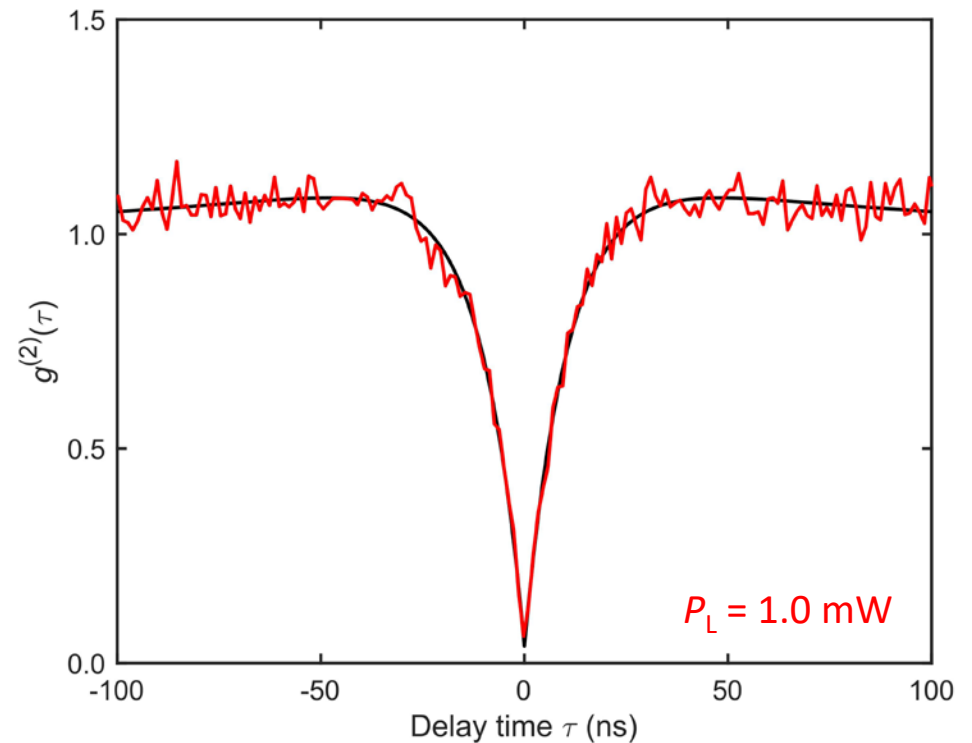


Photon statistics

C.B. ($E_g = 5.47 \text{ eV} = 227 \text{ nm}$)



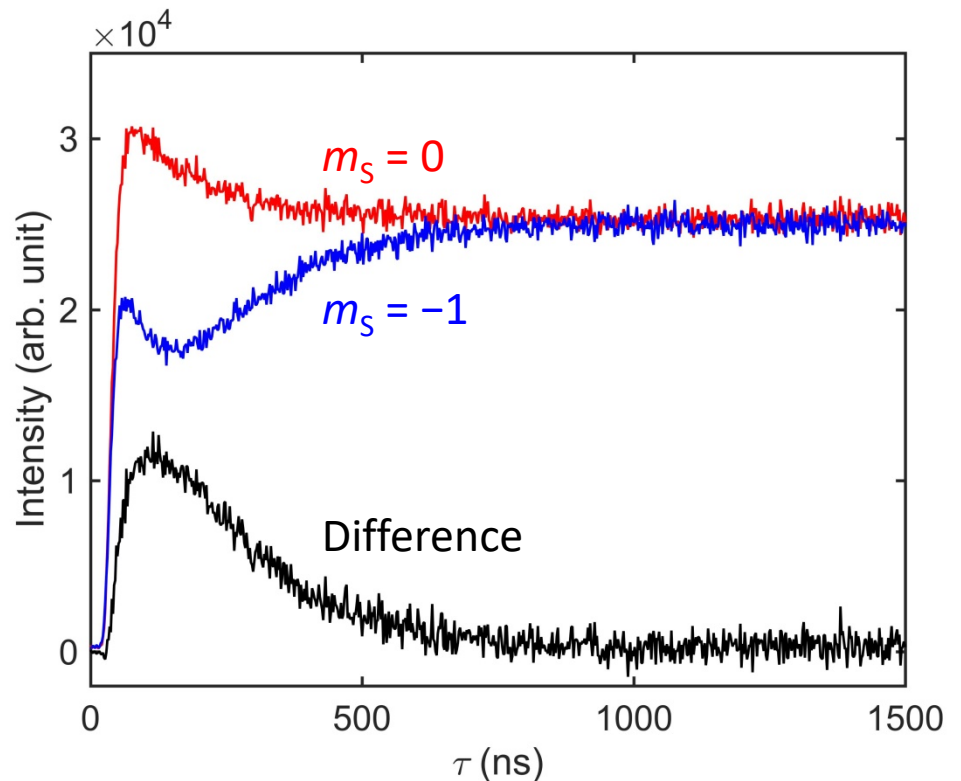
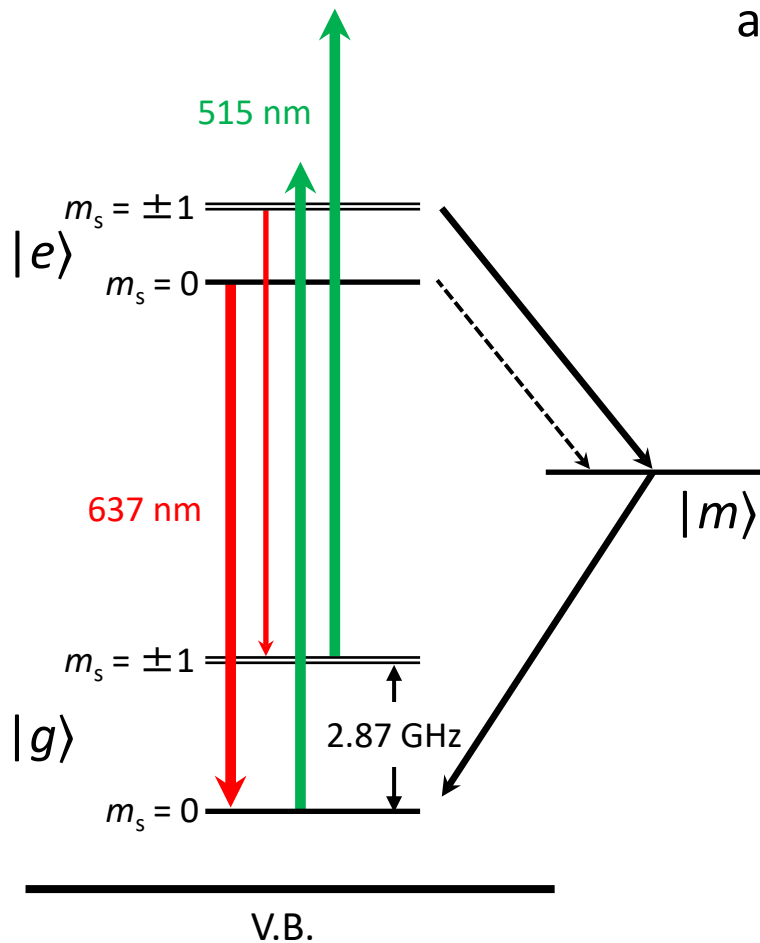
One photon at a time



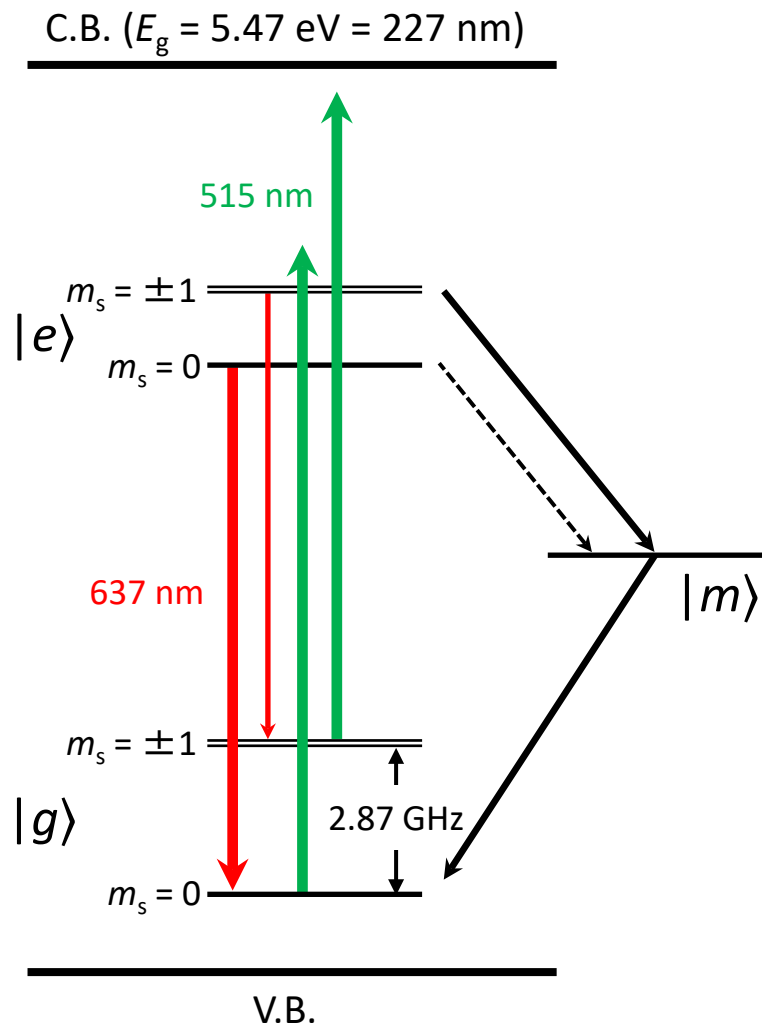
Time-resolved fluorescence

C.B. ($E_g = 5.47 \text{ eV} = 227 \text{ nm}$)

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

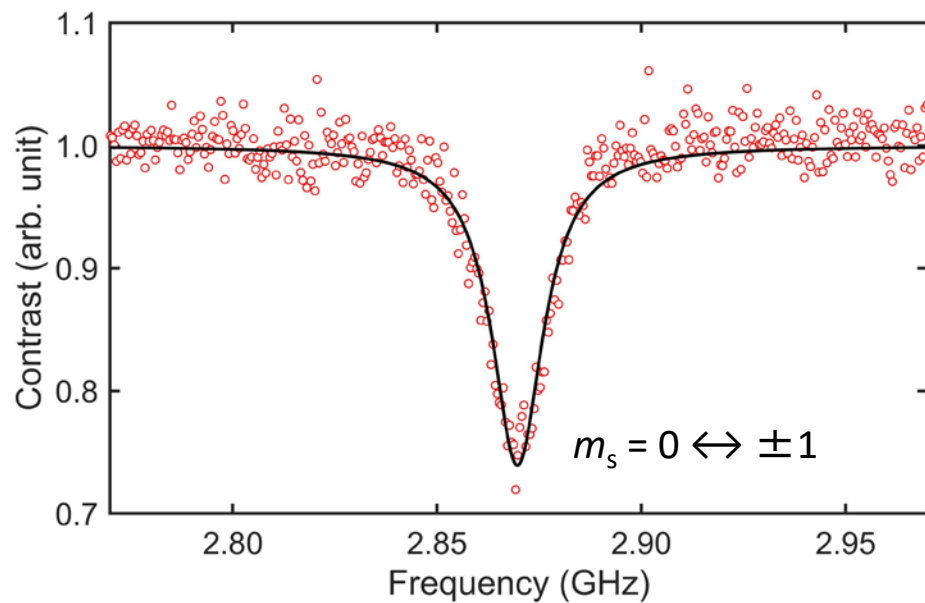


CW ODMR at $B_0 = 0$



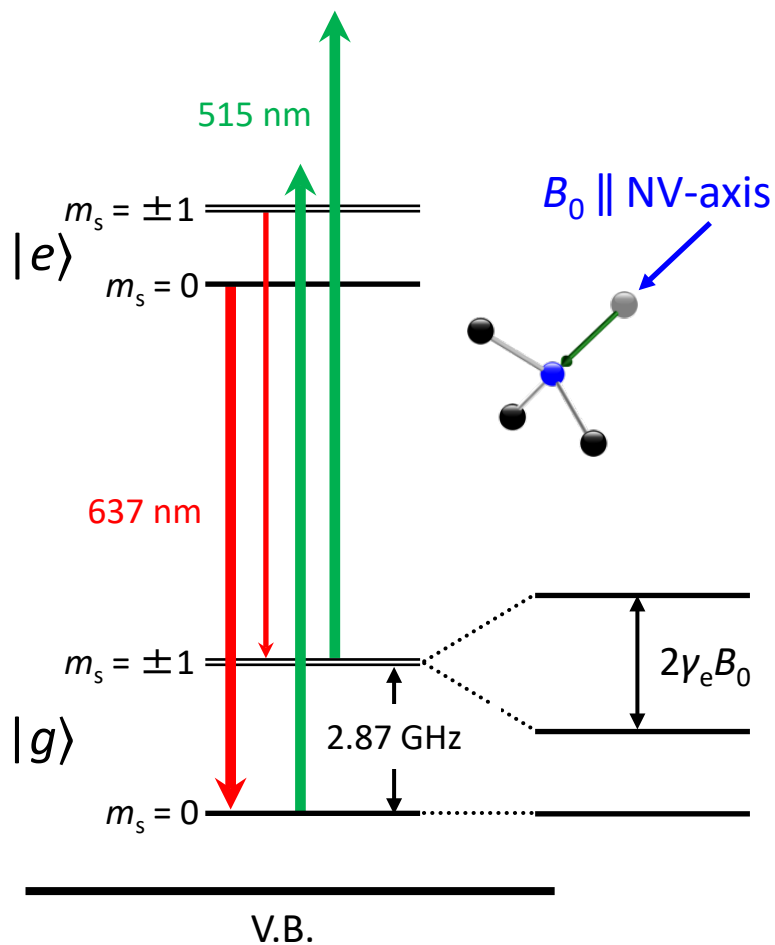
Zero-field splitting $H = DS_Z^2$

$$D = 2.87 \text{ GHz}$$



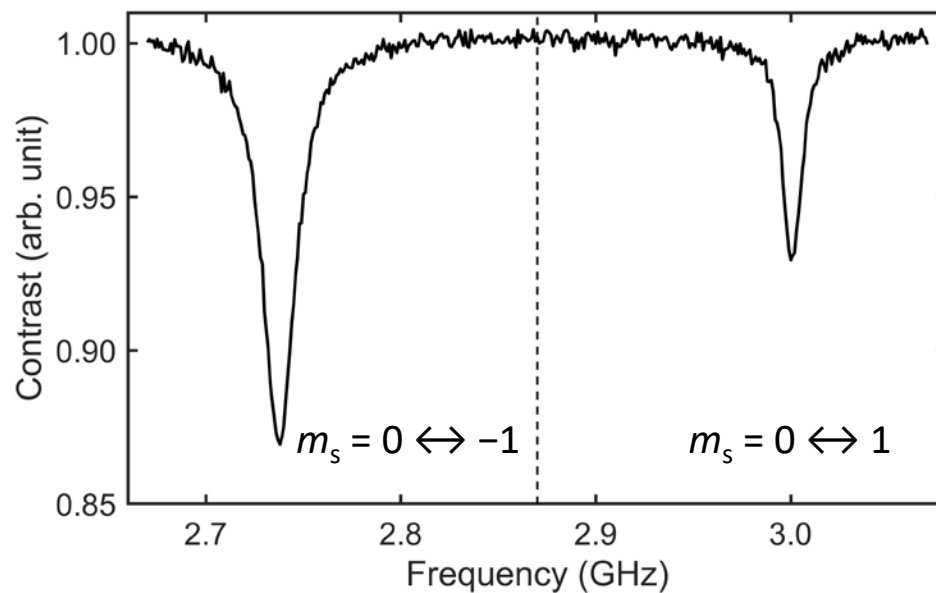
CW ODMR at $B_0 > 0$

C.B. ($E_g = 5.47 \text{ eV} = 227 \text{ nm}$)



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

$$\gamma_e = 28 \text{ MHz/mT}$$



$$B_0 = 4.7 \text{ mT } (2.87 \pm 0.132 \text{ GHz})$$

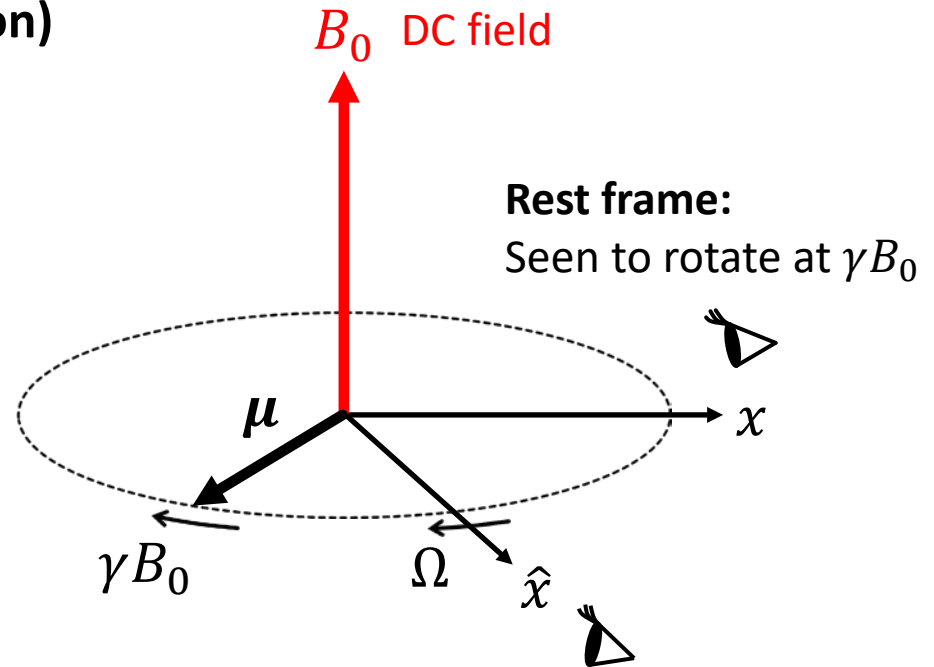
Magnetic resonance

Torque equation (Larmor precession)

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

Gyromagnetic ratio

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



Rest frame:

Seen to rotate at γB_0

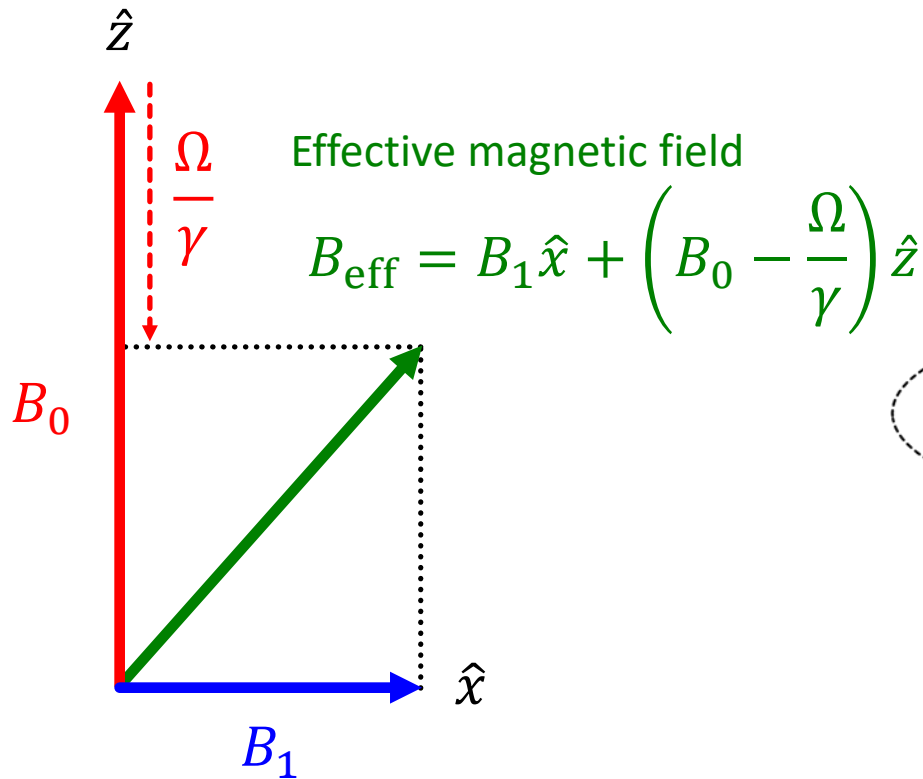
Frame rotating at angular velocity Ω :

Rotate slower...why?

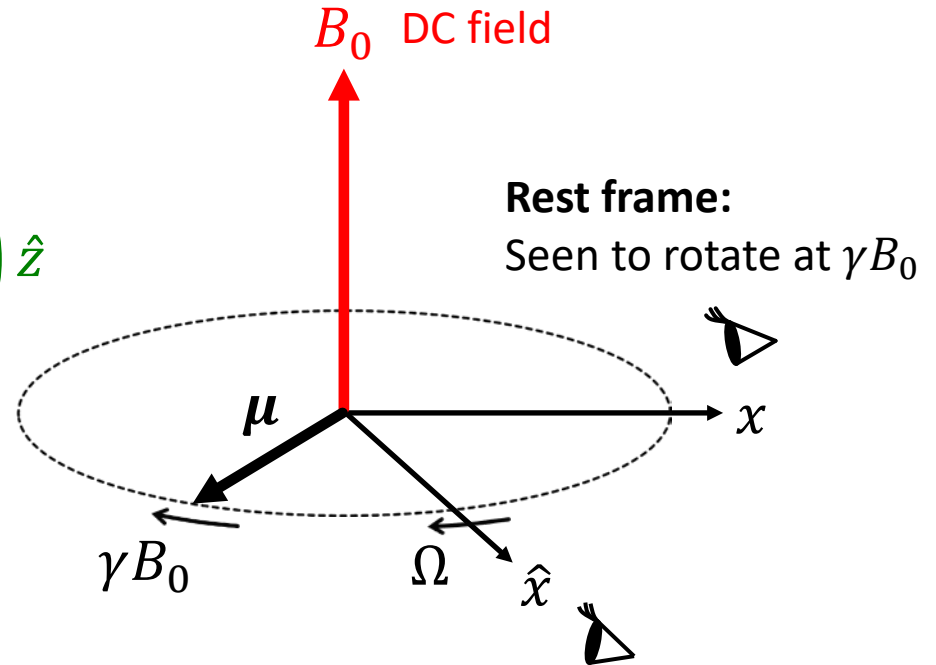


DC field along the z direction becomes weaker

Magnetic resonance



AC field rotating in the xy plane at Ω



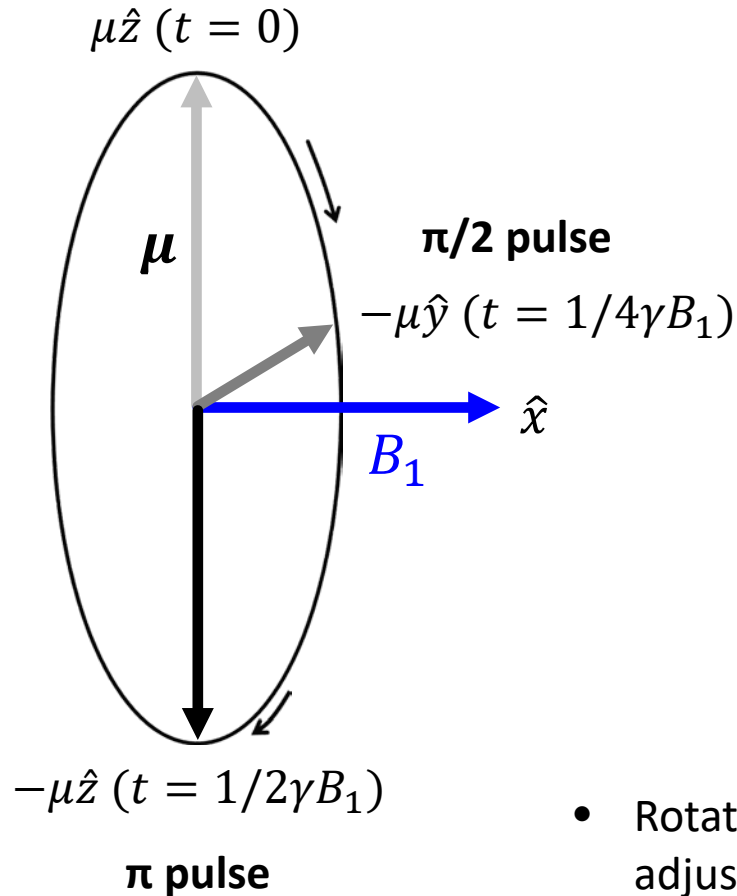
Frame rotating at angular velocity Ω :
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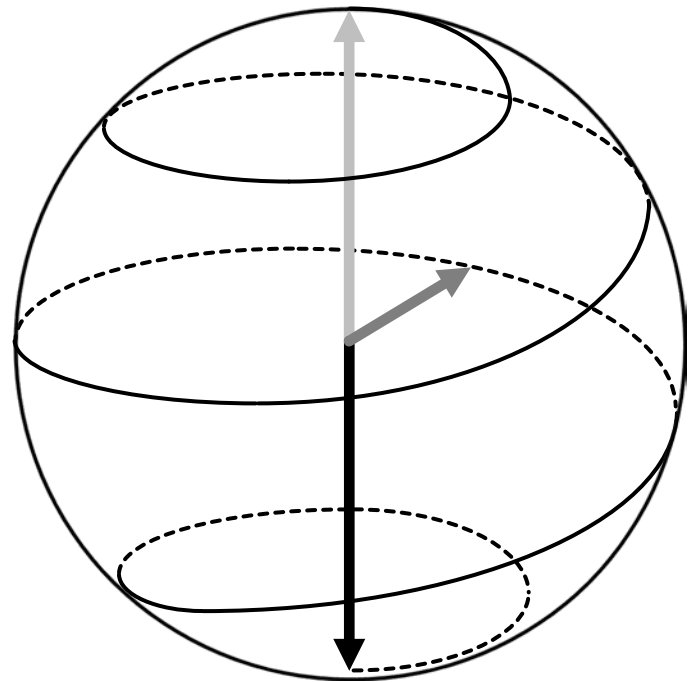
DC field along the z direction becomes weaker

Magnetic resonance

Frame rotating at $\Omega = \gamma B_0$



Rest (non-resonant) frame



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

Quantum bit

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

Superposition state

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

$$|\psi\rangle = \alpha|0\rangle + \beta|1\rangle$$

$$|\alpha|^2 + |\beta|^2 = 1$$



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

Global phase

$$0 \leq \theta \leq \pi$$

$$0 \leq \gamma, \phi < 2\pi$$



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

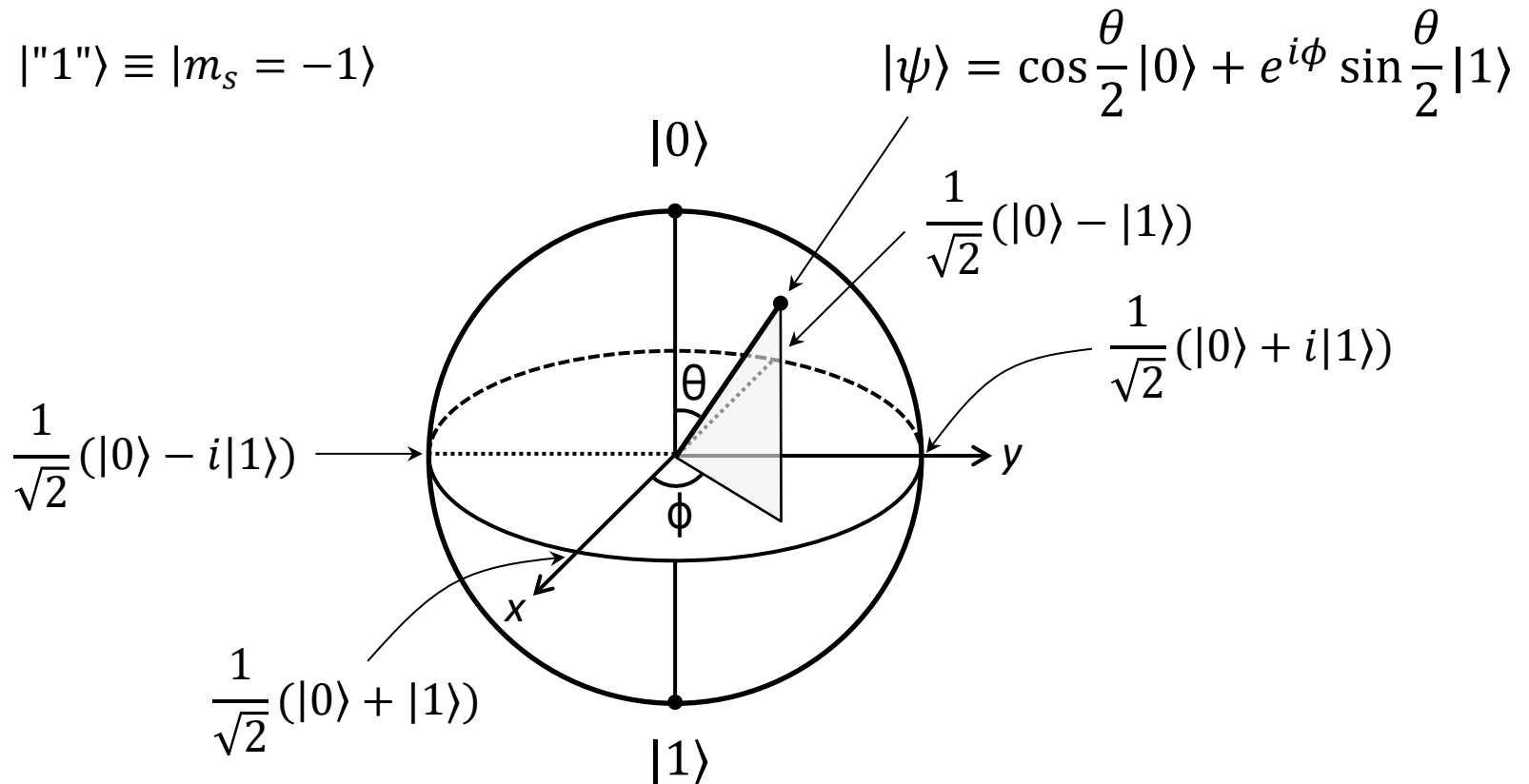
$$0 \leq \theta \leq \pi$$

$$0 \leq \phi < 2\pi$$

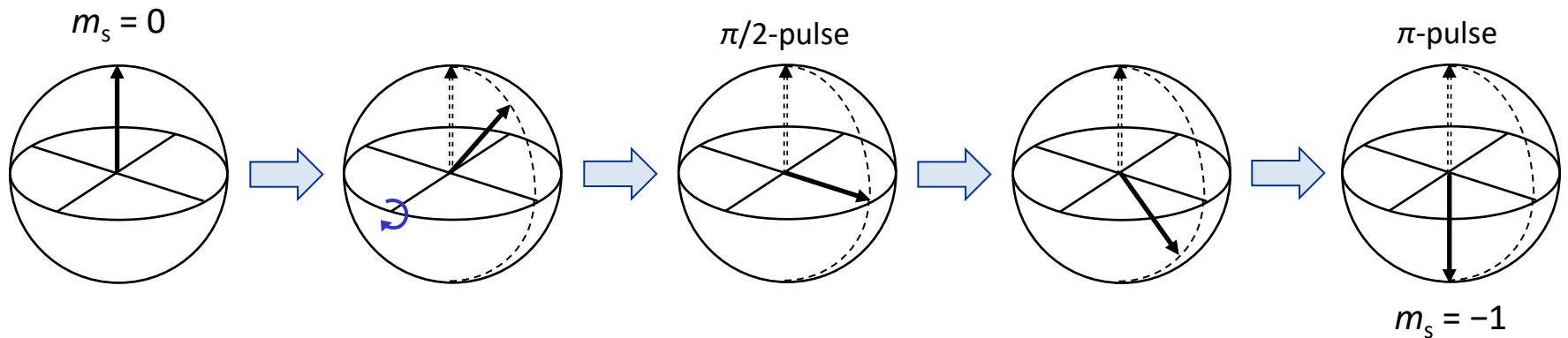
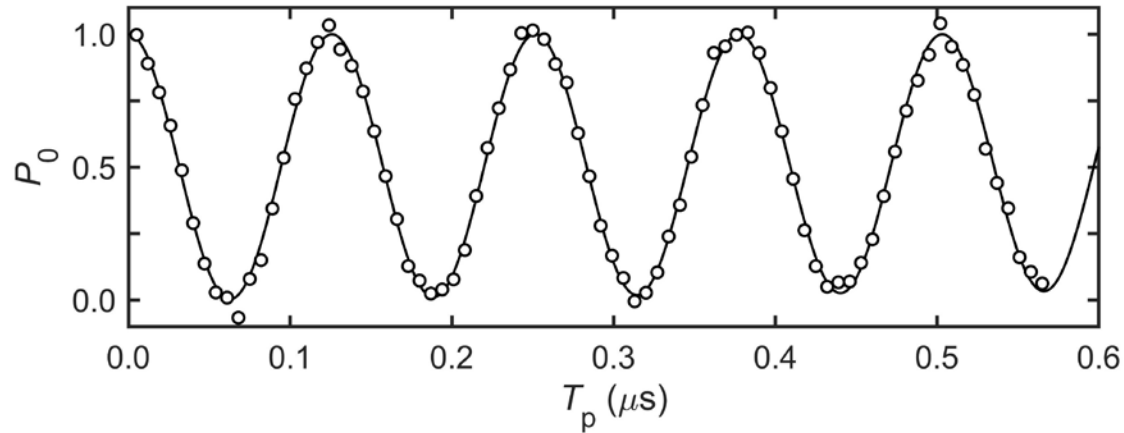
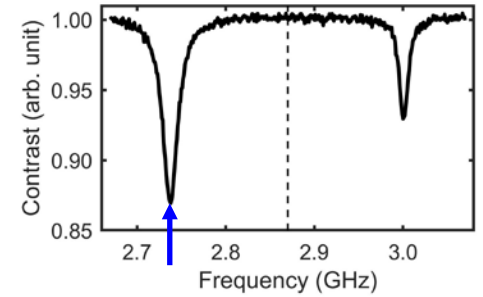
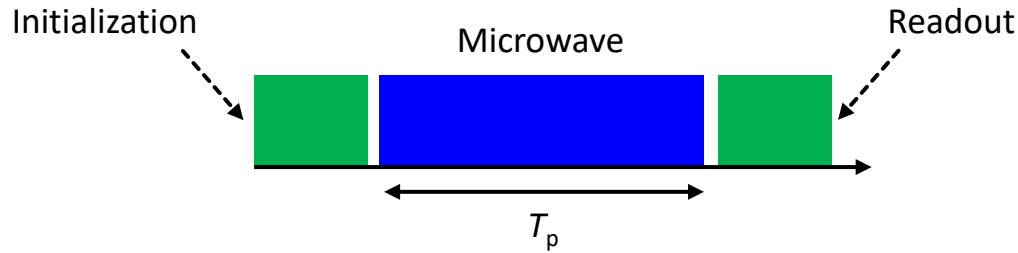
Bloch sphere

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

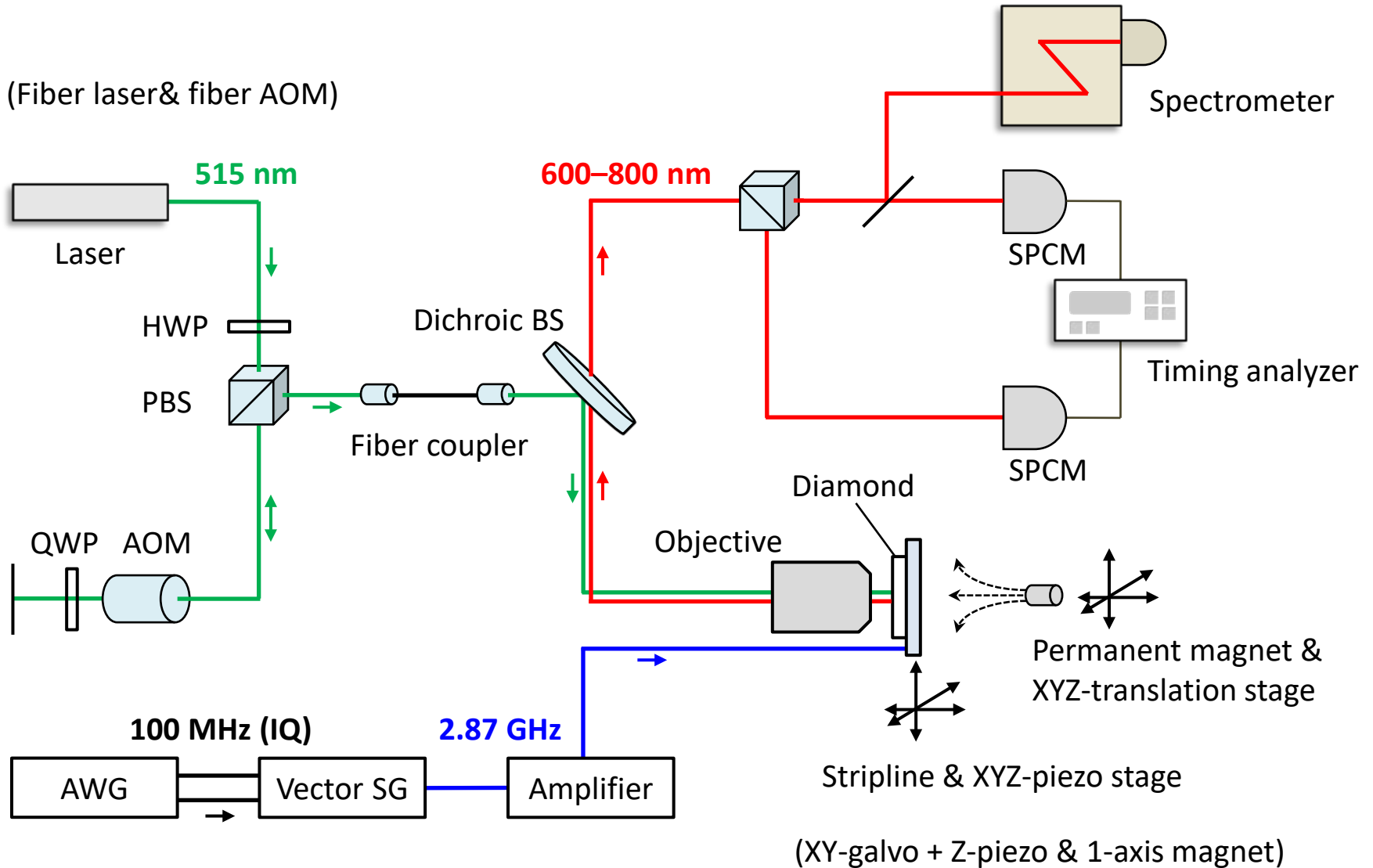
$$\begin{cases} |"0"> \equiv |m_s = 0> \\ |"1"> \equiv |m_s = -1> \end{cases}$$



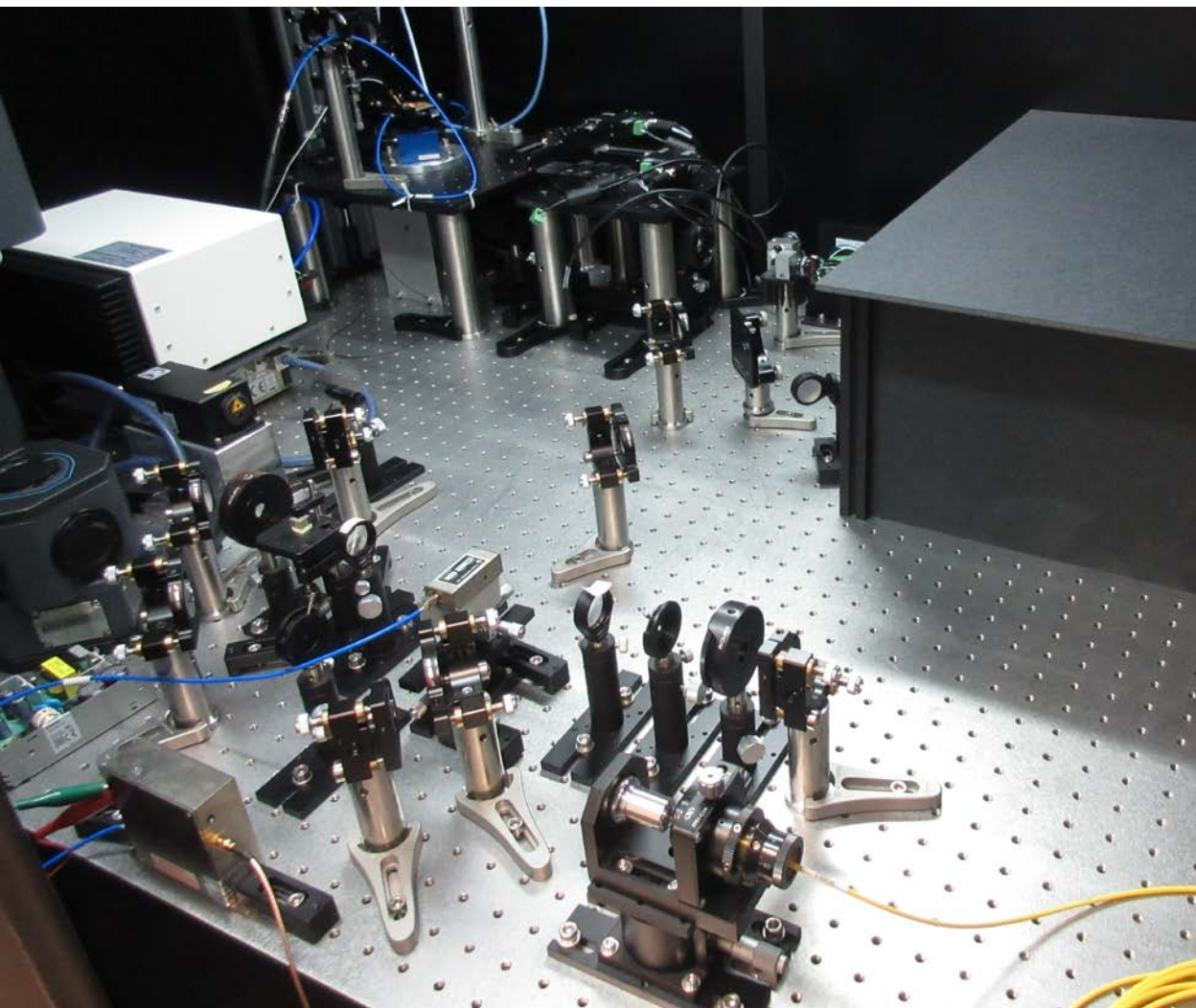
Rabi oscillation



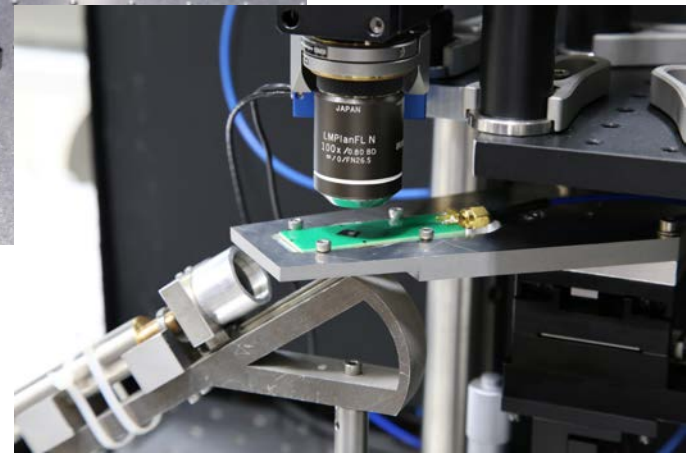
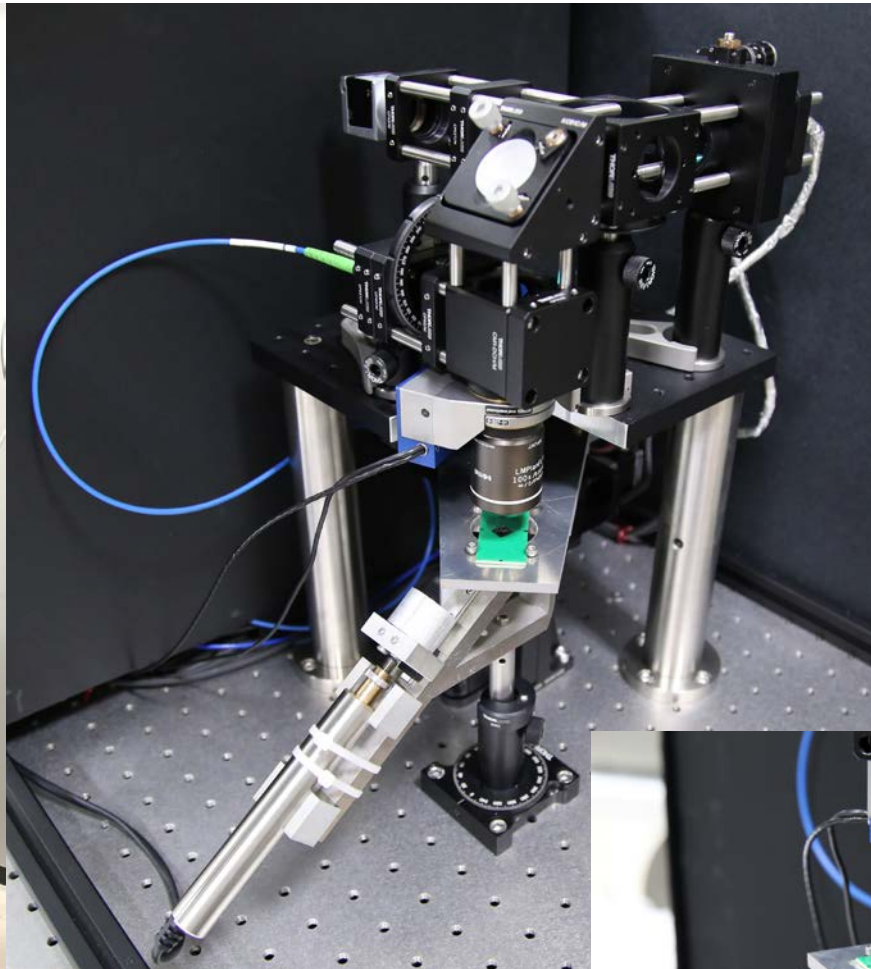
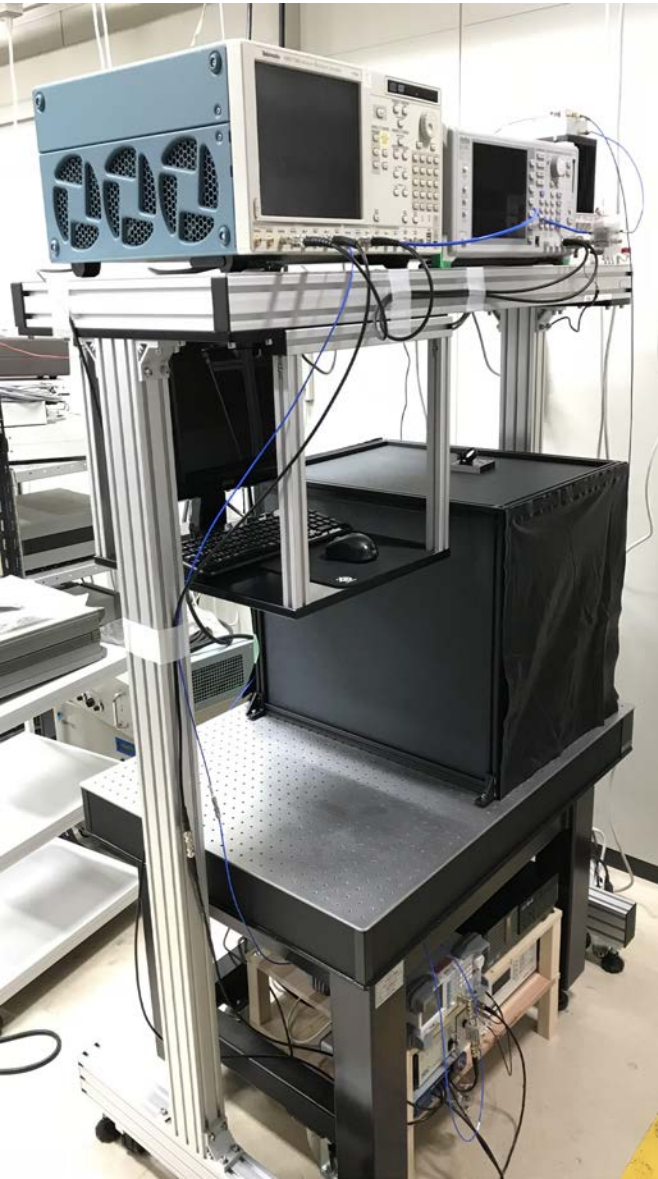
Experimental setup



Experimental setup



Experimental setup



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

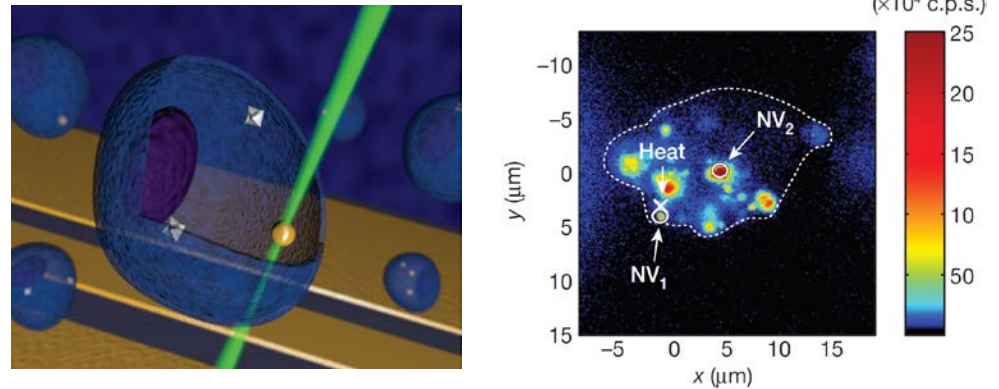
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Quantum sensing with NV centers

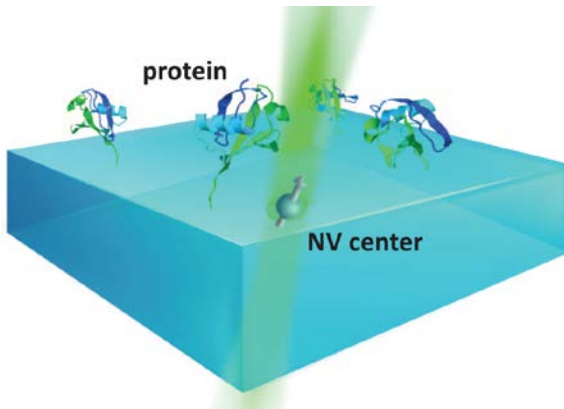
- $B, E, T, S...$
- DC & AC modes
- Wide temperature range
- Nondestructive
- High spatial resolution
- Various modalities

Nanodiamond & biology



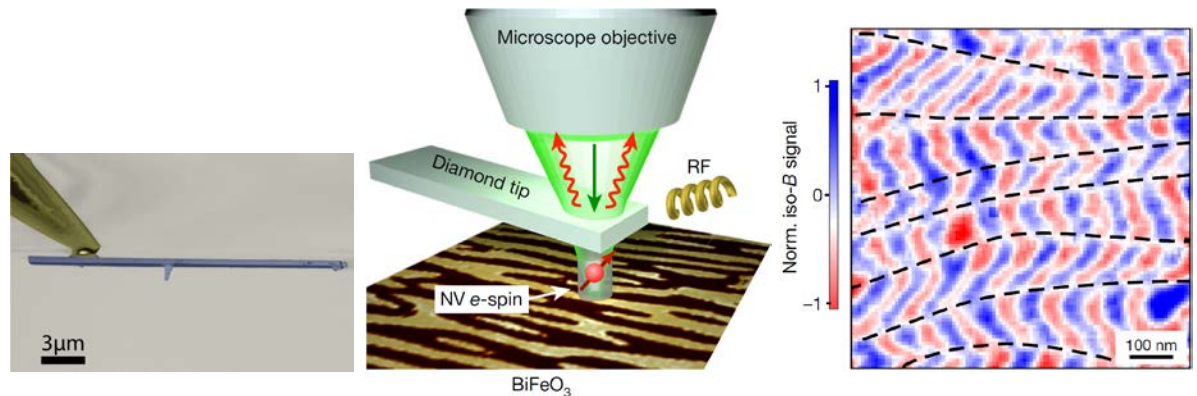
Nature **500**, 54 (2013)

Near-surface NV center & NMR



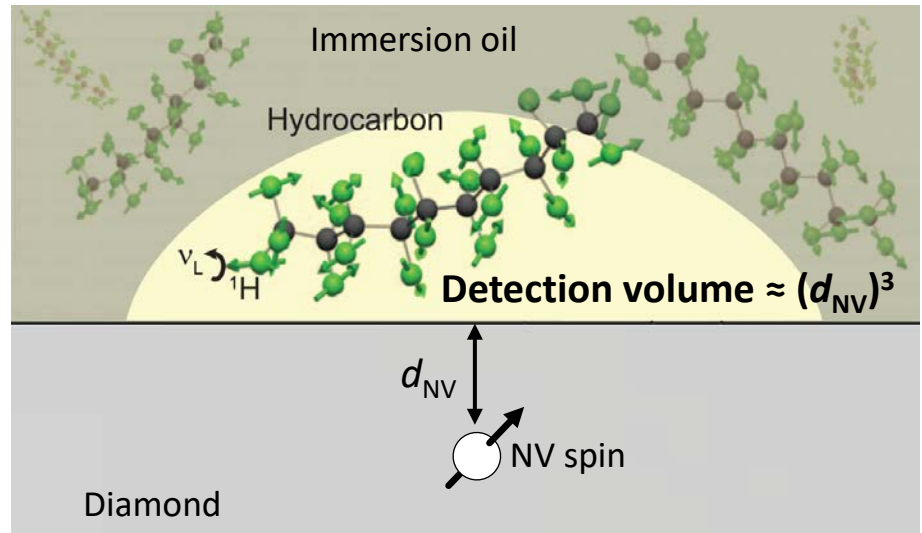
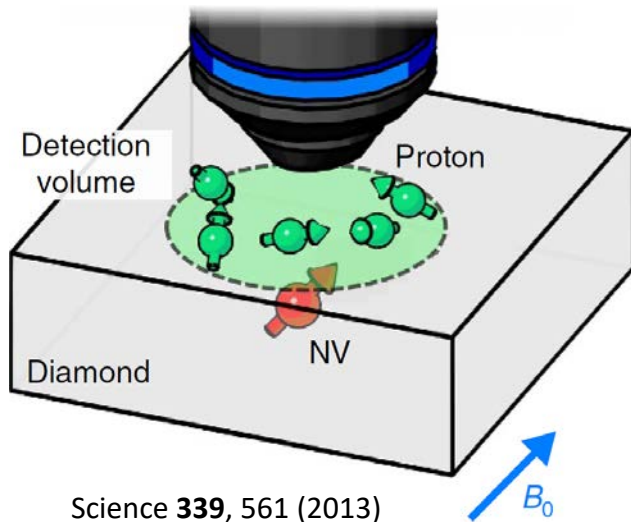
Science **351**, 836 (2016)

Scanning probe & condensed matter



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

Nuclear spin sensing



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

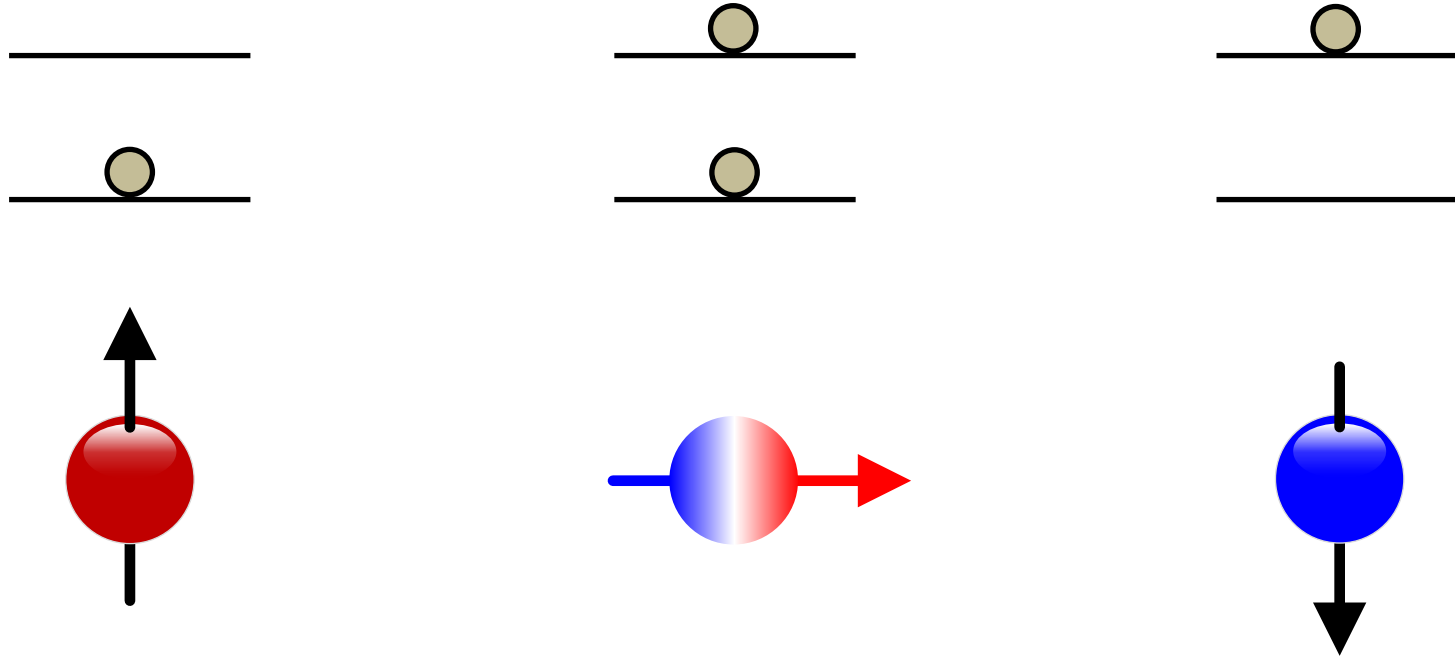


Weak AC magnetic field on the NV spin



Detect using **quantum coherence**

Quantum coherence



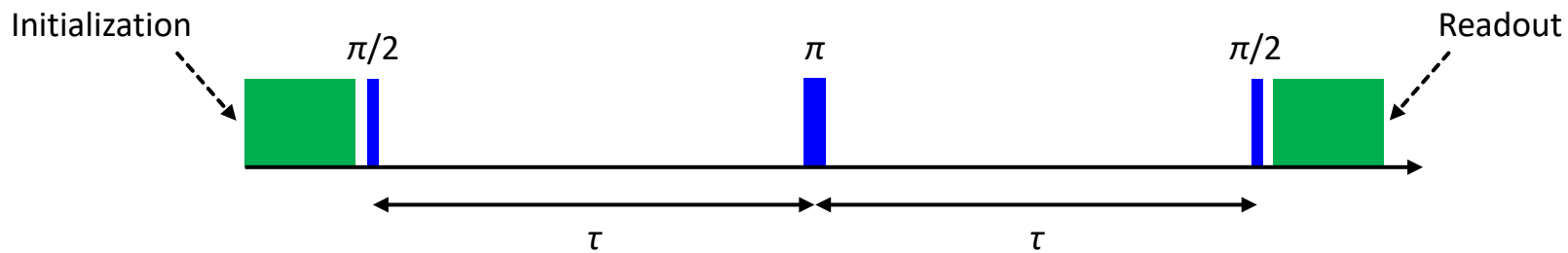
$$|0\rangle \equiv |m_s = 0\rangle$$

$$|\Psi\rangle = \alpha|0\rangle + \beta|1\rangle$$

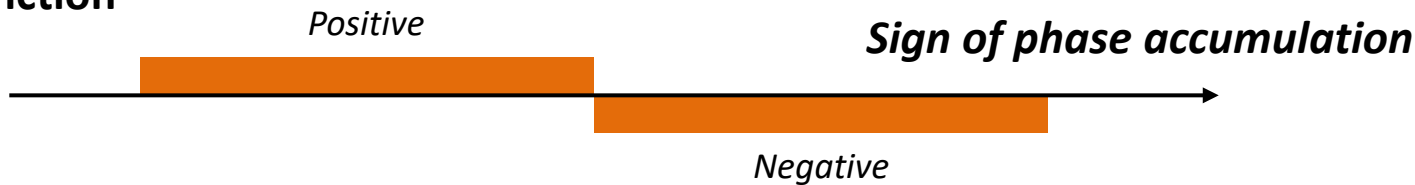
$$|1\rangle \equiv |m_s = -1\rangle$$

T_2 : measure of how long a superposition state is preserved

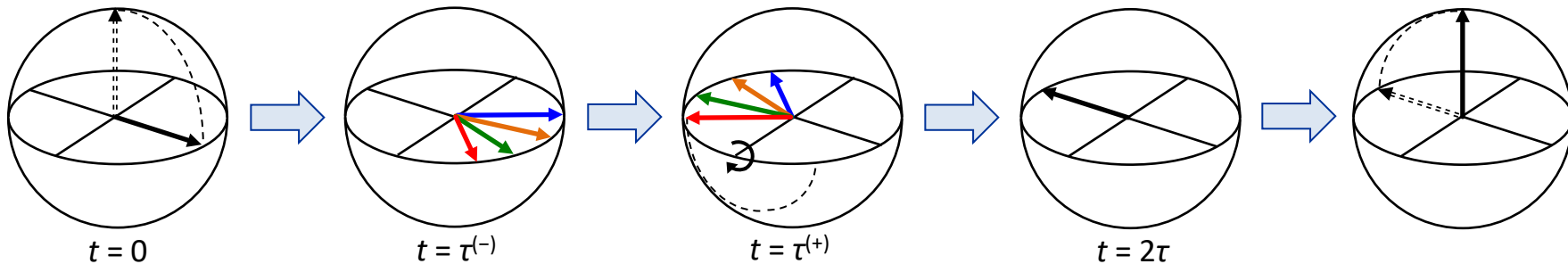
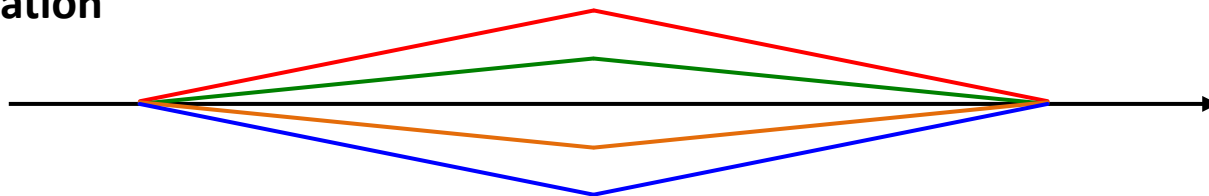
Spin echo



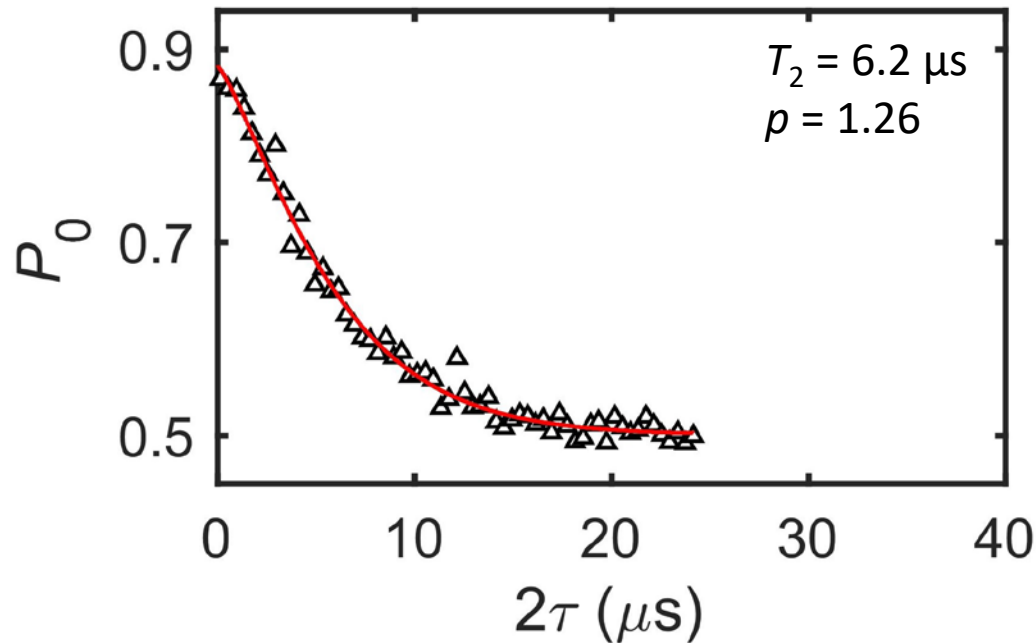
Modulation function



Phase accumulation by DC field



Coherence time



Stretched exponential decay

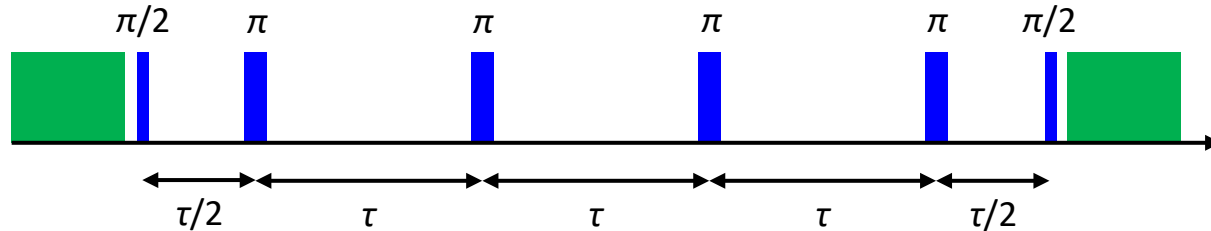
$$\exp\left[-\left(\frac{2\tau}{T_2}\right)^p\right]$$

Near-surface NV center

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

AC magnetometry

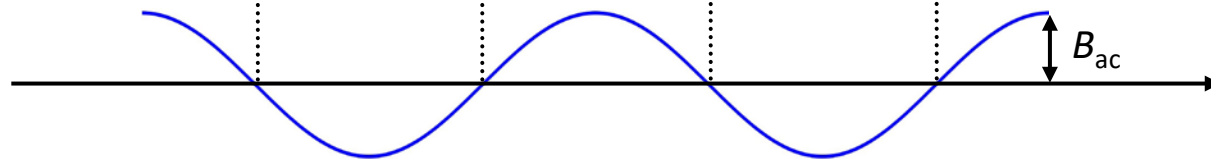
CP ($N = 4$)



Modulation function

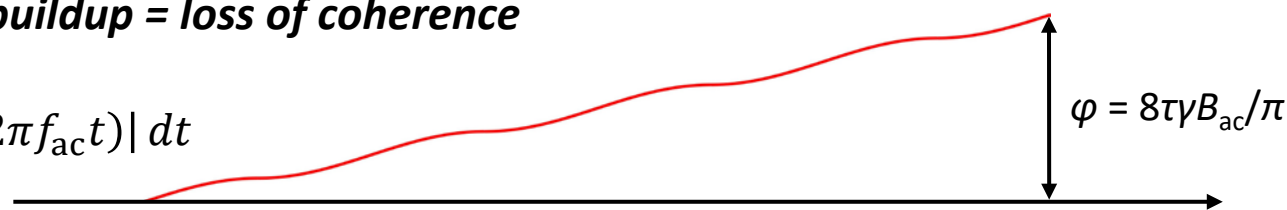


AC field at $f_{ac} = 1/2\tau$

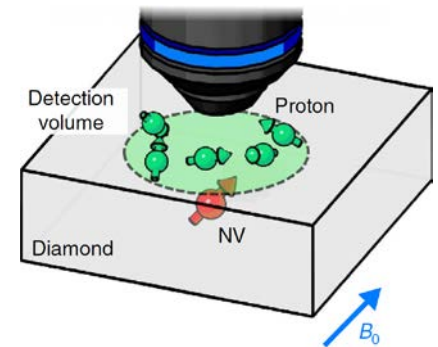
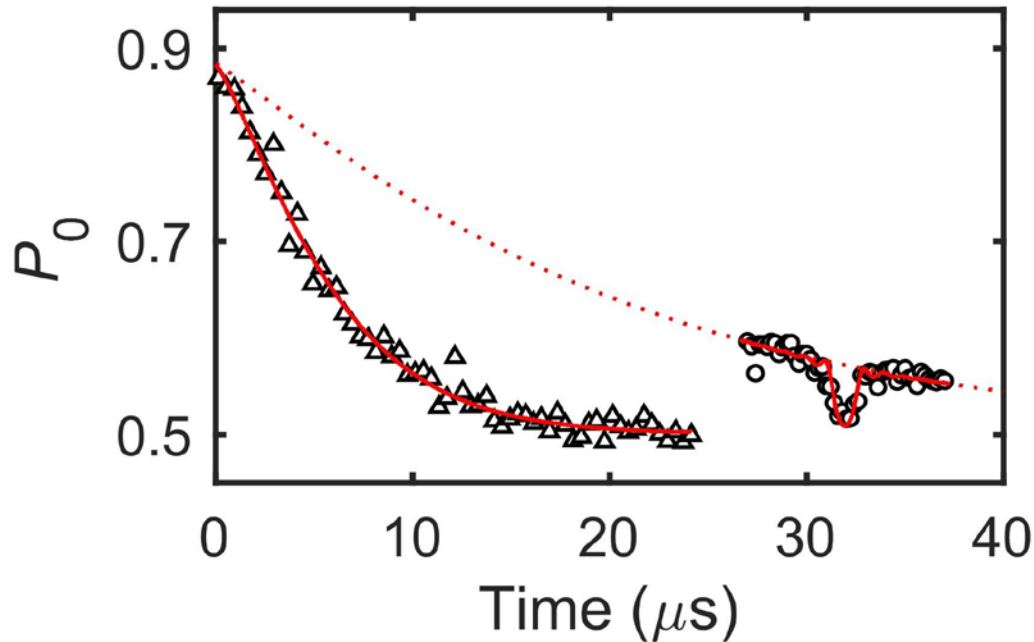


Sensor phase buildup = loss of coherence

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

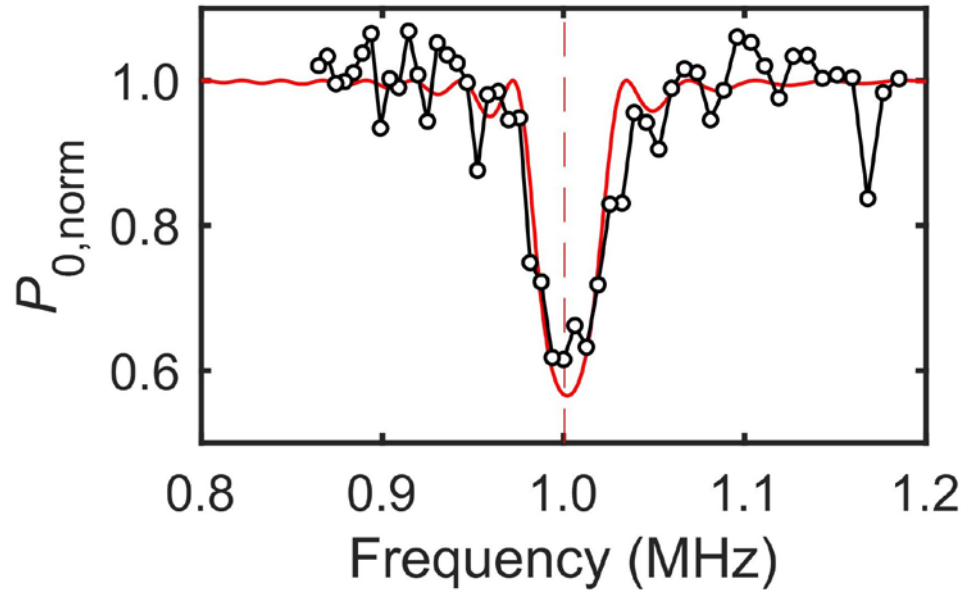


Nuclear spin sensing



- $T_2 = 6.2 \mu\text{s} @ B_0 = 23.5 \text{ mT}$
- $N = 64$ (XY16)
- $(2\tau)^{-1} = 64 / (2 \times 32 \mu\text{s}) = 1 \mu\text{s}$
 $\rightarrow \gamma_H B_0 = (42.577 \text{ kHz/mT}) \times B_0 = 1.00 \text{ MHz}$

Nuclear spin sensing

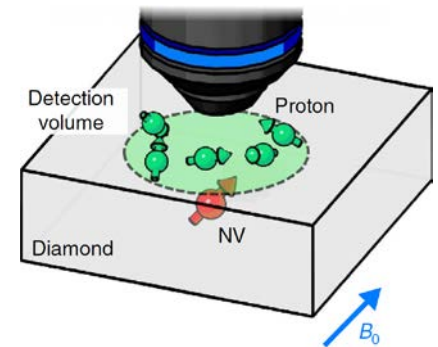


$$C(\tau) = f(B_{\text{rms}})$$

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

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

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



Toward single-molecular imaging

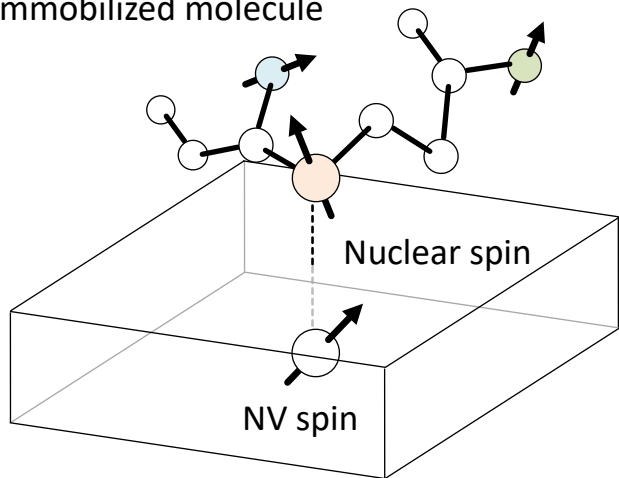
- **Strategy**

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

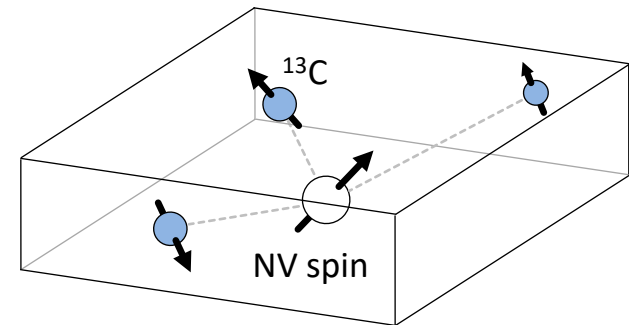
- **Practical issues**

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

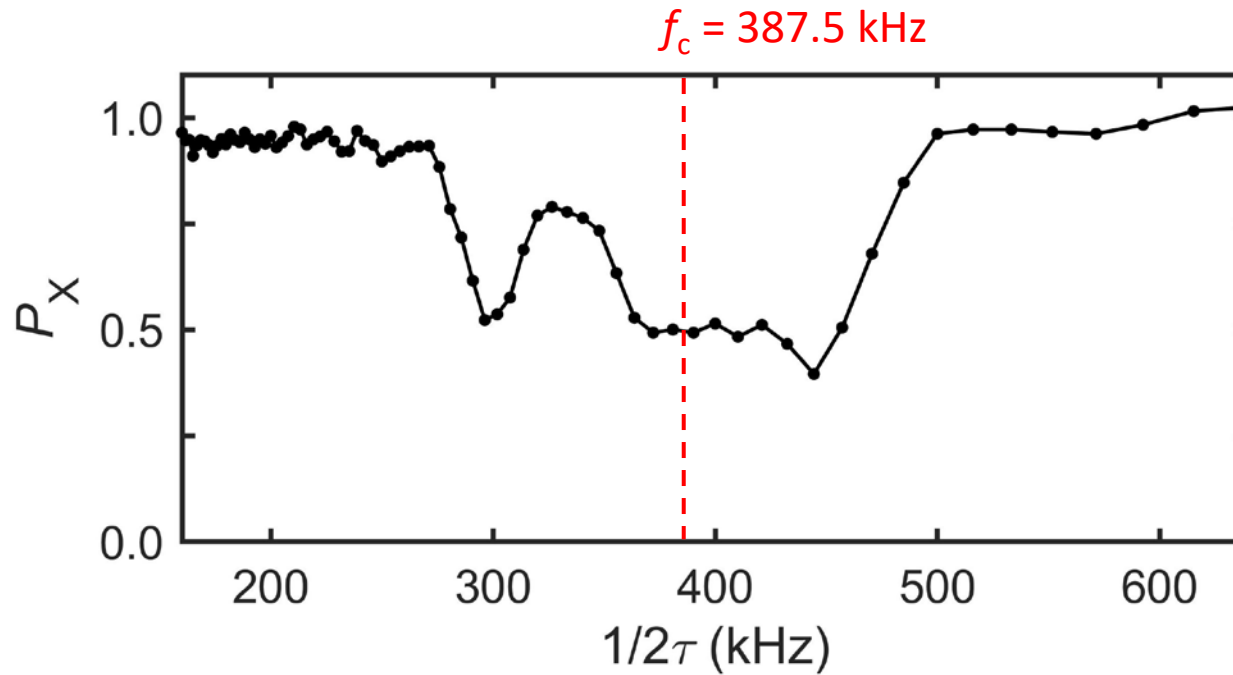
Immobilized molecule



Use ^{13}C (1.1%) in diamond as a testbed



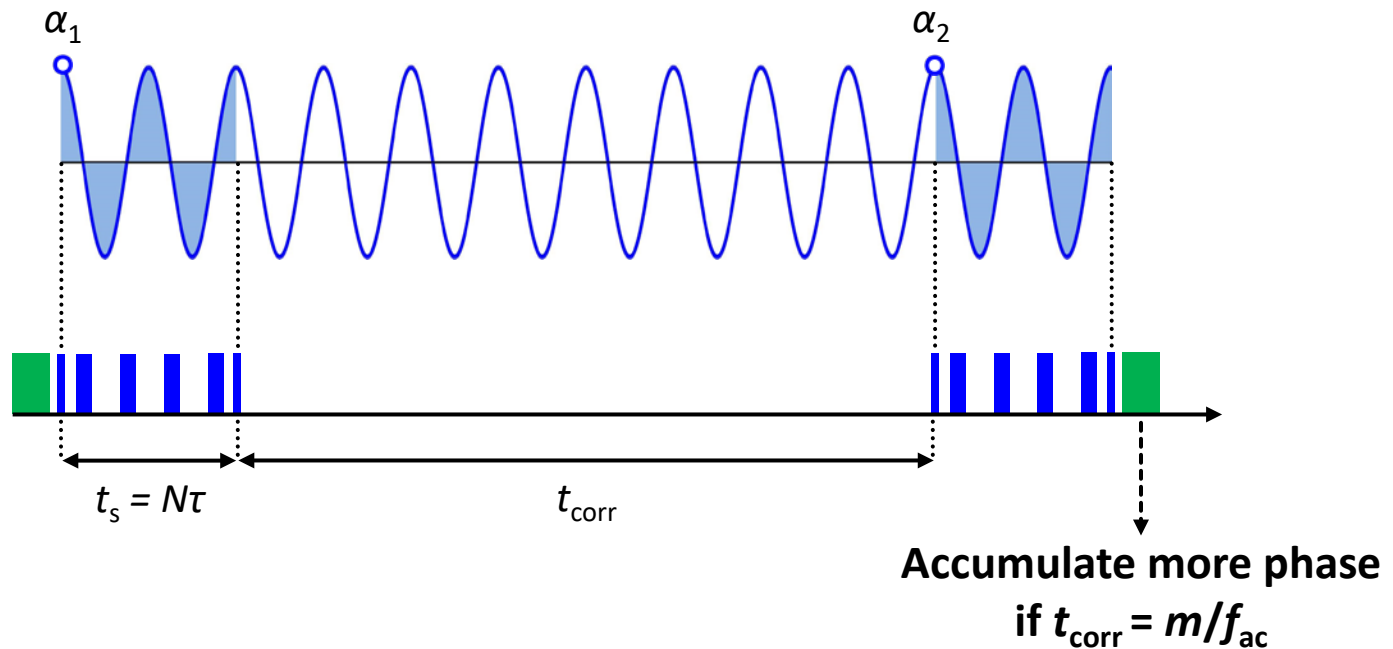
Nuclear spin sensing



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

Correlation spectroscopy

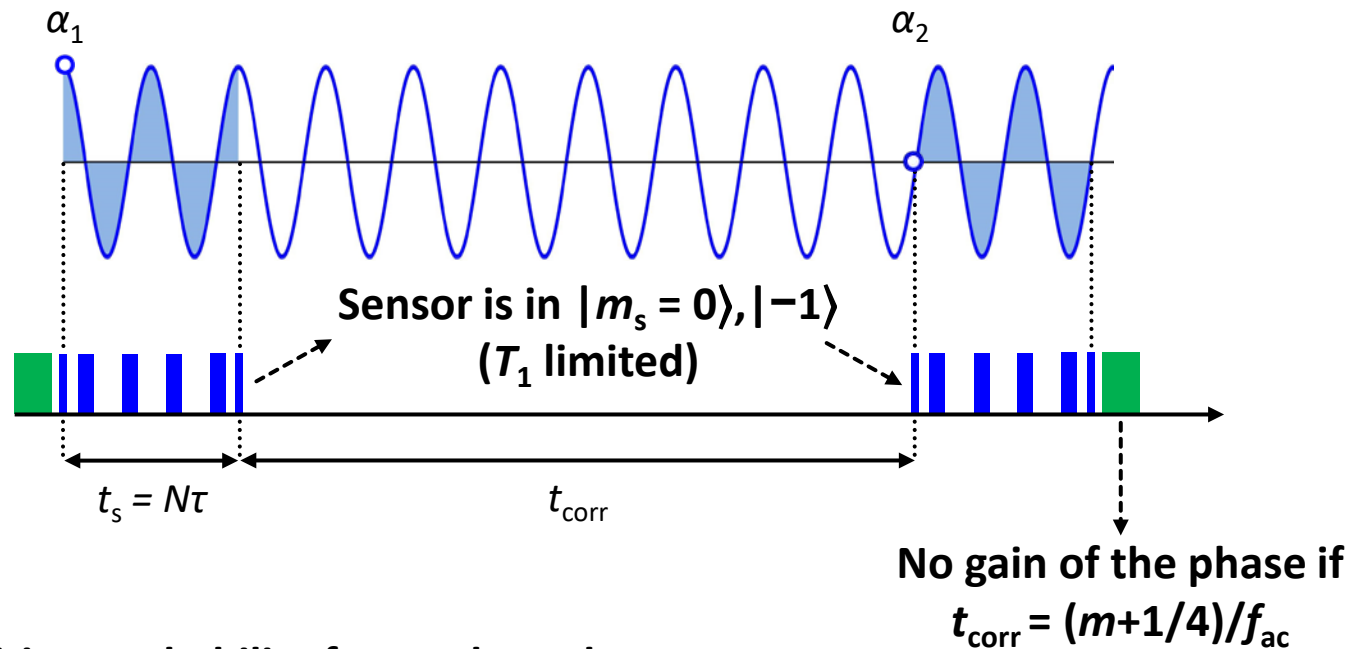
AC field at f_{ac}



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

AC field at f_{ac}



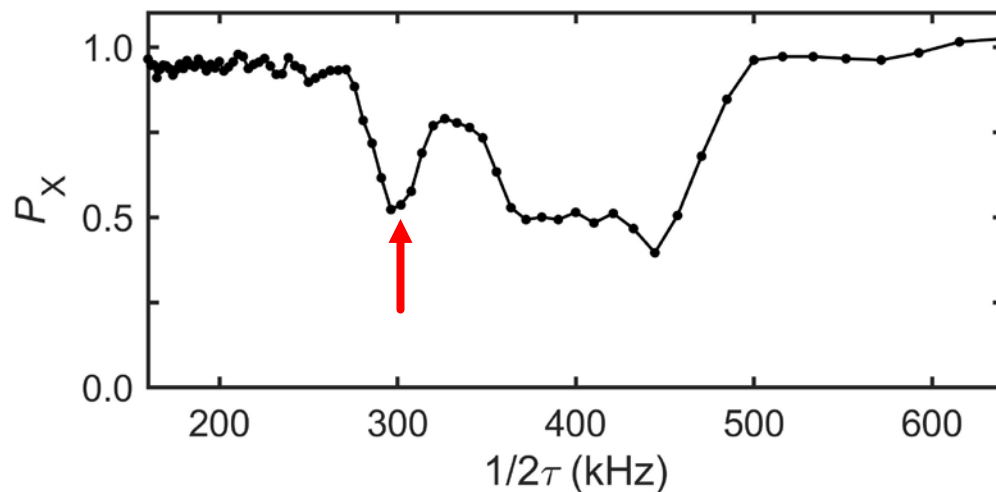
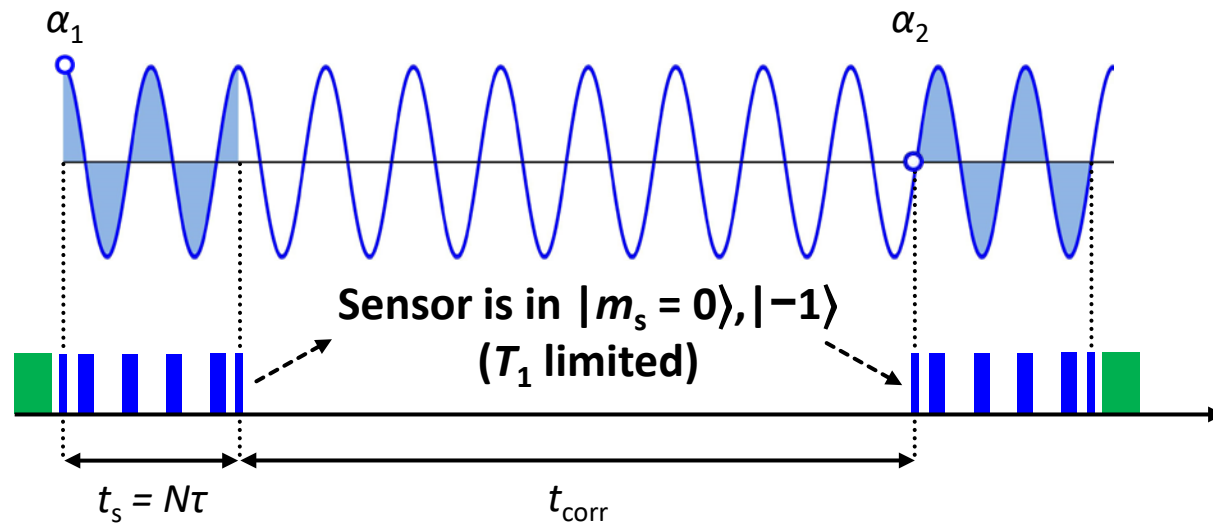
The transition probability for random phases

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

Nature Commun. **4**, 1651 (2013) Laraoui *et al.*
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Correlation spectroscopy

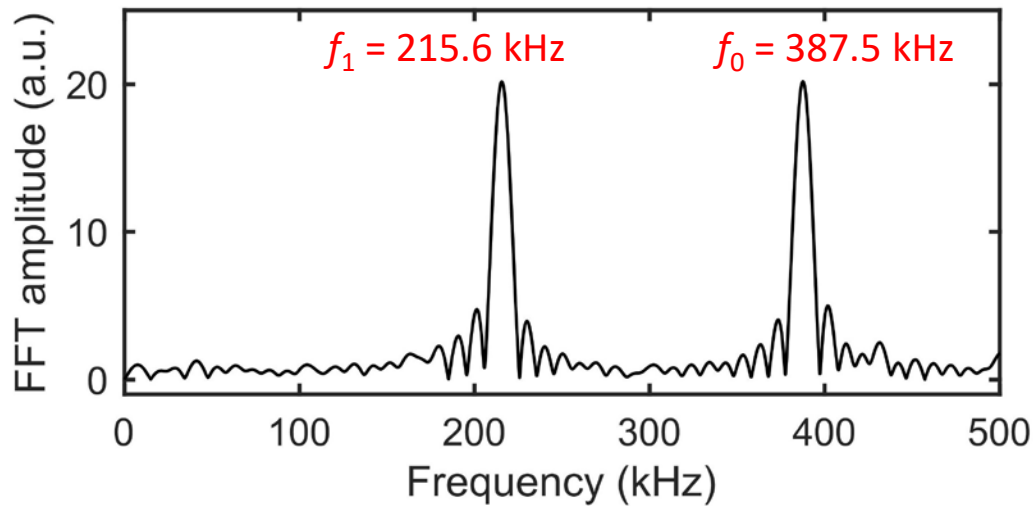
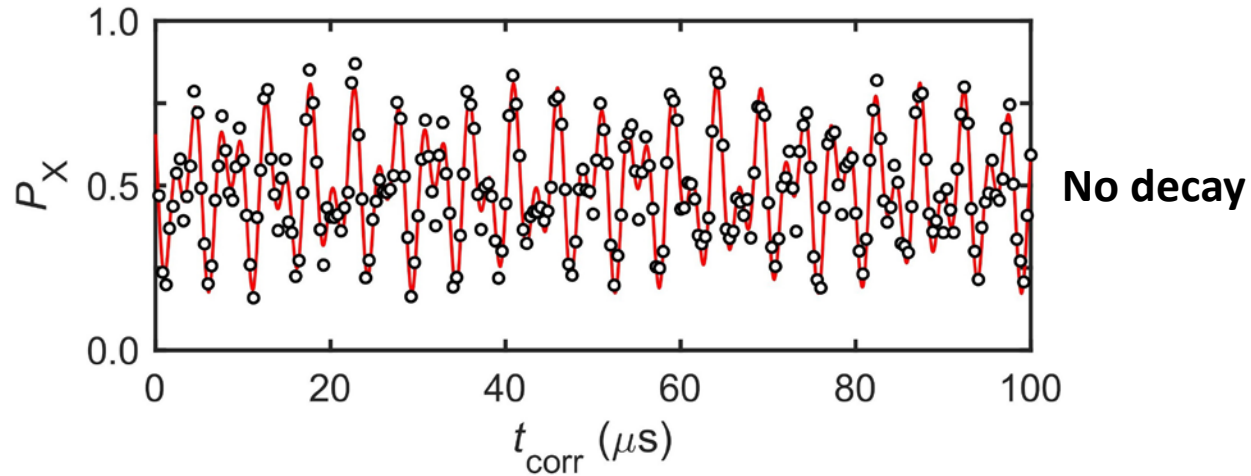
AC field at f_{ac}



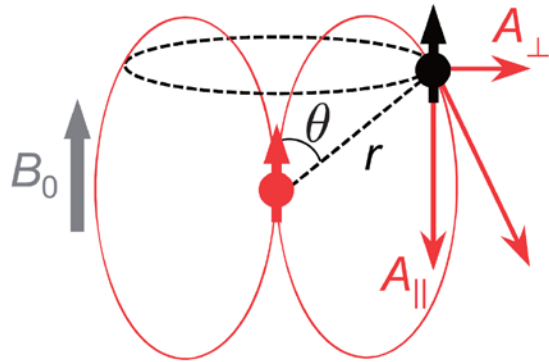
Where to look at?

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

Correlation spectroscopy of a nucleus



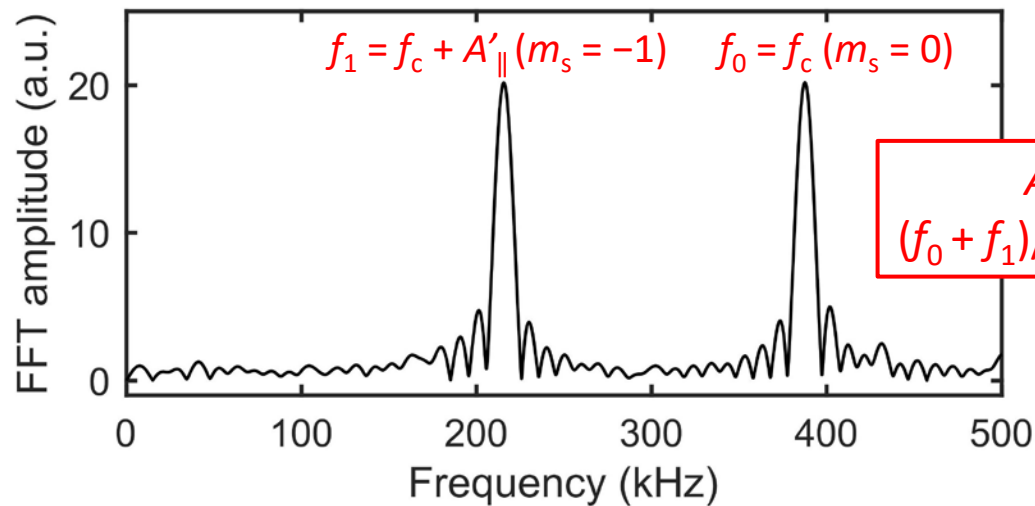
Correlation spectroscopy of a nucleus



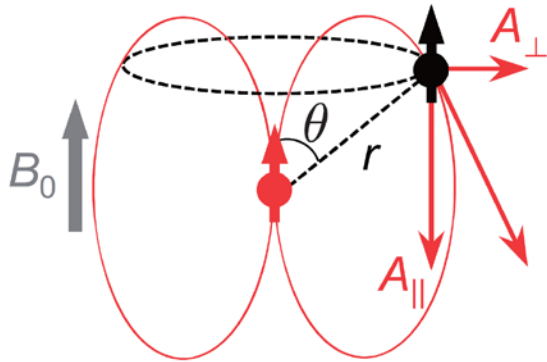
Hamiltonian of NV-¹³C coupled system

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

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



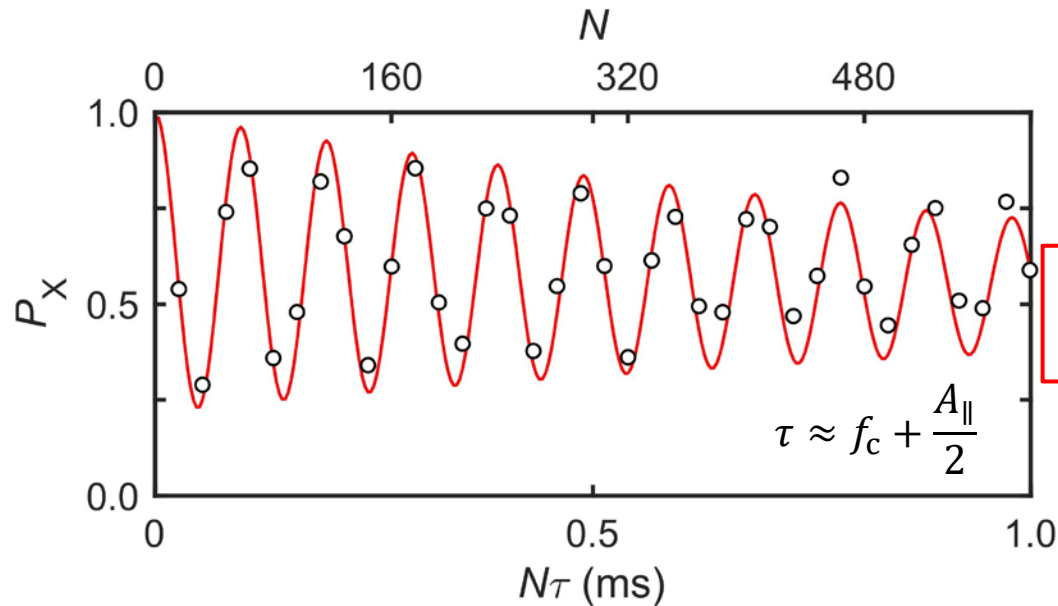
Coherent control of a nuclear spin



Hamiltonian of NV- ^{13}C coupled system

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

→ The single ^{13}C n -spin rotates about the A_{\perp} axis

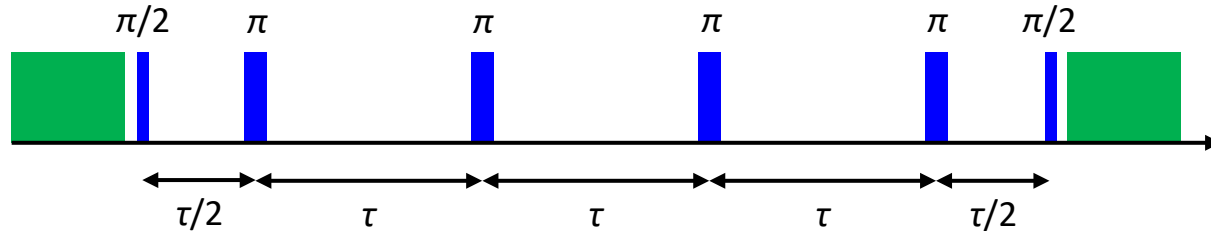


$$f_{\text{osc}} = 10.2 \text{ kHz} \approx A'_{\perp}/2$$

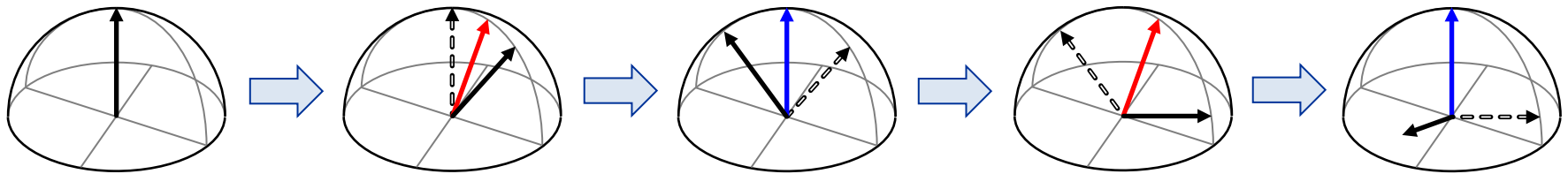
$$P_x < 0.5 \rightarrow \text{single}$$

Conditional rotation of a nuclear spin

CP ($N = 4$)

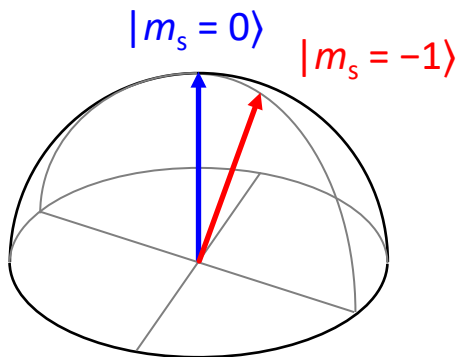


Evolution of n -spin vector

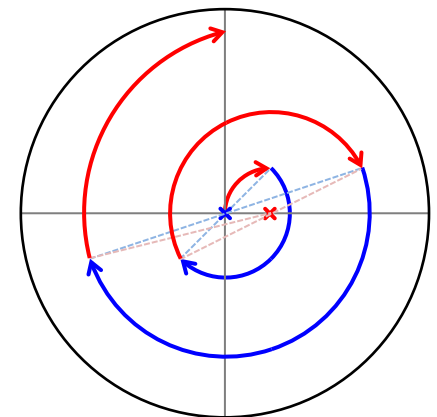
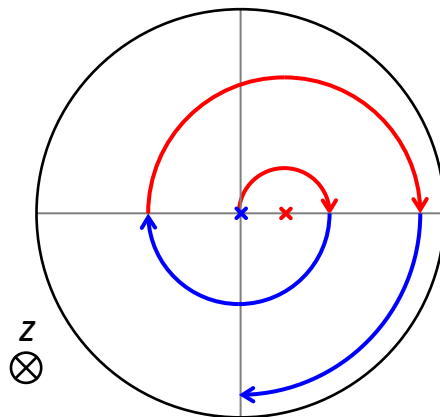


Start from $|m_s = 0\rangle$

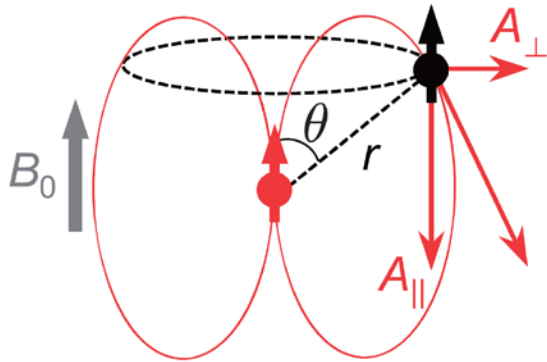
Start from $|m_s = -1\rangle$



Q-axis of n -spin



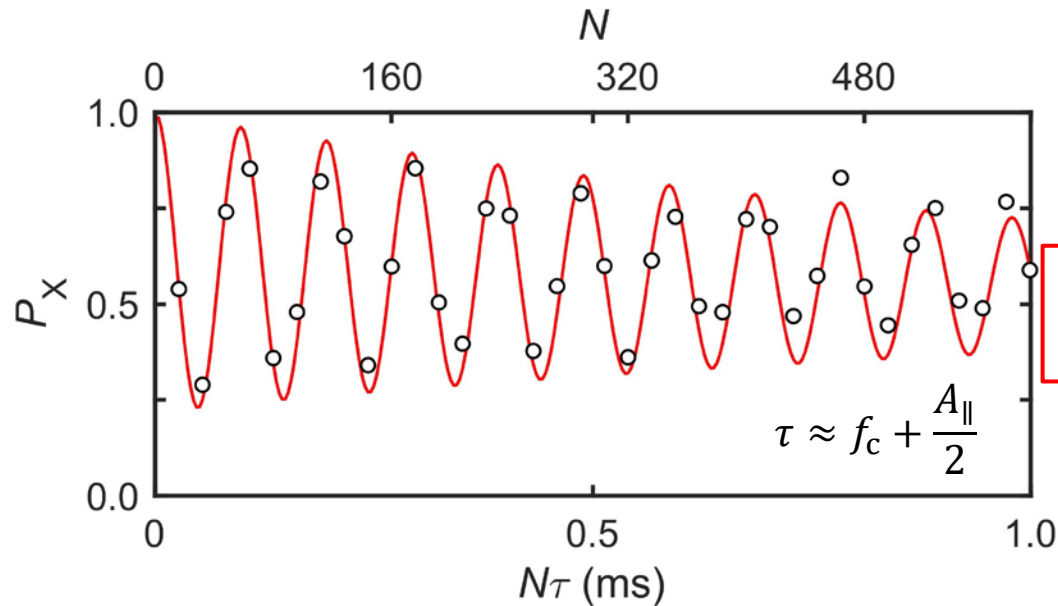
Coherent control of a nuclear spin



Transition probability of the NV spin

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

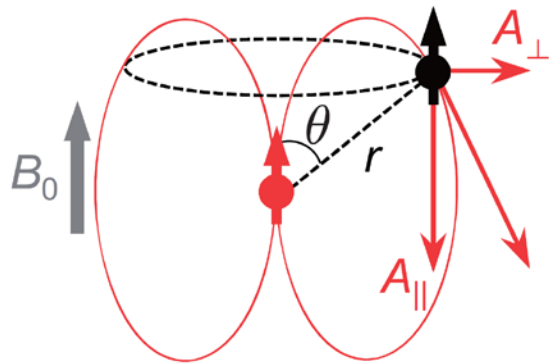
Phys. Rev. Lett. **109**, 137602 (2012) Taminiau *et al.*



$f_{osc} = 10.2 \text{ kHz} \approx A'_{\perp}/2$
 $P_X < 0.5 \rightarrow \text{single}$

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

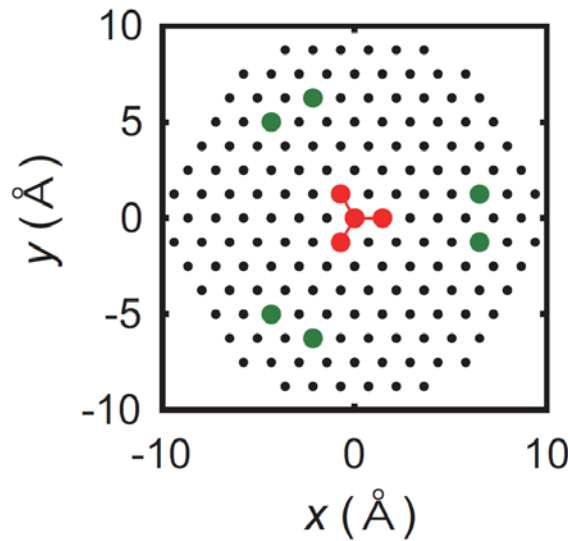
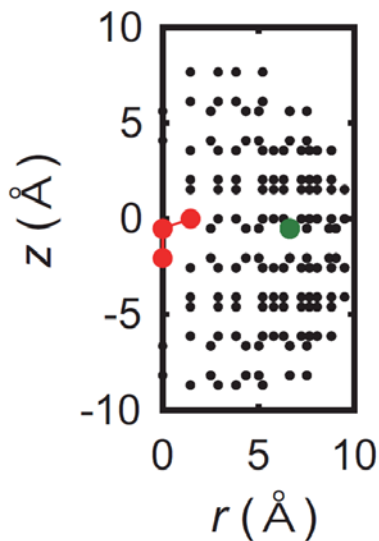
Determination of hf constants



Magnetic dipole int. + contact hf int.

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

$$A_{\perp} \propto \frac{3 \cos \theta \sin \theta}{r^3}$$



$$(r, \theta) = (6.84 \text{ \AA}, 94.8^\circ)$$

$$A_{\parallel} = -173.1 \text{ kHz}$$

$$A_{\perp} = 22.3 \text{ kHz}$$



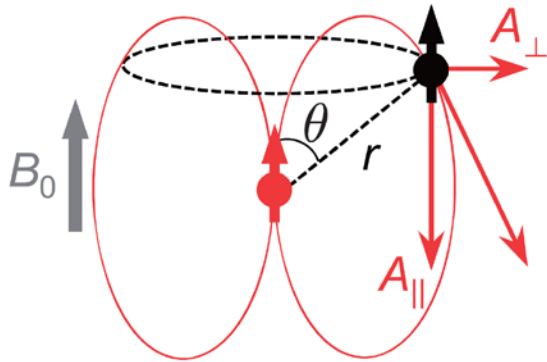
$$A_{\parallel} = -175.1 \pm 2.1 \text{ kHz}$$

$$A_{\perp} = 21.9 \pm 0.2 \text{ kHz}$$

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

How to determine ϕ ?

(azimuthal angle)

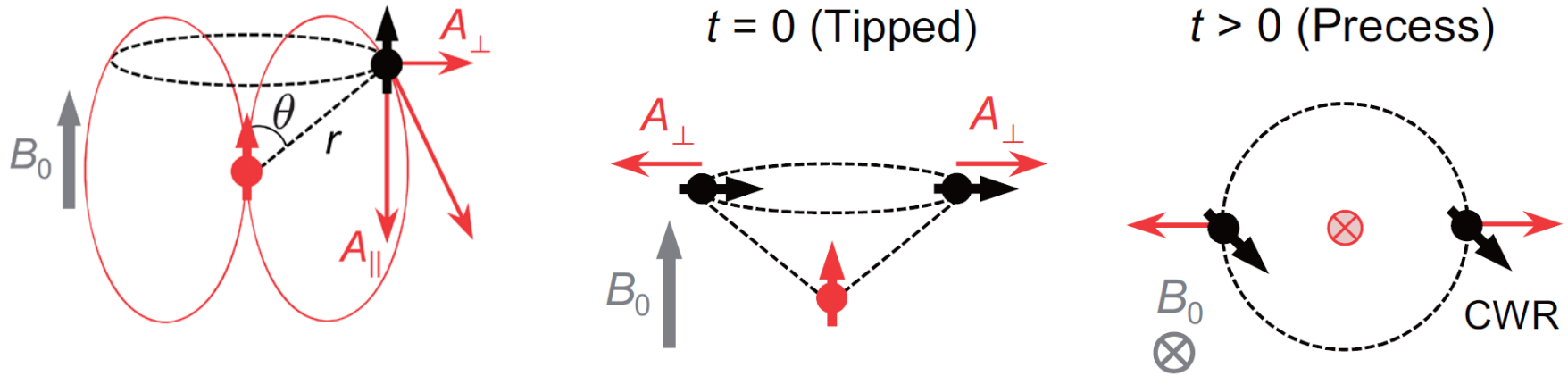


Magnetic dipole int.

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

$$A_{\perp} \propto \frac{3 \cos \theta \sin \theta}{r^3}$$

How to determine ϕ ?



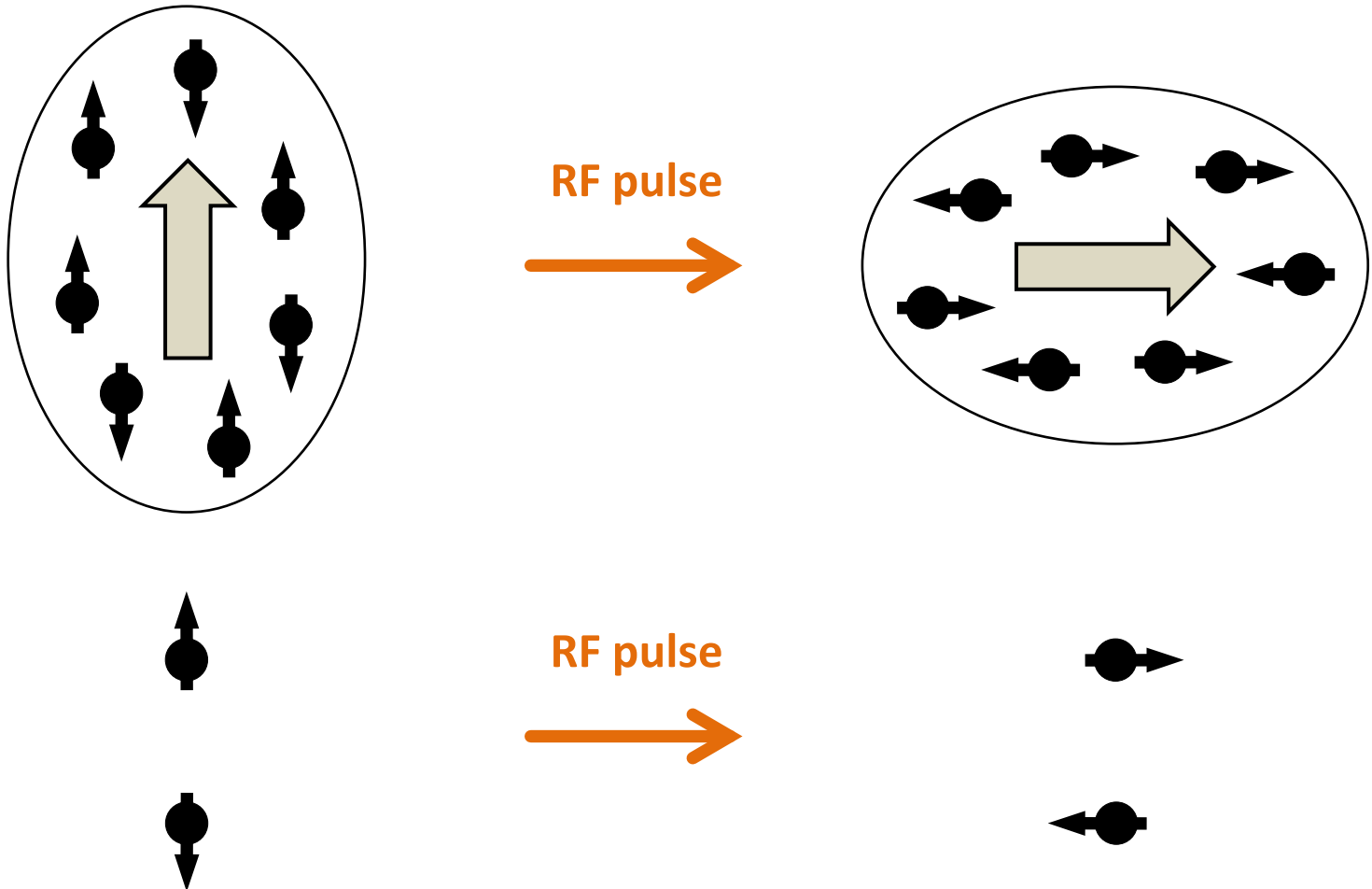
Transition probability of the NV spin after the detection of a single nuclear spin

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



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

Ensemble vs. single

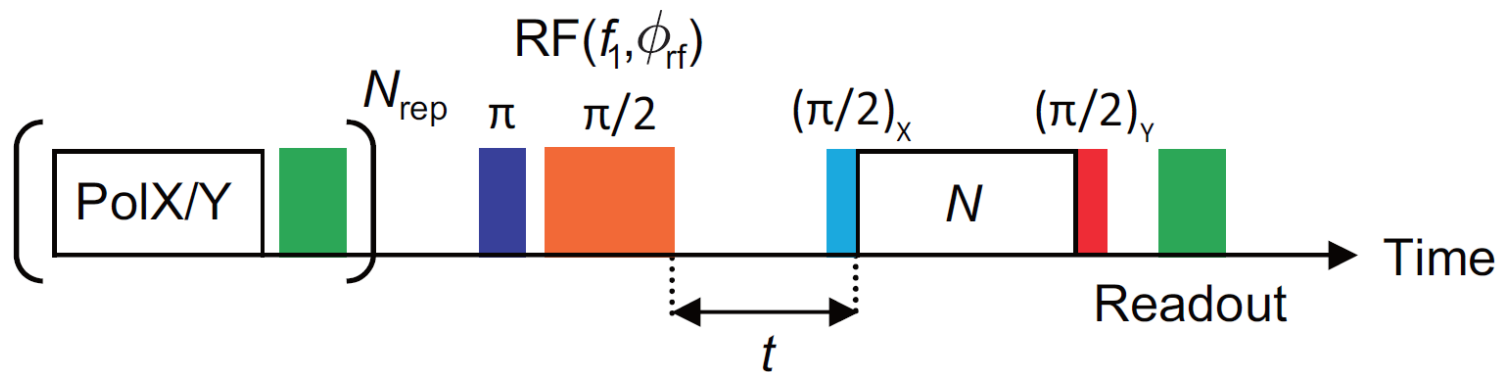
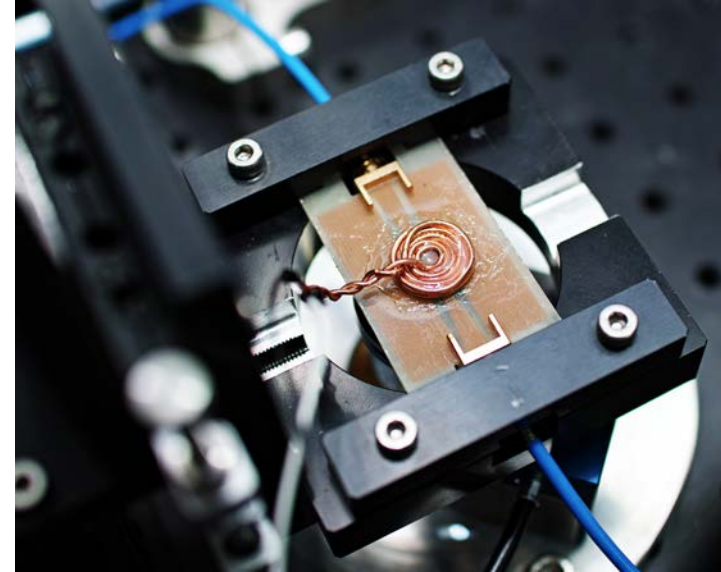


The initial state matters

→ Dynamic nuclear polarization (DNP)

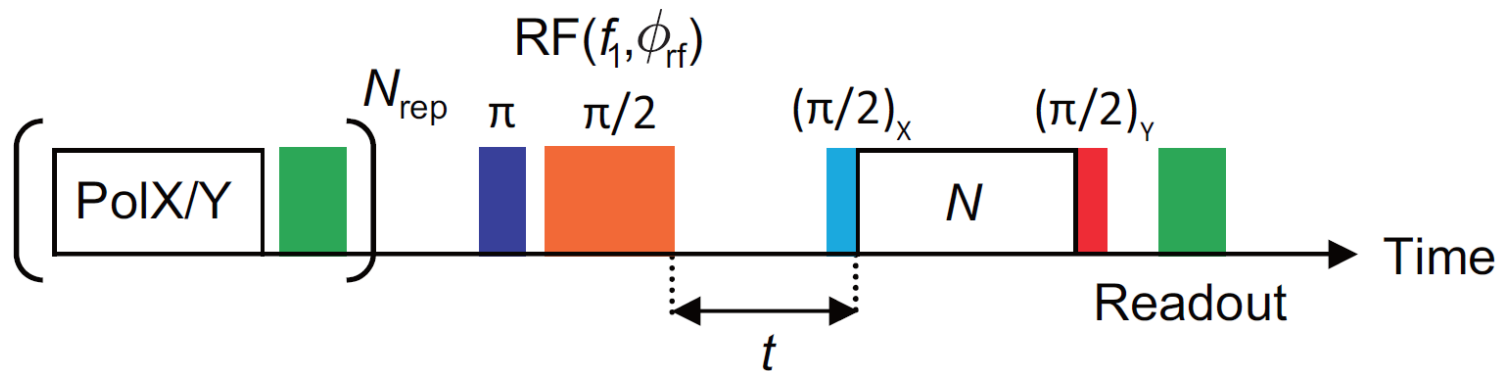
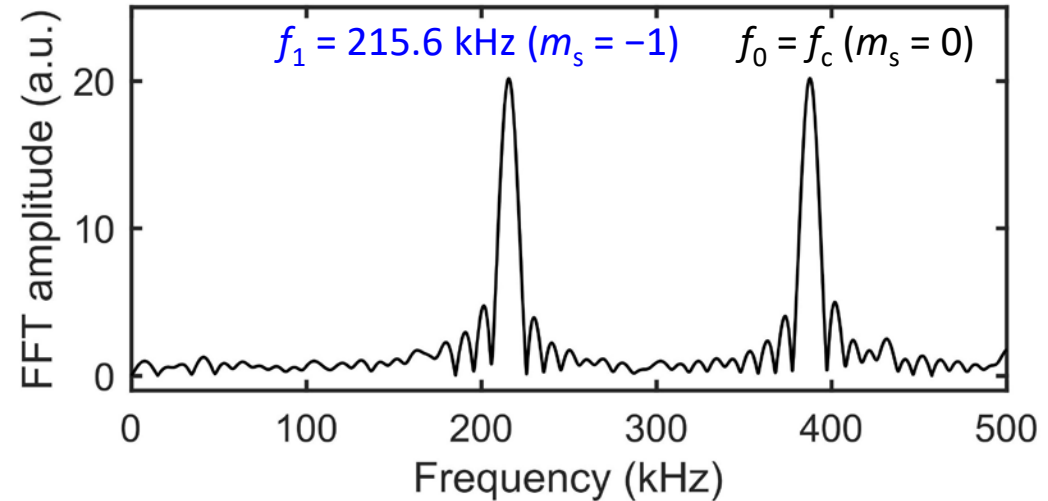
Determination of ϕ of a ^{13}C n -spin

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

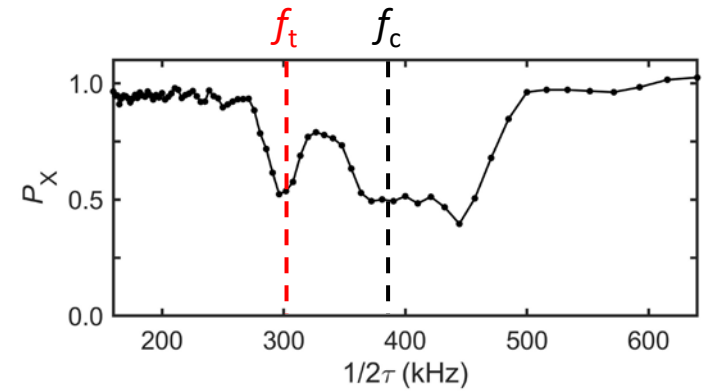
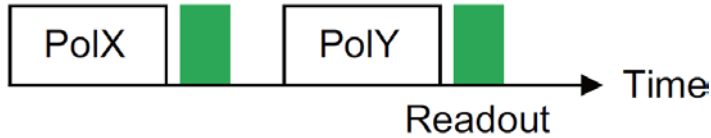
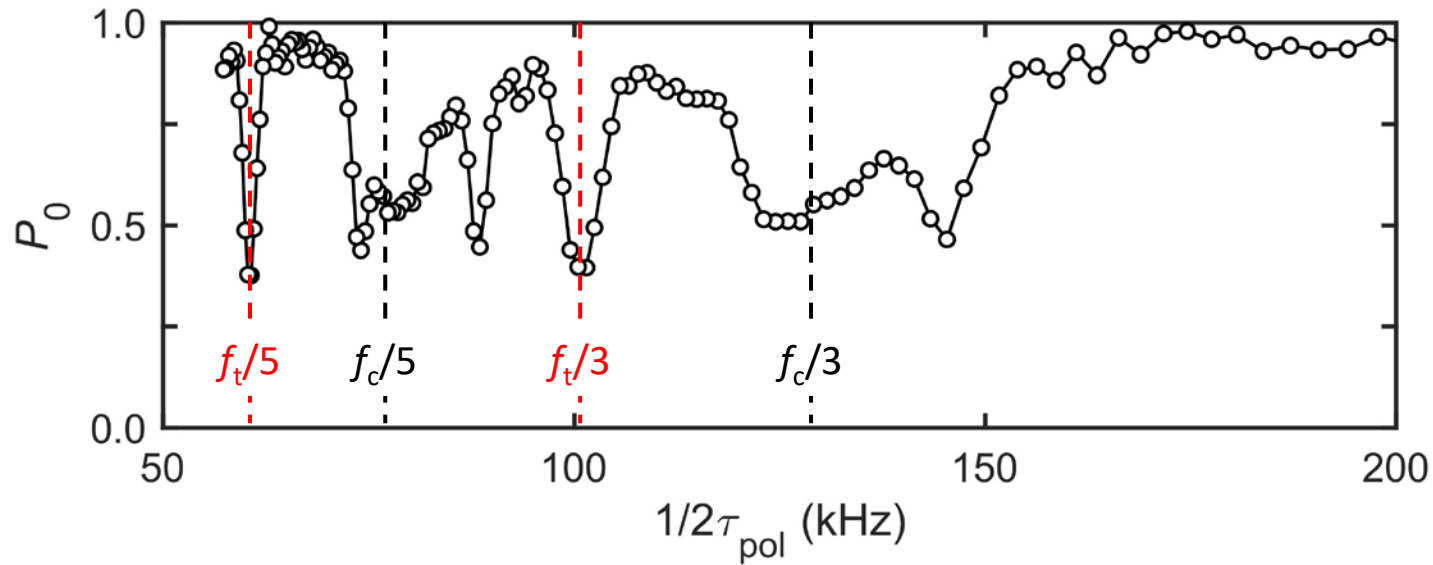


Determination of ϕ of a ^{13}C n -spin

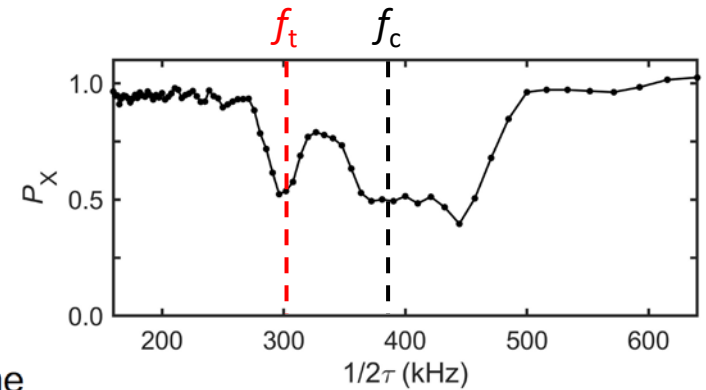
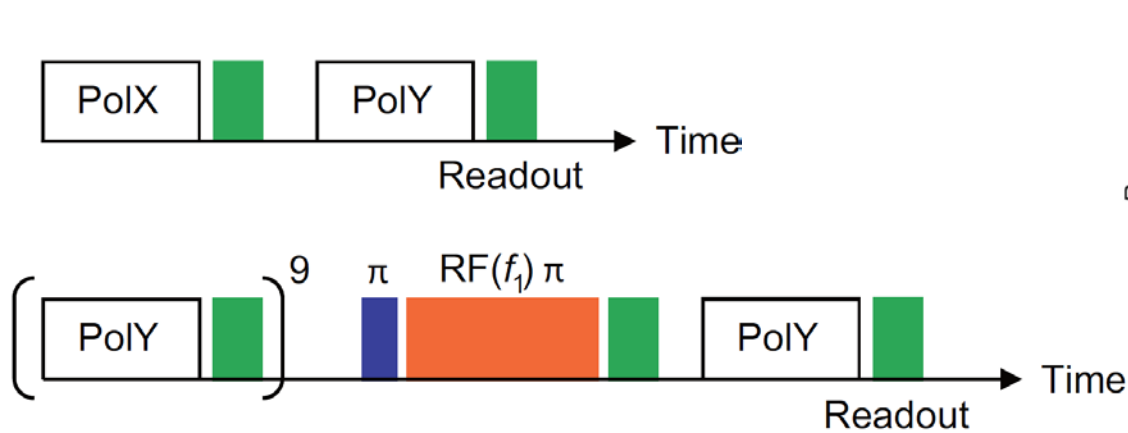
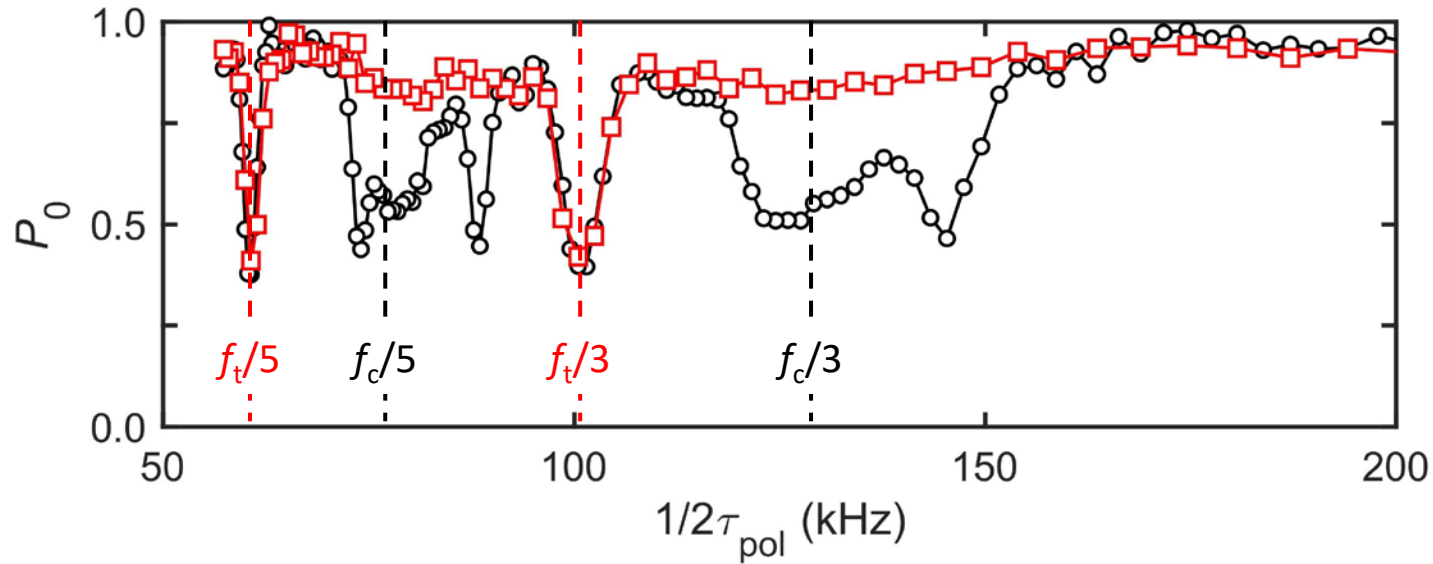
1. DNP (PulsePol)
2. RF pulse@ $m_s = -1$
3. Wait t (n -spin precesses)
4. AC sensing



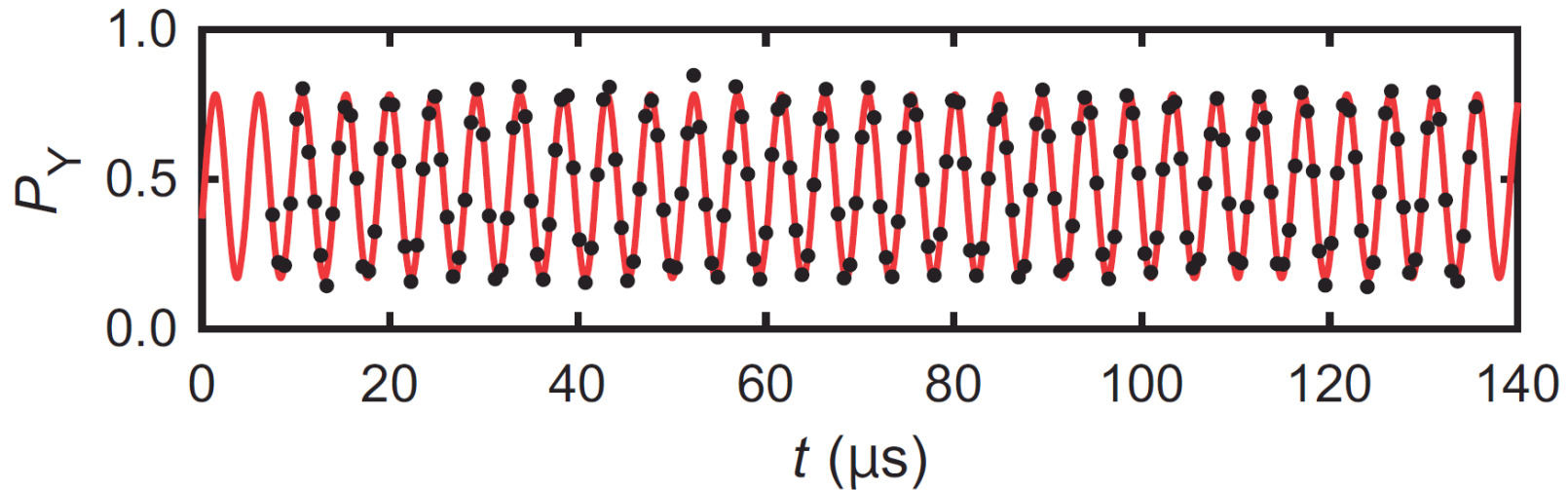
PulsePol



PulsePol

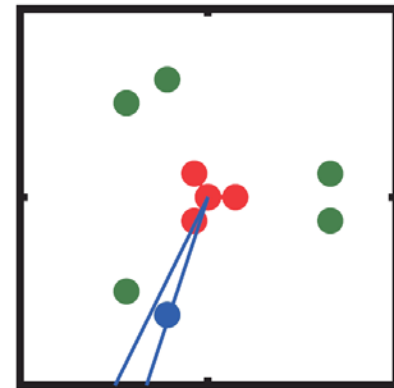


Determination of ϕ of a ^{13}C n -spin



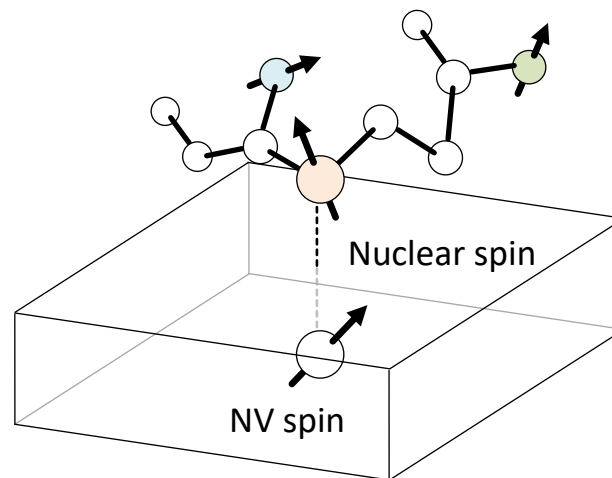
- ✓ $t \rightarrow 1$ ms (undersampling)
- ✓ $f_p = 215.79$ kHz $\approx f_1 = 215.6$ kHz
- ✓ $\phi - \phi_n(0) = 334.0^\circ$
- ✓ $\phi_n(0) = 89.2^\circ$ (Real-space n -spin trajectory)

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



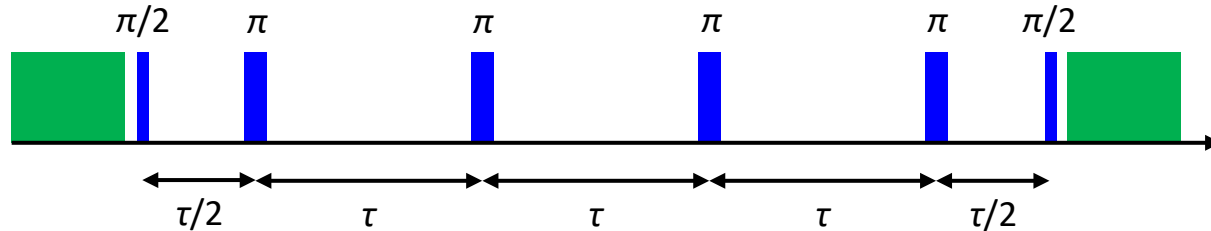
Toward single-molecular imaging

- **Information of the positions of the individual nuclei**
 - Accurate measurement of $e-n$ int. const's (A_{\parallel}, A_{\perp}) $\approx (r, \theta)$
 - Lack of information on the azimuthal angle ϕ
- **Spectral resolution**
 - Easy to resolve isotopes
 - Need to measure J -couplings & chemical shifts (ppm!)
 - Limited by sensor/memory lifetimes ($T_{2e/n}, T_{1e/n}$)

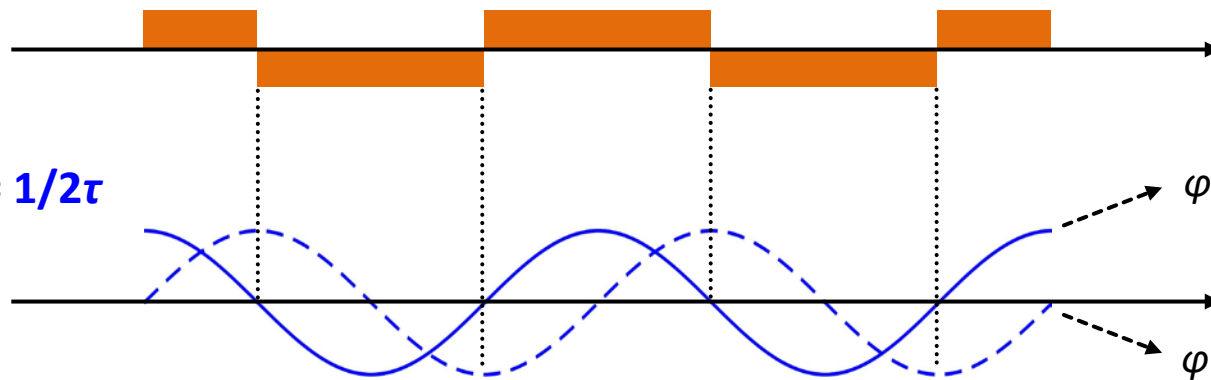


AC magnetometry

CP ($N = 4$)

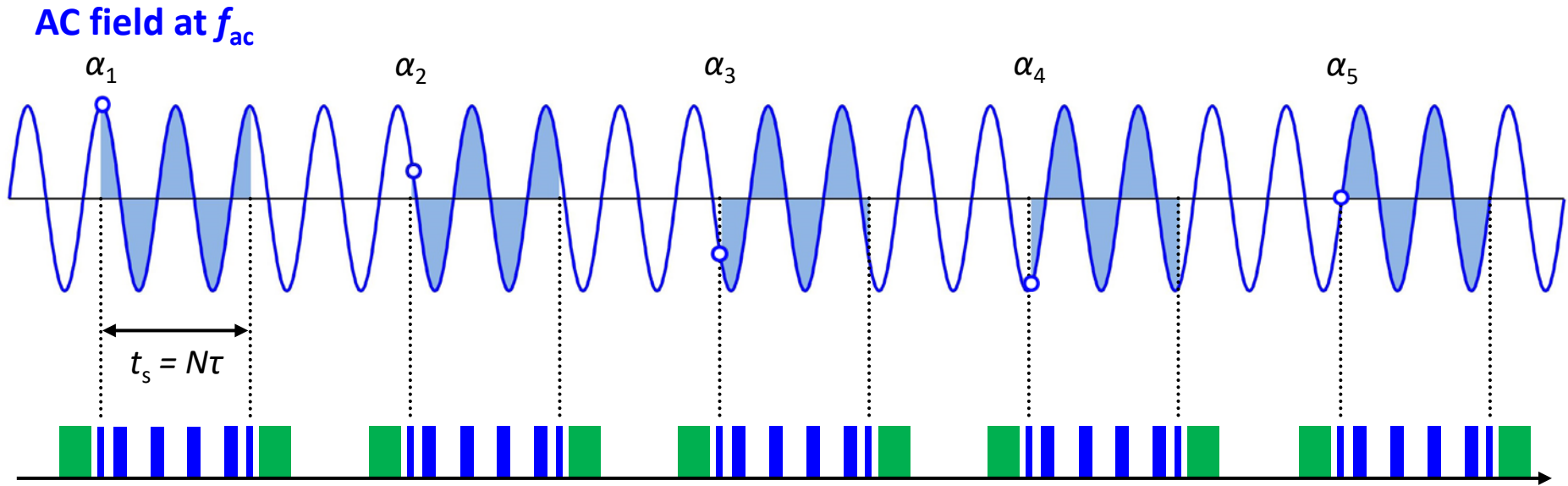


Modulation function



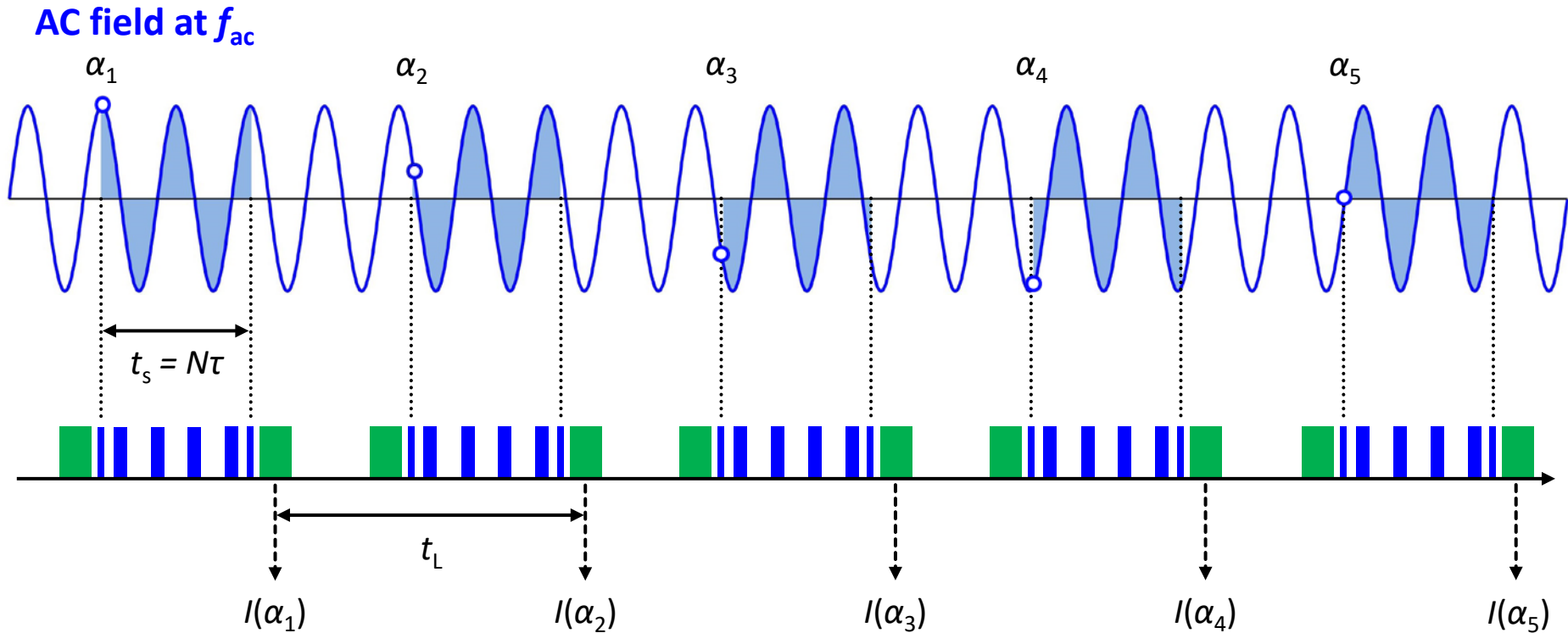
- φ depends on the **initial phase α** of the AC field ($\varphi \propto \cos \alpha$)

AC magnetometry



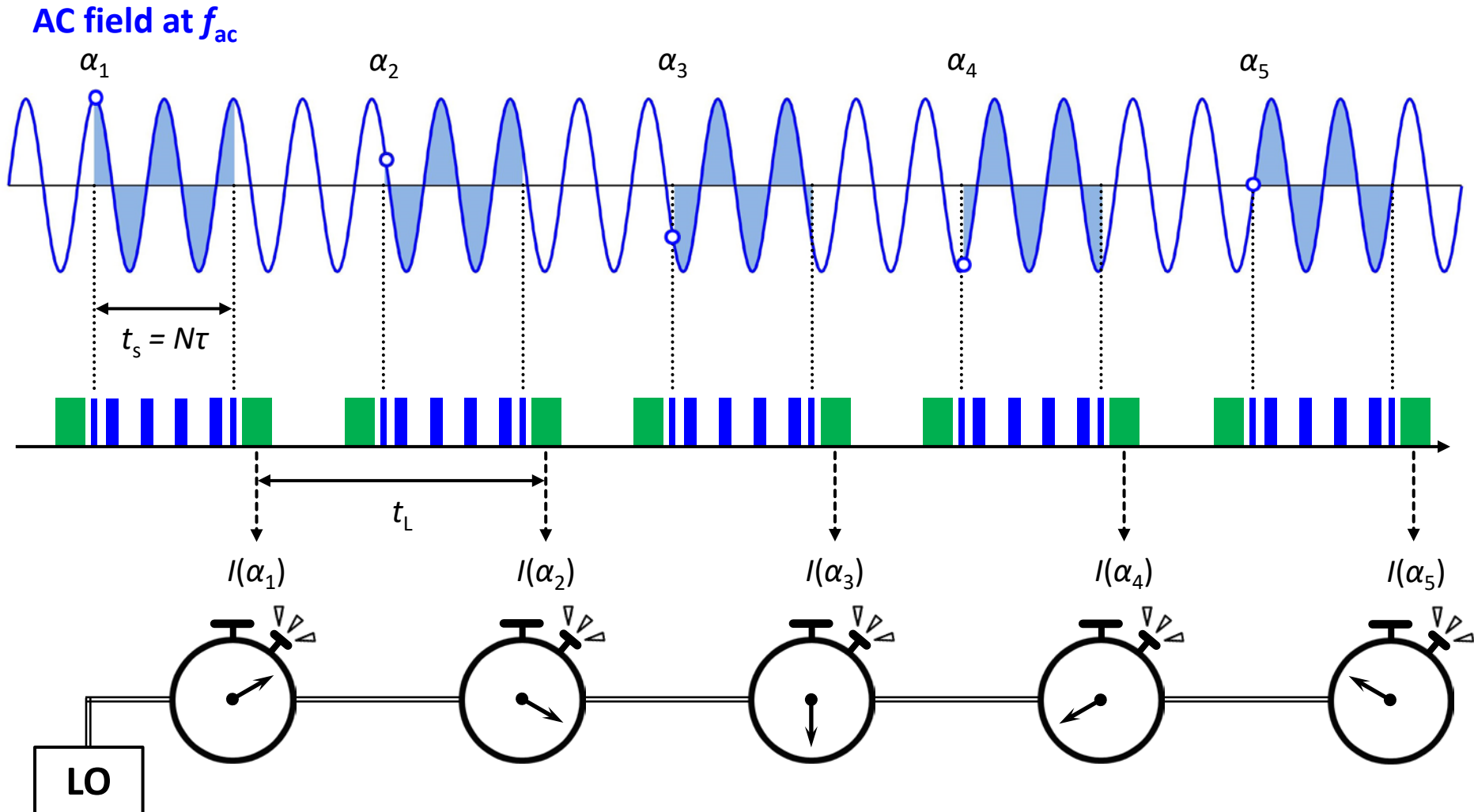
- φ depends on the **initial phase α** of the AC field ($\varphi \propto \cos \alpha$)
- Average over **random α**

Ultrahigh resolution sensing



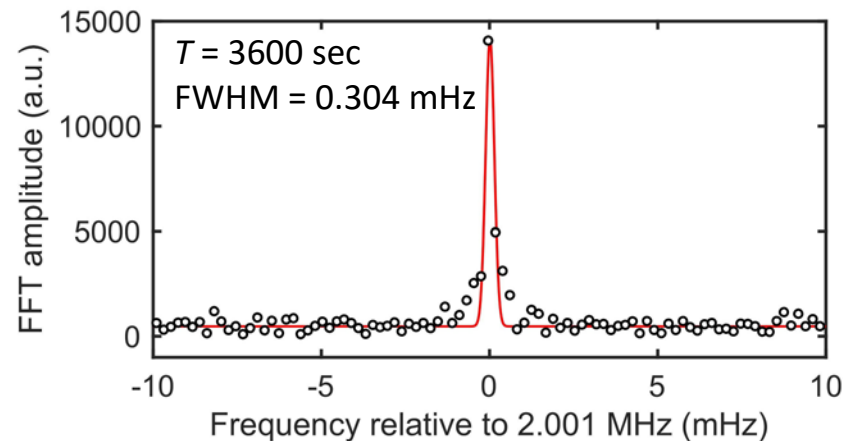
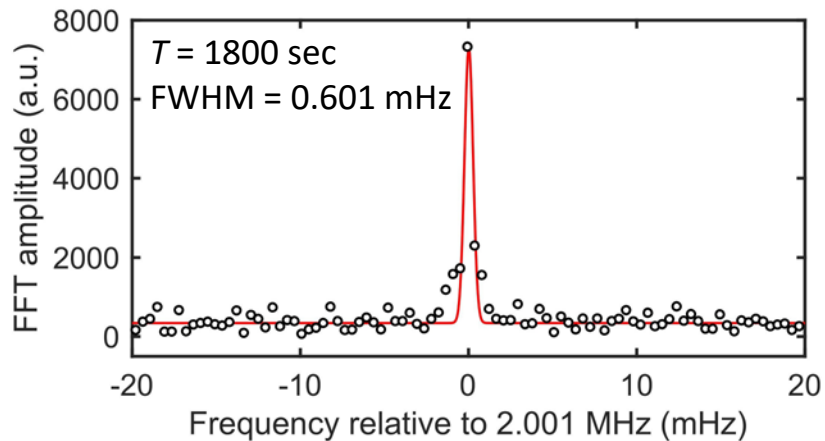
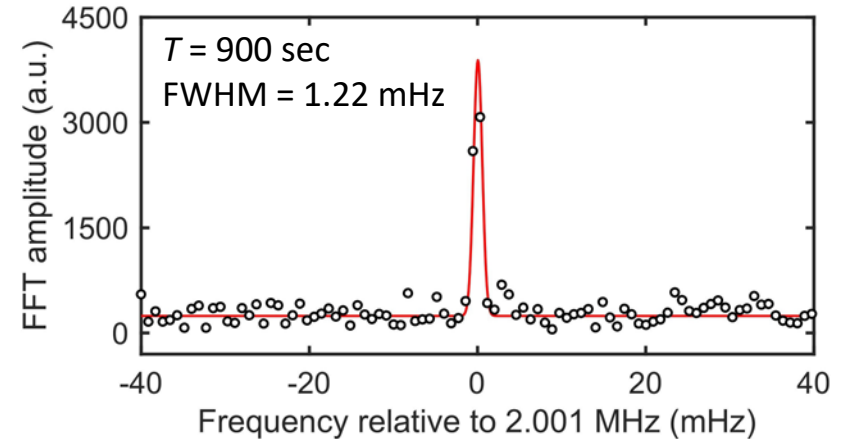
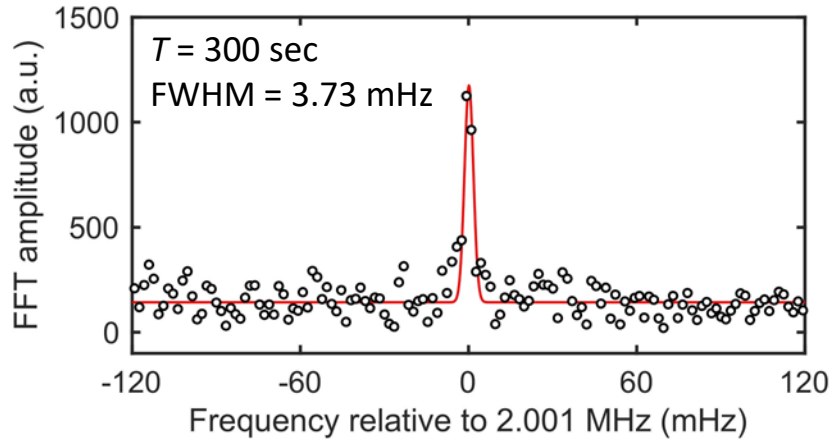
- φ depends on the **initial phase α of the AC field** ($\varphi \propto \cos \alpha$)
- Average over **random α**
- **If the data acq. is periodic**, adjacent α 's are related by $\alpha_{k+1} = 2\pi f_{ac} t_L + \alpha_k$

Ultrahigh resolution sensing

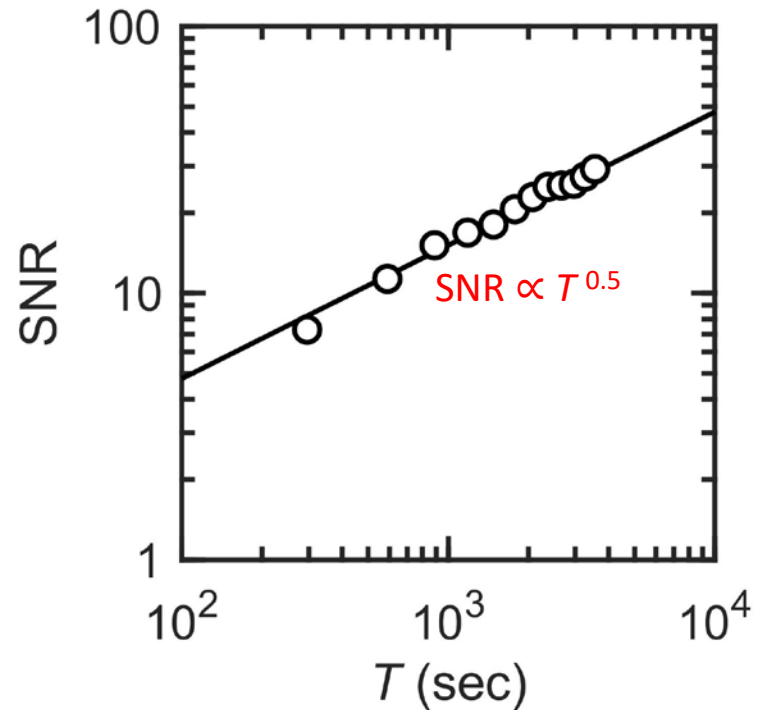
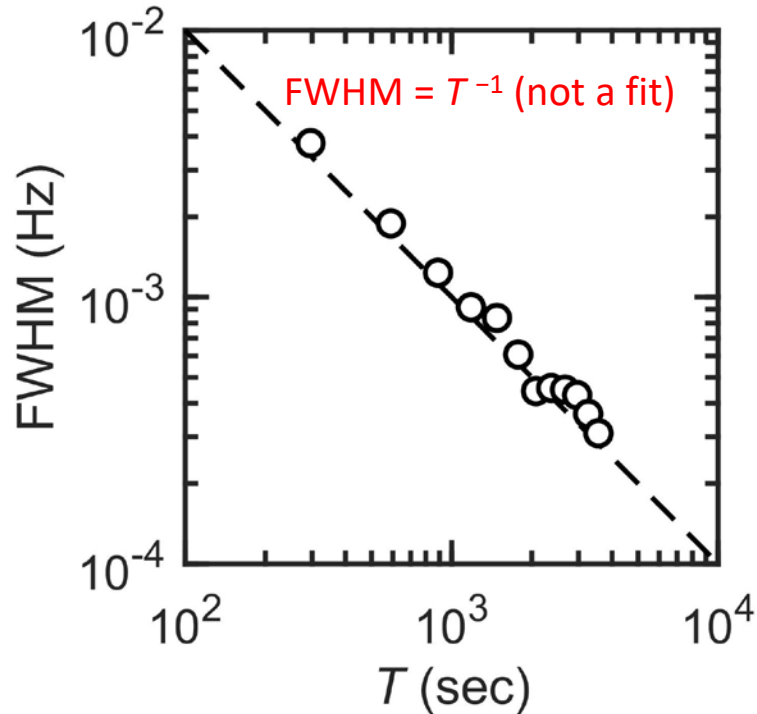


Ultrahigh resolution sensing

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



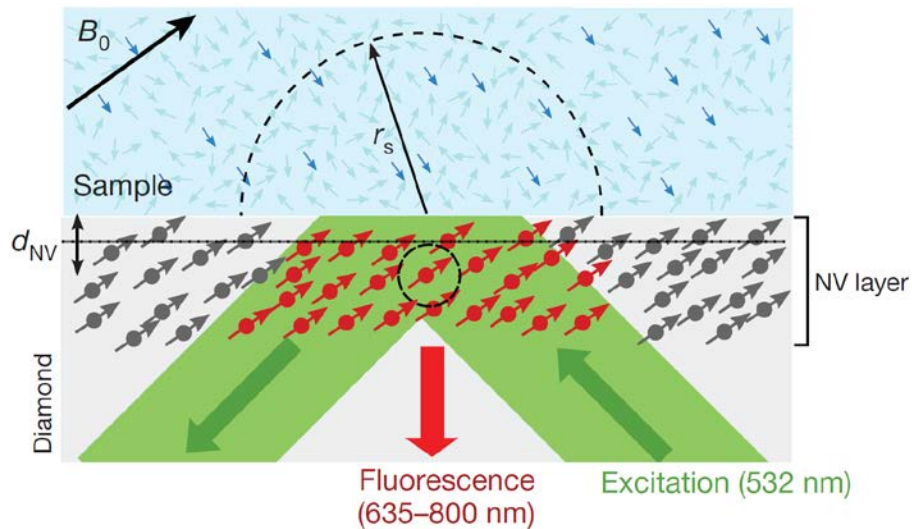
Ultrahigh resolution sensing



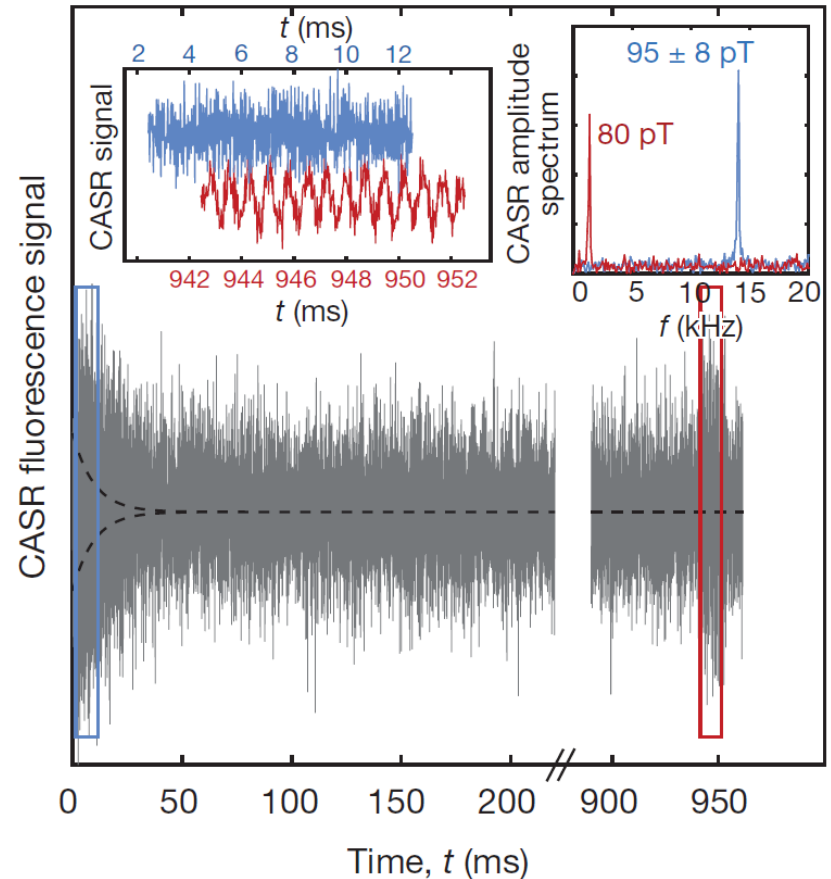
- Spectral resolution not limited by sensor/memory lifetimes ($T_{2e/n}$, $T_{1e/n}$)
- Only limited by the stability of LO (essentially infinite)
- Resolution = T^{-1} & SNR $\propto T^{0.5}$ \rightarrow Precision $\propto T^{-1.5}$

NMR spectroscopy

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



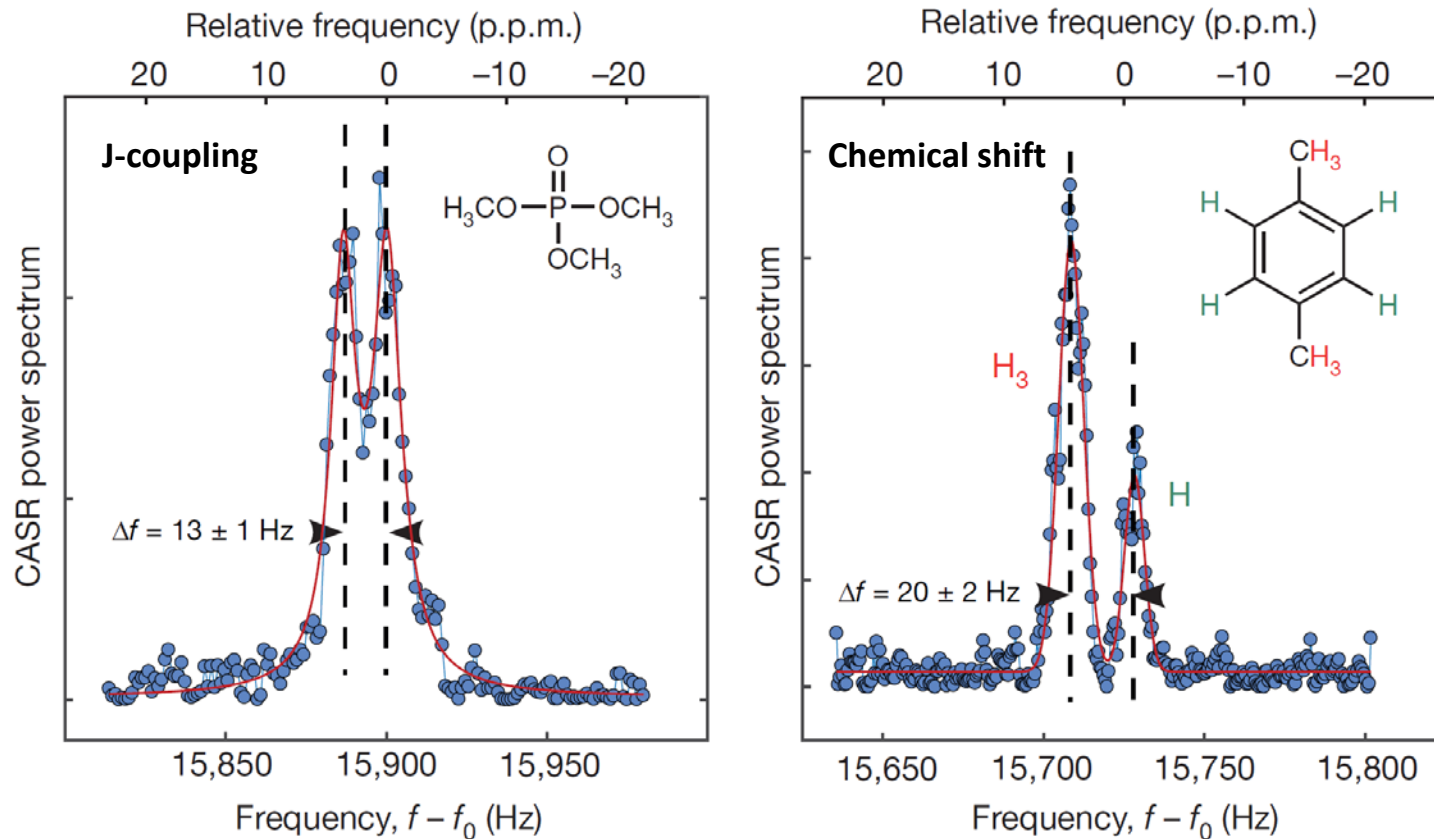
- $[NV] \approx 3 \times 10^{17} \text{ cm}^{-3}$
- # of NV $\approx 5 \times 10^9$
- $V_{\text{detect}} \approx 25 \text{ pL}$
- # of protons $\approx 2.5 \times 10^{15}$
- RF pulse \rightarrow FID



See also: Science **357**, 67 (2017) Aslam *et al.* (Wrachtrup, Stuttgart)
 $[B_0 = 3 \text{ T}, f_e = 87 \text{ GHz}, T_{1n} = 260 \text{ s}]$

NMR spectroscopy

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



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

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

Summary

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

[1] *Phys. Rev. B* **98**, 121405 (2018) Sasaki *et al.* (Keio)

[2] *Phys. Rev. Lett.* **121**, 170801 (2018) Zopes *et al.* (ETH)

[3] *Nature* **576**, 411 (2019) Abobeih *et al.* (Delft)

[4] *Science* **356**, 832 (2017) Schmitt *et al.* (Ulm)

[5] *Science* **356**, 837 (2017) Boss *et al.* (ETH)

[6] *Nature* **555**, 351 (2018) Glenn *et al.* (Harvard)

[7] *Science* **357**, 67 (2017) Aslam *et al.* (Stuttgart)

[8] *Nature Commun.* **10**, 594 (2019) Pfender *et al.* (Stuttgart)

[9] *Nature* **571**, 230 (2019) Cujia *et al.* (ETH)