Quenching spin decoherence in diamond and single-molecule magnets

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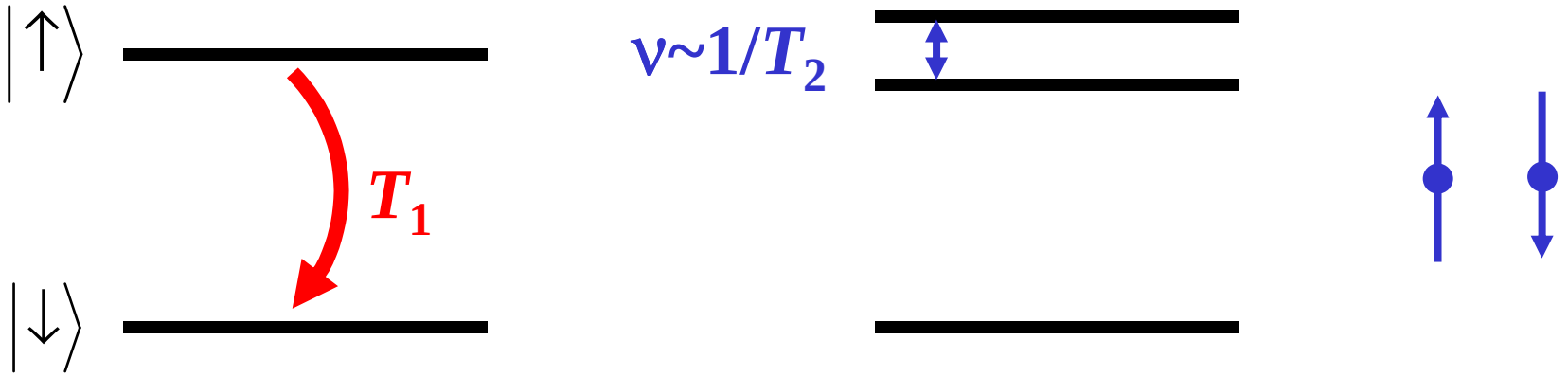
Spin relaxation times T_1 and T_2

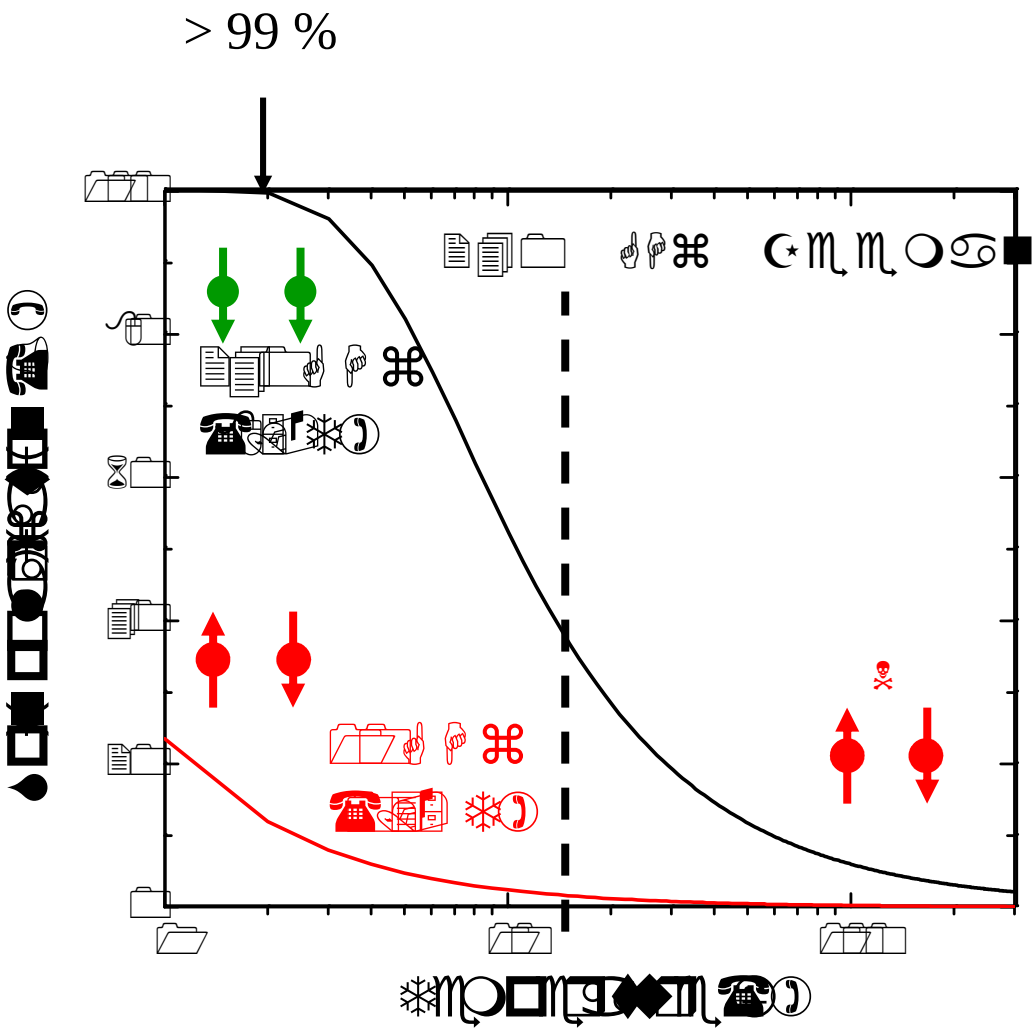
- T_1: Relaxation from the excited state to the ground state. The total magnetization is changed (Energy-costing process). Typically caused by spin-lattice interactions.

- T_2: Phase relaxation of spin precession. The total magnetization is NOT changed (Energy-conserving process). Typically caused by temporal spin-spin interactions (spin flip-flop).



High frequency EPR

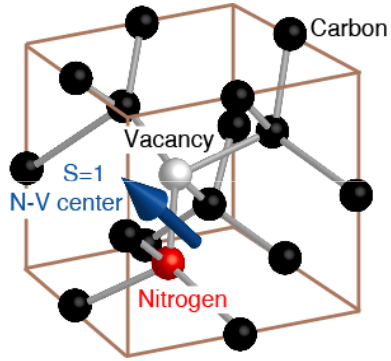
- Spin polarization @ 2K
  - 240 GHz: 99.4 %
  - 10 GHz: 12 %
- Spin flip-flops are main decoherence source.
- Spin flip-flop rate ∝ # of the up- and down-spin pair
- High polarization suppress spin decoherence



Outline

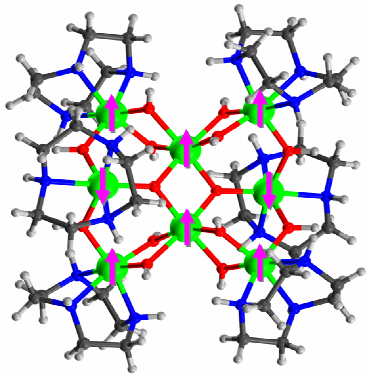
1. EPR with VDI source (P~30 mW)

- NV centers in diamond



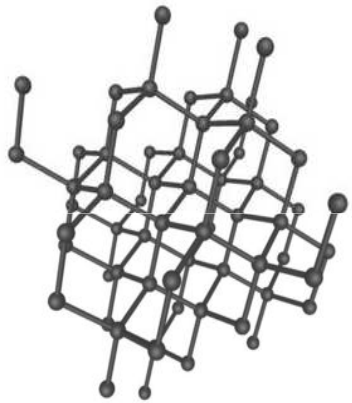
- Single-molecule magnets

2. FEL-based pulsed EPR (P~1kW)

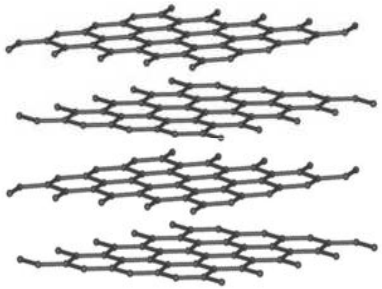


Diamond and impurities

- Hardest material
- Excellent thermal conductor
- A diamond is a crystal of tetrahedrally bonded carbon atoms.
- Diamond is classified by impurity contents.



Diamond

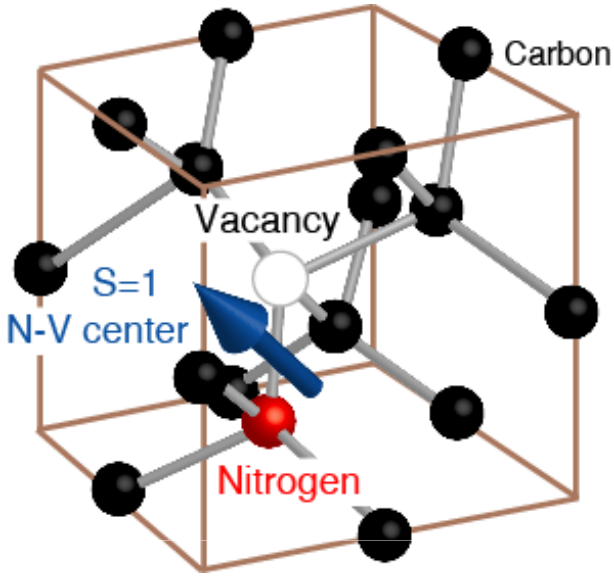


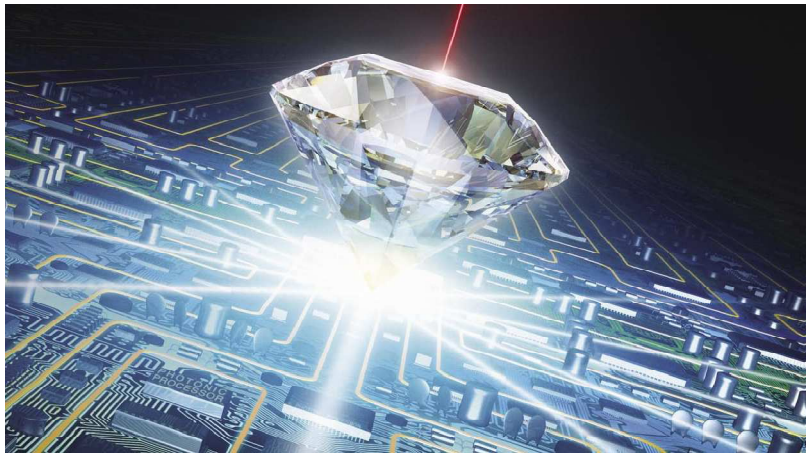
Graphite

Type	Ia	Ib	IIa	IIb
Natural abundance	~98 %	~0.1 %	1~2 %	~0 %
Nitrogen (ppm)	~2◈10^3	1~10^2	~1	~1
Others (ppm)				~100 (B)
Color	Clear~Yellow	Yellow	Clear	Blue

NV centers in Diamond

- Quantum information processing
- Single photon source
- Single spin read-out
- Rapid spin polarization
- Long spin coherence time at room temperature
  - T. A. Kennedy *et al.*, *Appl. Phys. Lett.* **83**, 4190 (2003)
  - T. Gaebel *et al.*, *Nature Phys.* **2**, 408 (2006)

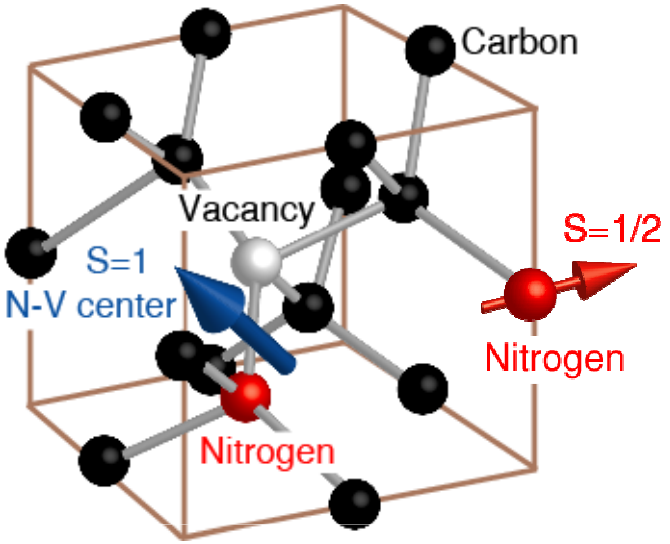


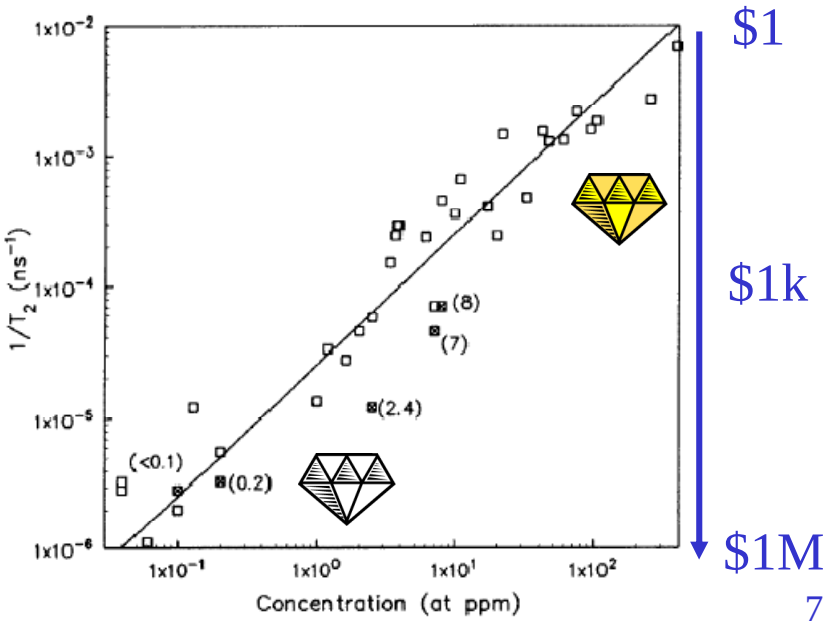


(D. D. Awschalom *et al.*, *Scientific American* October 2007)

Decoherence of NV center

- N electron spin flip-flops
  - J. A. van Wyk *et al.*, *J. Phys. D: Appl. Phys.* **30**, 1790 (1997).
  - T. A. Kennedy *et al.*, *Appl. Phys. Lett.* **83**, 4190 (2003)
  - R. Hanson *et al.*, *Phys. Rev. B* **74**, 161203R (2006))
- No temperature dependence of T_2 @ 10 GHz
  - E. C. Reynhardt *et. al.*, *J. Chem. Phys.* **109**, 8471 (1998))



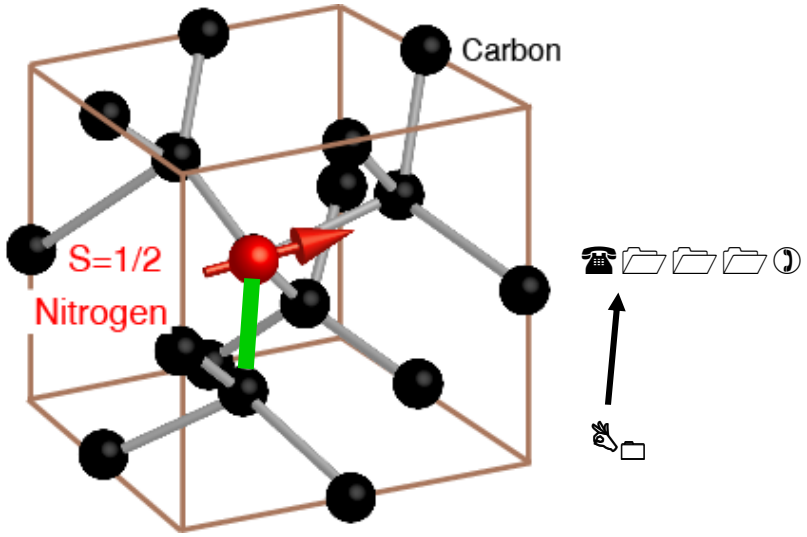


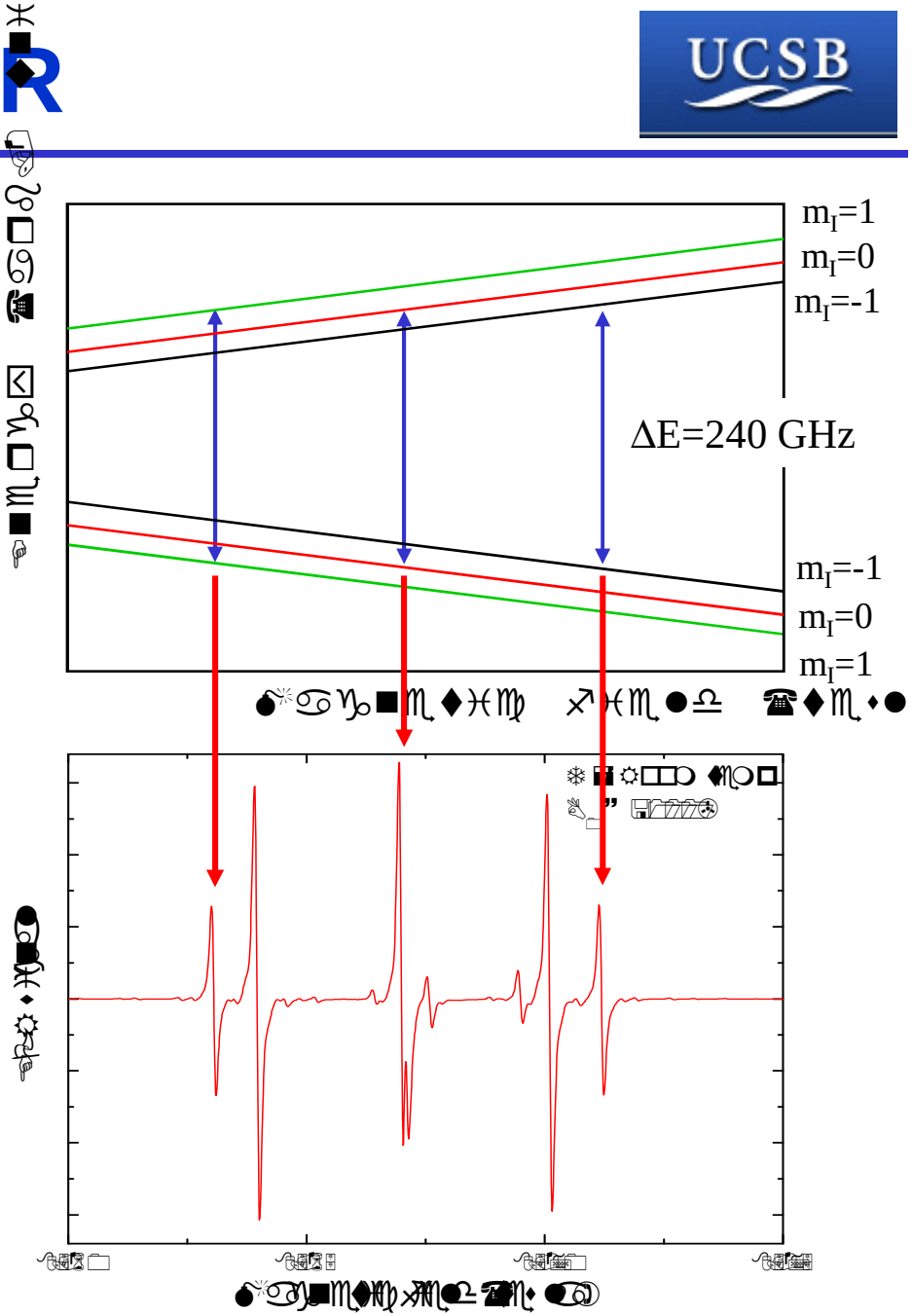
Continuous wave EPR

- N (single N) (S=1/2)

$$H_N = g\mu_B \mathbf{B}\cdot\mathbf{S} + \mathbf{S}\cdot\overleftrightarrow{\mathbf{A}}\cdot\mathbf{I}$$

  - ^{14}N (I=1) hyperfine couplings





Continuous wave EPR

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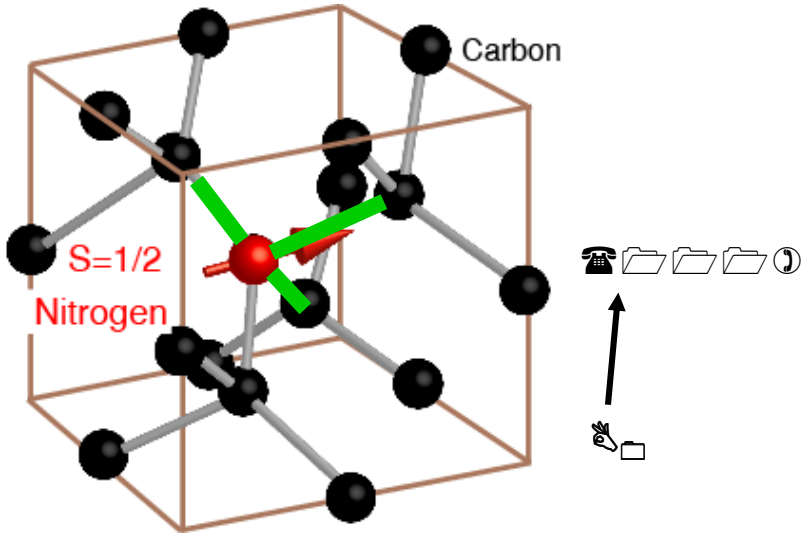
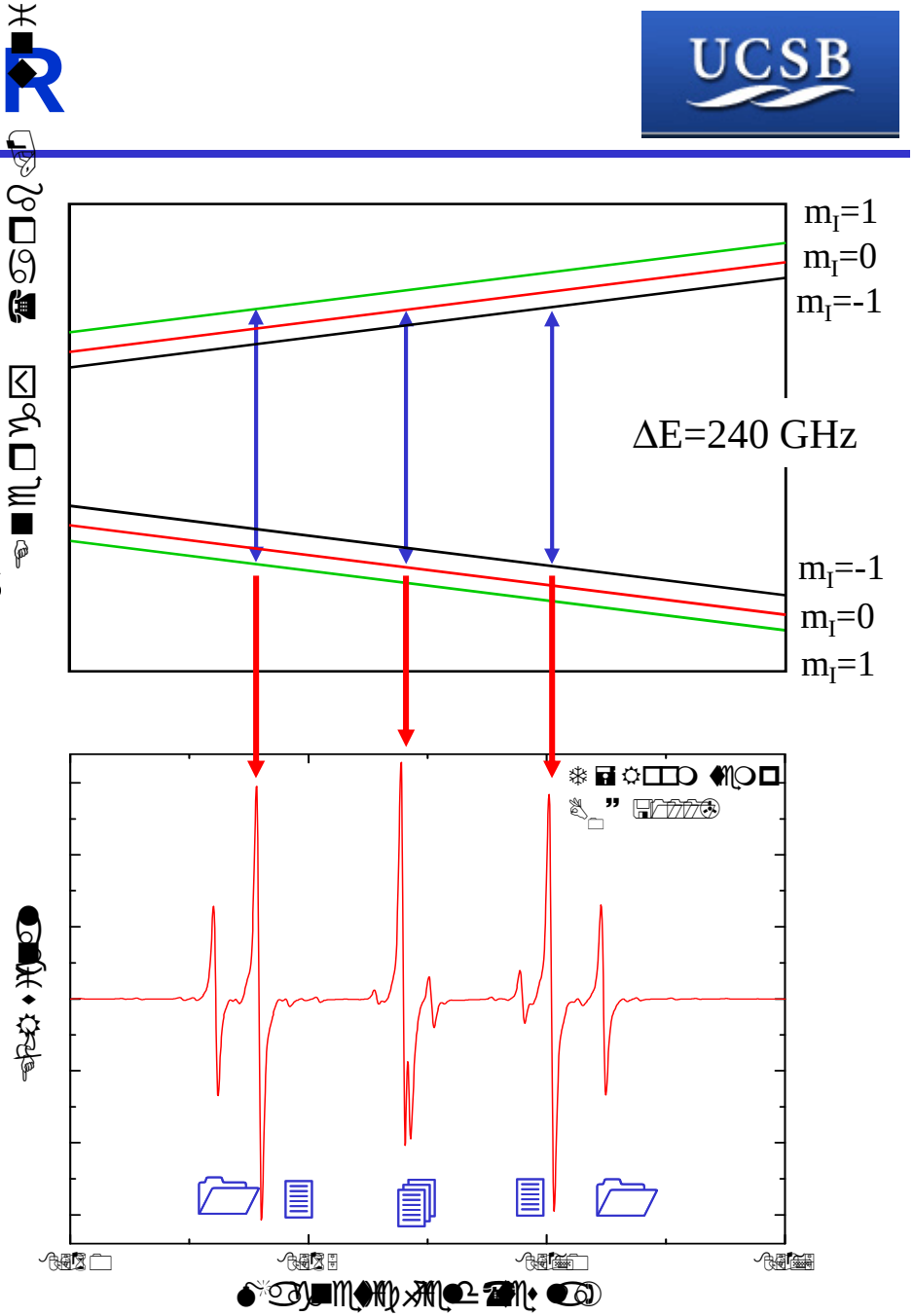
$$H_N = g\mu_B \mathbf{B}\cdot\mathbf{S} + \mathbf{S}\cdot\overleftrightarrow{\mathbf{A}}\cdot\mathbf{I}$$

  - ^{14}N (I=1) hyperfine couplings
  - Signal ratio=1:3:4:3:1



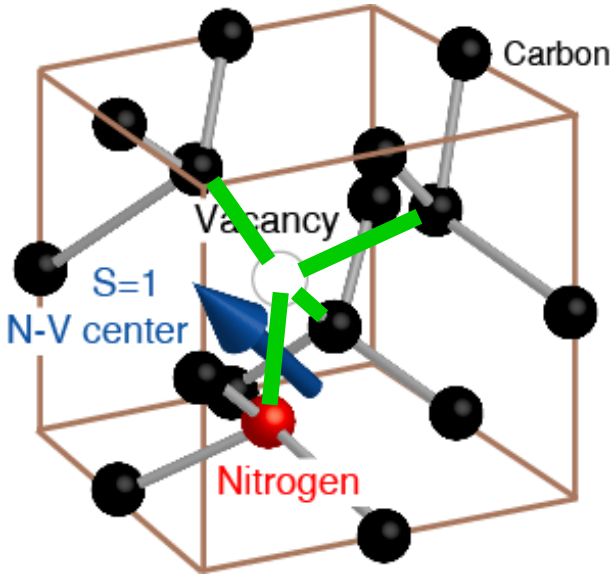


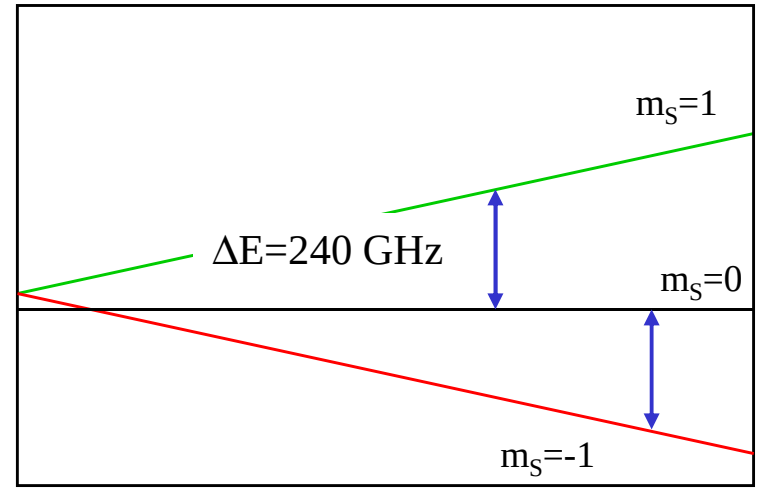
Continuous wave EPR

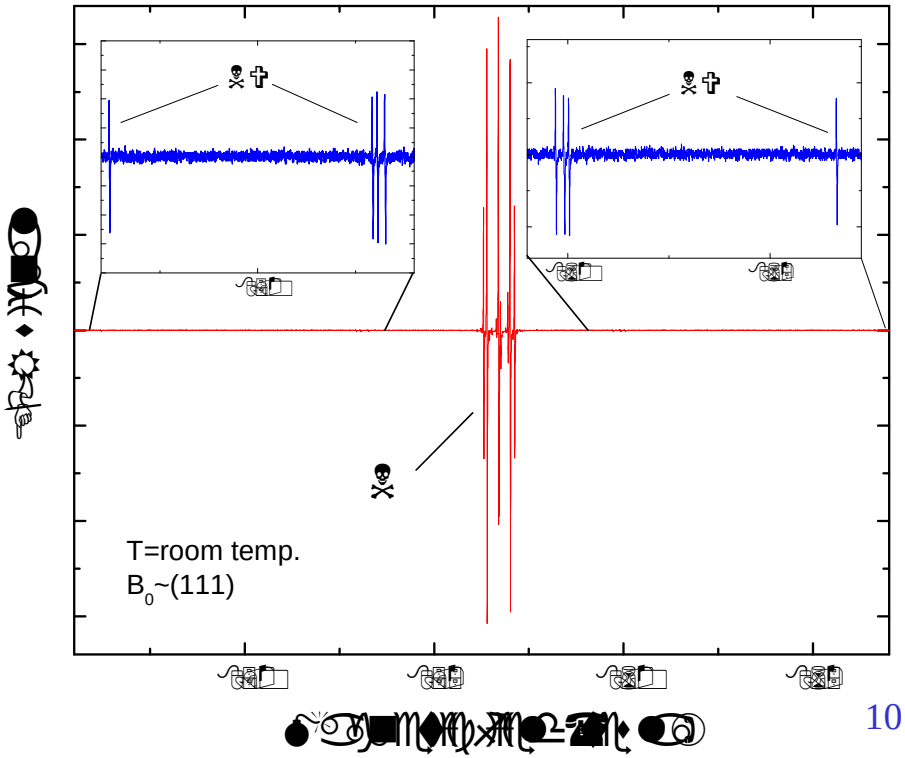
- NV center (S=1)

$$H_{NV} = g\mu_B \mathbf{B}\cdot\mathbf{S} + D(S_z^2 + 1/3S(S+1))$$

  - Zero-field splittings

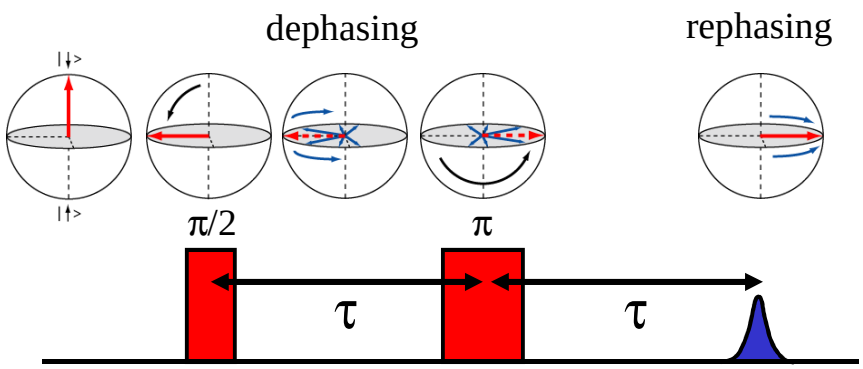






Temperature dependence of T_2

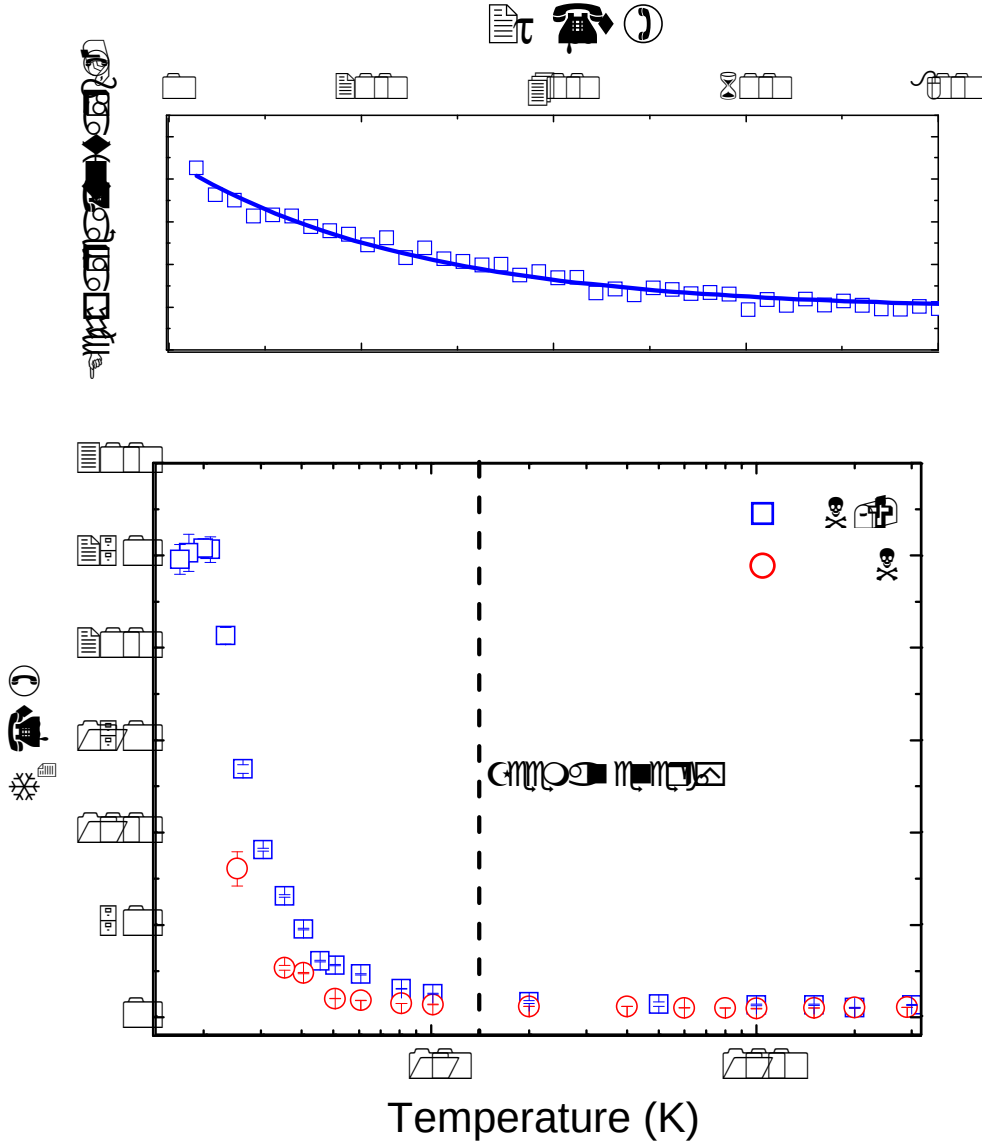
- Hahn echo sequence



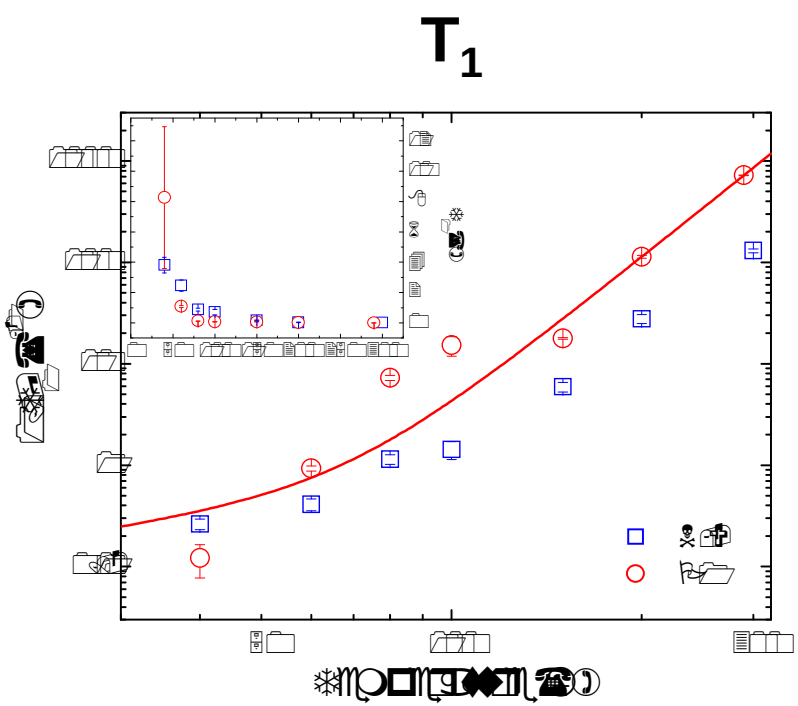
- T_2 is obtained by a single exponential fit

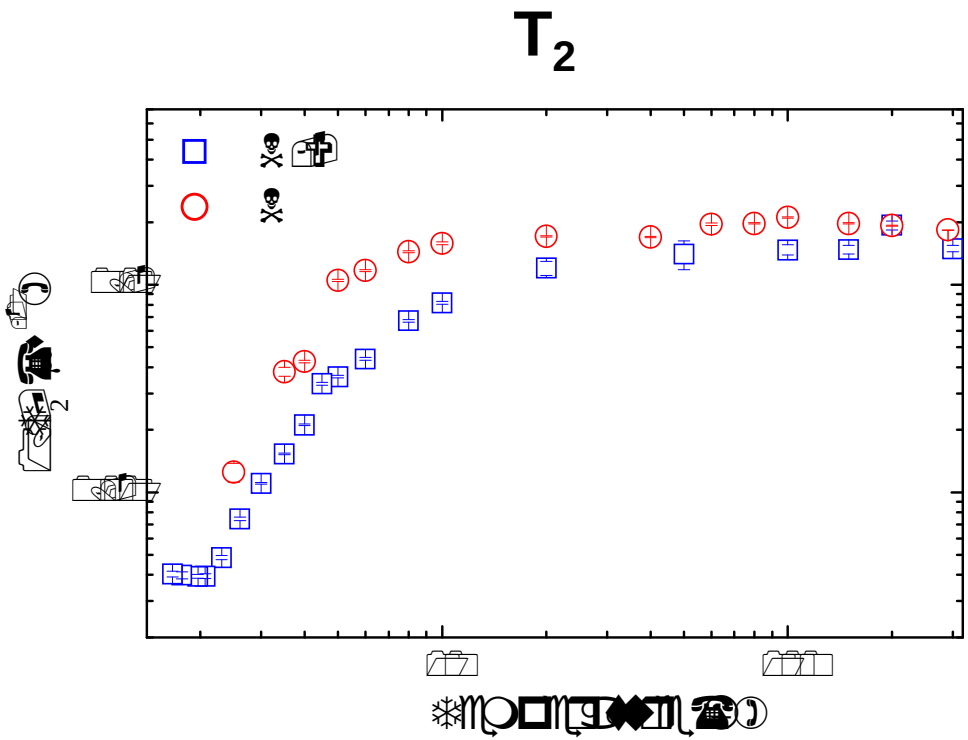
- N-V:
  - T>11.5 K : T_2 = 6.7 μs → 8.3 μs
  - T < 2 K : T_2 ~ 250 μs

- N:
  - T>11.5 K : T_2 = 5.5 μs → 5.8 μs
  - T = 2.5 K : T_2 ~ 80 μs



Quenching spin bath decoherence





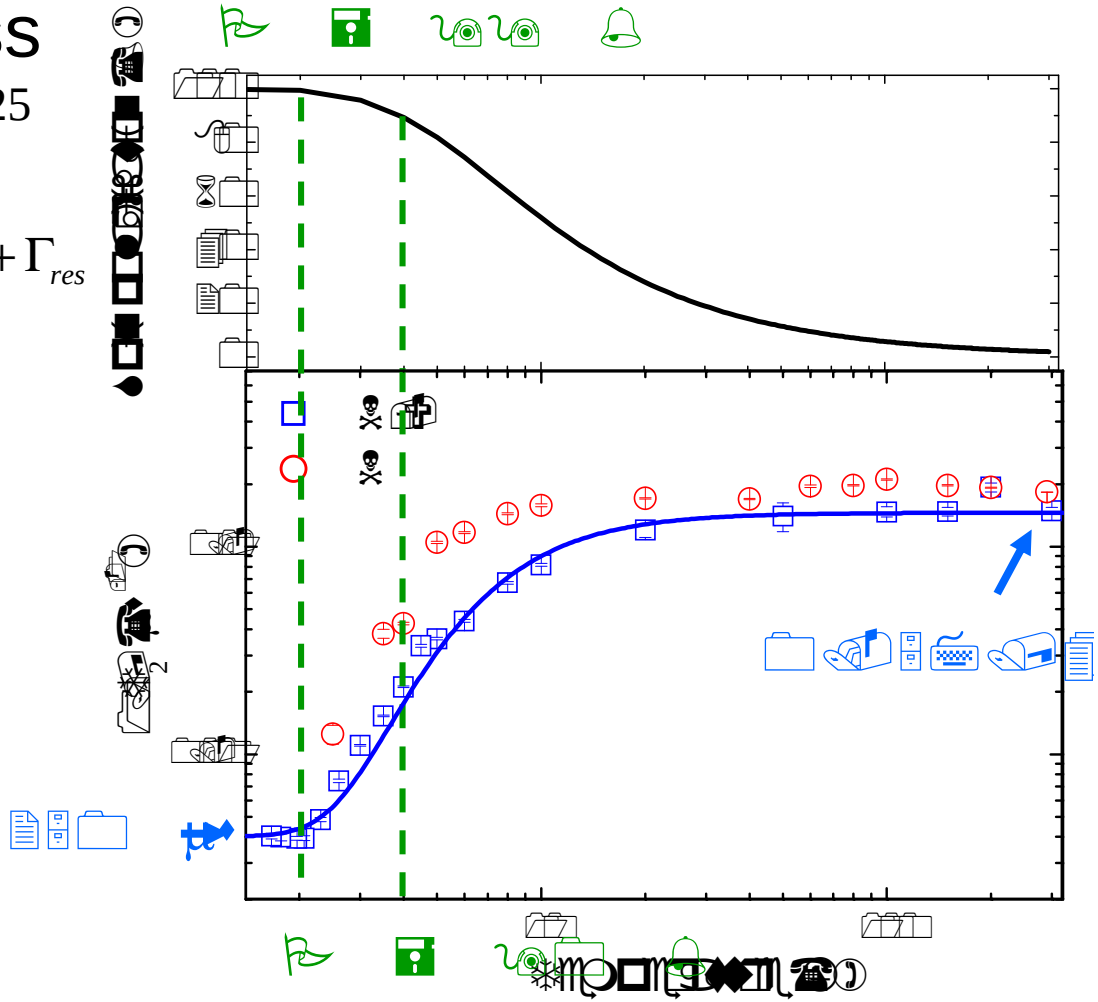
Quenching spin bath decoherence

- N spin flip-flop process

(C. Kutter *et. al.*, *Phys. Rev. Lett.* **74**, 2925 (1995))

$$\frac{1}{T_2} = CP_{\uparrow}P_{\downarrow} + \Gamma_{res} = \frac{C}{(1+e^{T_{Ze}/T})(1+e^{-T_{Ze}/T})} + \Gamma_{res}$$

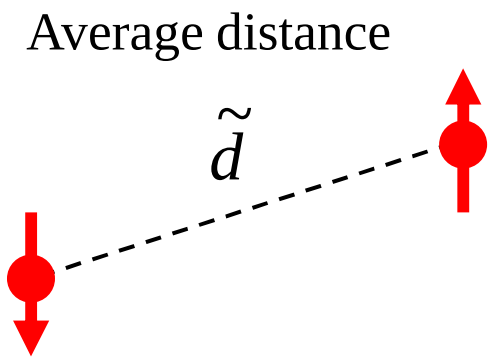
- 90 % for 10 x T_2
- 99 % for quenching
- C=0.57 MHz
- $1/\Gamma_{res}$ = 250 μs



Dipole-dipole interaction

- C=0.57 MHz

$$\frac{1}{T_2} \propto P_\uparrow P_\downarrow + \Gamma_{res} = \frac{C}{(1+e^{T_{Ze}/T})(1+e^{-T_{Ze}/T})} + \Gamma_{res}$$



- Dipole-dipole interaction energy

$$C = \frac{U_d}{h} \cong \left\langle \frac{\mu_0}{4\pi} \frac{\mathbf{m_1} \cdot \mathbf{m_2} - 3(\mathbf{n} \cdot \mathbf{m_1})(\mathbf{n} \cdot \mathbf{m_2})}{\tilde{d}^3} \right\rangle / h$$

- $\tilde{d}$ = 2.8 nm → N contents ~ 25 ppm

- The sample crystal = 10 ~ 100 ppm

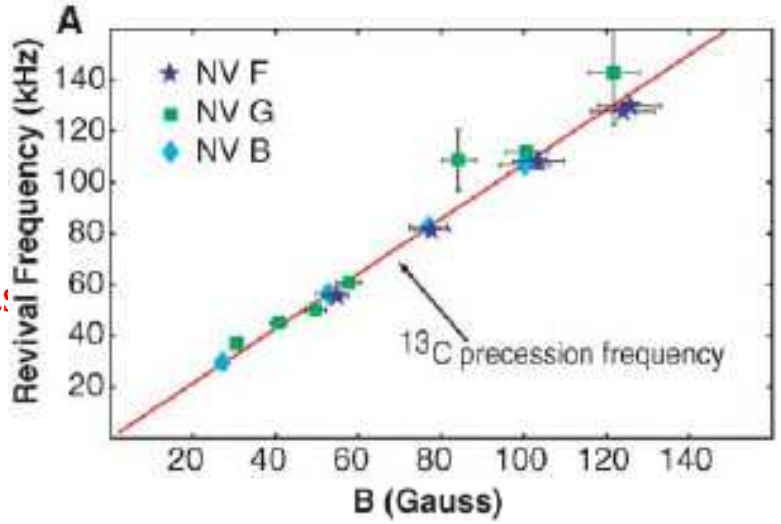
- **T_2-based distance measurement (Future plans)**

^{13}C nuclear spin bath fluctuations

- $1/\Gamma_{res}$ = 250 μs: Temperature independent relaxation rate

$$\frac{1}{T_2} \propto P_{\uparrow}P_{\downarrow} + \Gamma_{res} = \frac{C}{(1+e^{T_{Ze}/T})(1+e^{-T_{Ze}/T})} + \Gamma_{res}$$

$1/\Gamma_{res}$= 250 μs



L. Childress *et al.*, *Science* **314** 281 (2008)

- Decoherence time caused by ^{13}C nuclear spin flip-flop process

$$\frac{1}{T_2} = 0.49\sqrt{\frac{\gamma_e}{\gamma_n}}\frac{\Delta\omega_{nn}}{[I(I+1)]^{1/4}} \sim \gamma_e^{1/2}\gamma_n^{3/2}N[I(I+1)]^{1/4}$$

where $\Delta\omega_{nn}$ is NMR linewidth, N is the number of nuclear per volume.

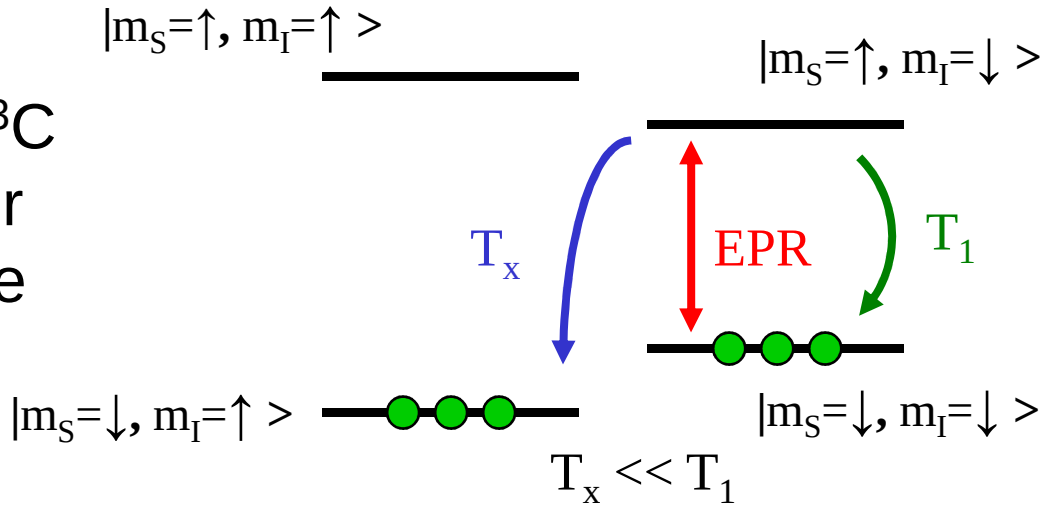
(I. M. Brown, Time domain electron spin resonance, p195, Wiley (1979).
A. Schweiger and G. Jeschke, Oxford university press (2001)).

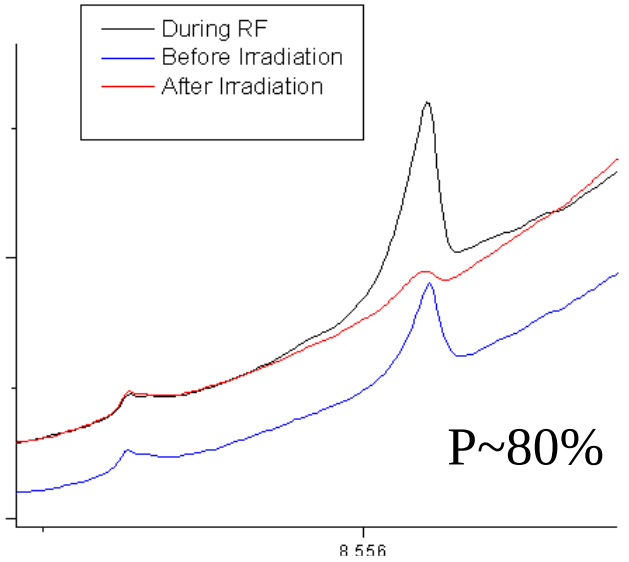
- T_2 ~ 380 μs for ^{13}C nuclear spin bath fluctuations

S. Takahashi *et al.*, *Phys. Rev. Lett.* **101**, 047601 (2008)

Polarizing ^{13}C nuclear spins

- Suppress fluctuations of ^{13}C nuclear spin bath to further increase spin decoherence time.
- Dynamic nuclear polarization (DNP) may be able to polarize the nuclear spin bath.
- High polarization of N electron spins is a key.





A. van Rynbach, S. Takahashi, J. van Tol *et al.*, unpublished

Summary - diamond

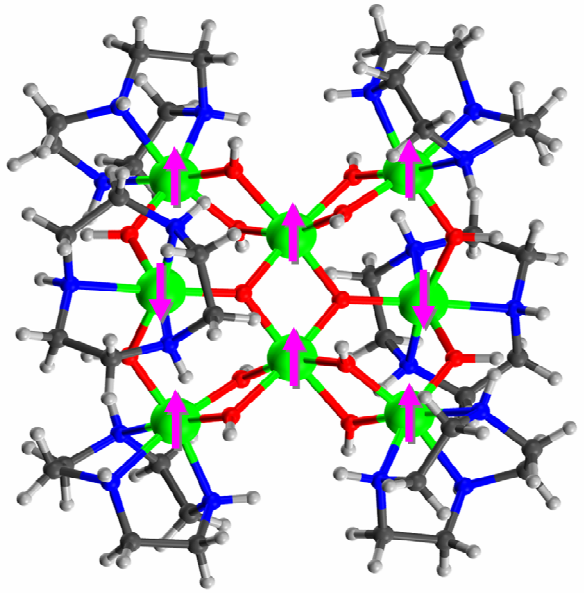
- We demonstrated that spin decoherence of electron spin bath can be quenched by high-fields and low-temperatures.
- We can access a nuclear spin bath decoherence.
- Temperature dependence of T_2 is potentially useful for distance measurements.

Outline

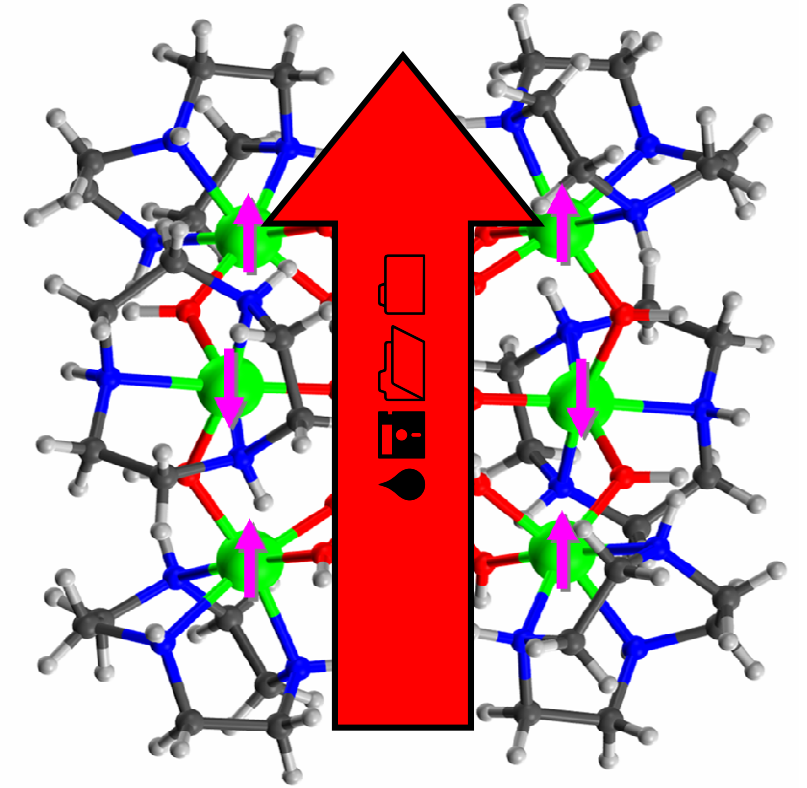
1. **EPR with VDI source (P~30 mW)**

- NV centers in diamond
- **Single-molecule magnets**

2. FEL-based pulsed EPR (P~1kW)



Single-molecule magnets



● : Fe^{3+} (S=5/2) ● : O ● : N

● : C ● : H

K. Wieghardt *et al.*, G. Angew. Chem., Int. Ed. Engl. 23, 77 (1984).

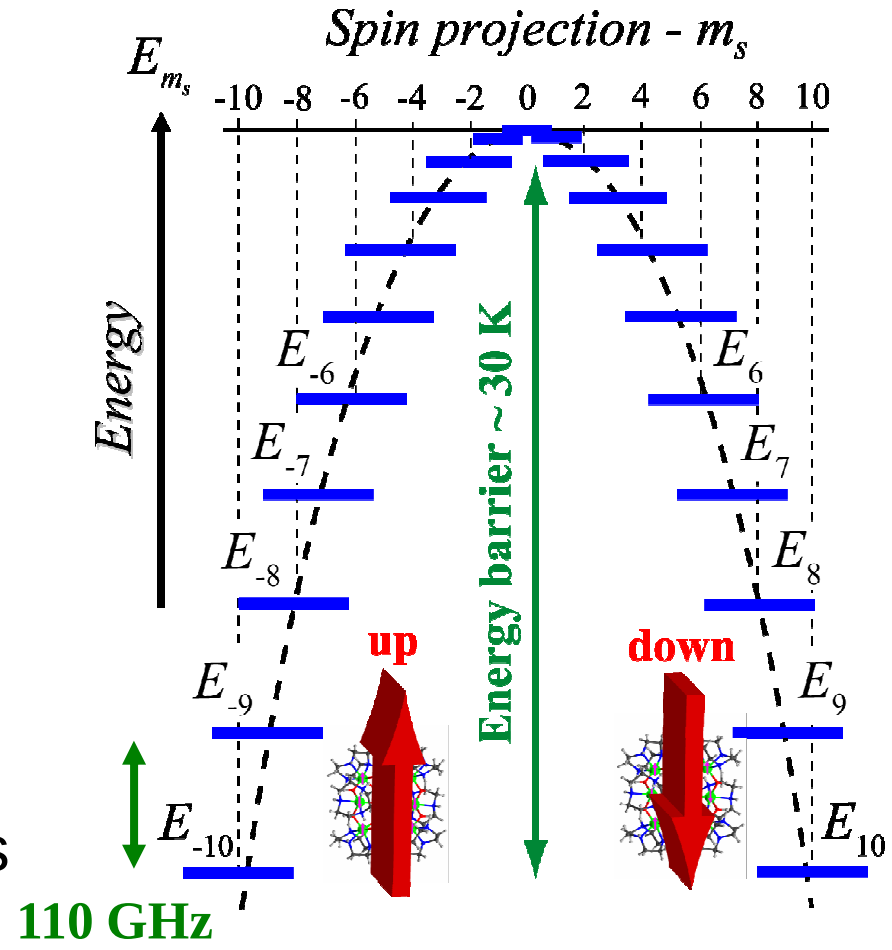
$[Fe_8O_2(OH)_{12}(C_6H_{15}N_3)_6]Br_7(H_2O)Br\cdot 8H_2O$

- High-spin molecular magnets made by metal-ion clusters
- Chemically fabricated quantum dots
- S=10 Fe_8 SMM

  Total spin = (6-2)×5/2=10
- Weakly interacts with each other, ensemble properties express themselves as a pseudo-giant single spin.

Energy barrier

- Anisotropy due to crystal field.
- For Fe_8, uniaxial anisotropy
- Energy barrier = DS_z^2 ~ 30K
- Superparamagnets at high T
- Magnetic relaxation becomes very slow at low T, so becomes magnets.



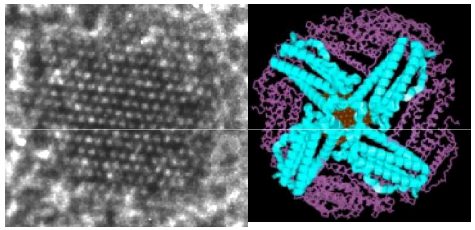
Quantum ↔ Classical

macroscale ⟷ nanoscale

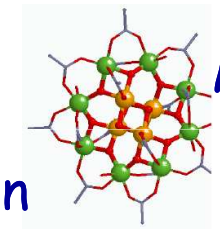
permanent magnets | micron particles | nanoparticles | clusters | Molecular clusters | Individual spins

100 nm | 10 nm | 1 nm

$S = 10^{23}$ 10^{10} 10^{8} 10^{6} 10^{5} 10^{4} 10^{3} 10^{2} 10 1



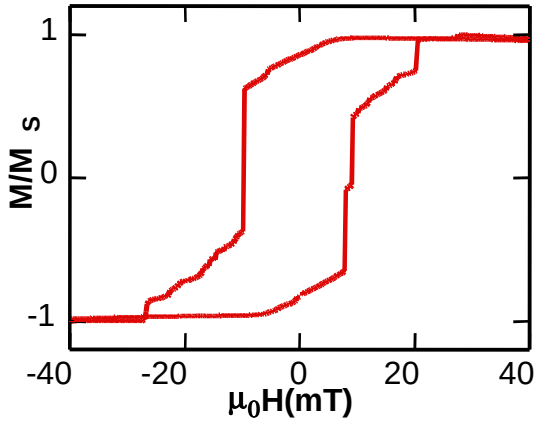
Ferritin



Mn_{12}-ac

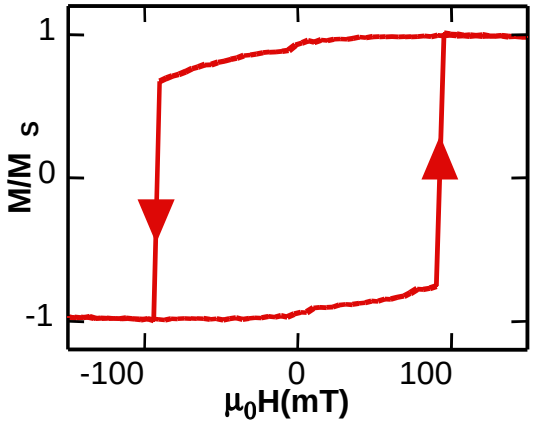
multi - domain

nucleation, propagation and annihilation of domain walls



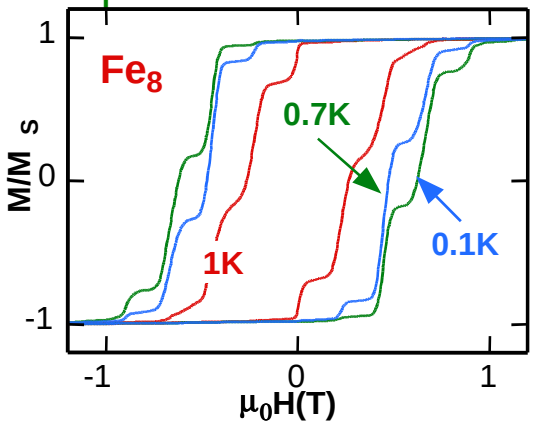
single - domain

uniform rotation



magnetic moment

quantum tunneling, quantum interference



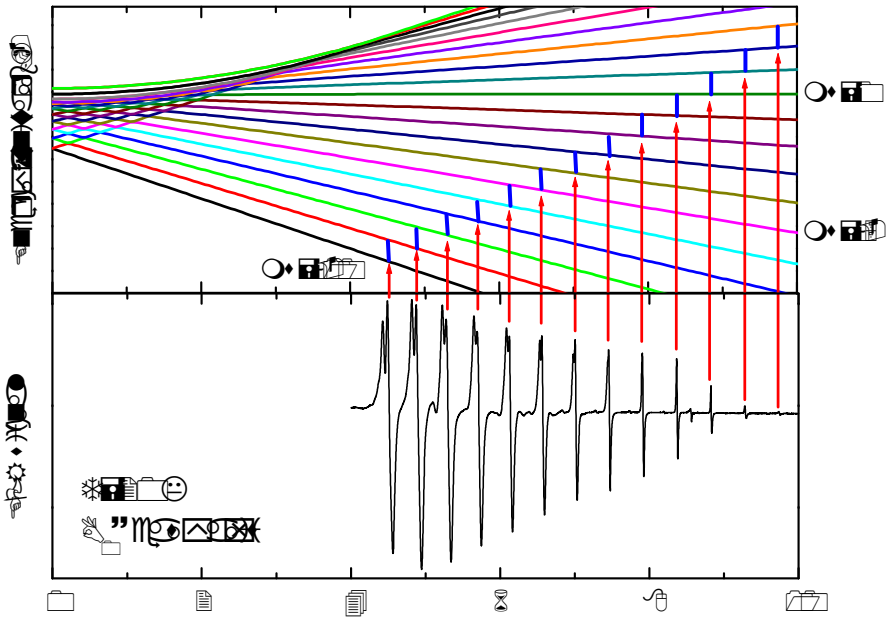
cw EPR – angle dependence

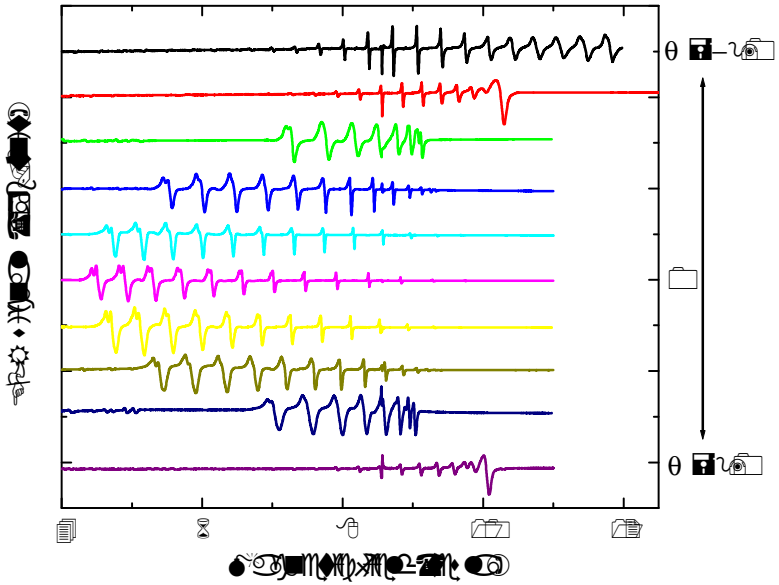
- Spin Hamiltonian for individual Fe_8 SMM

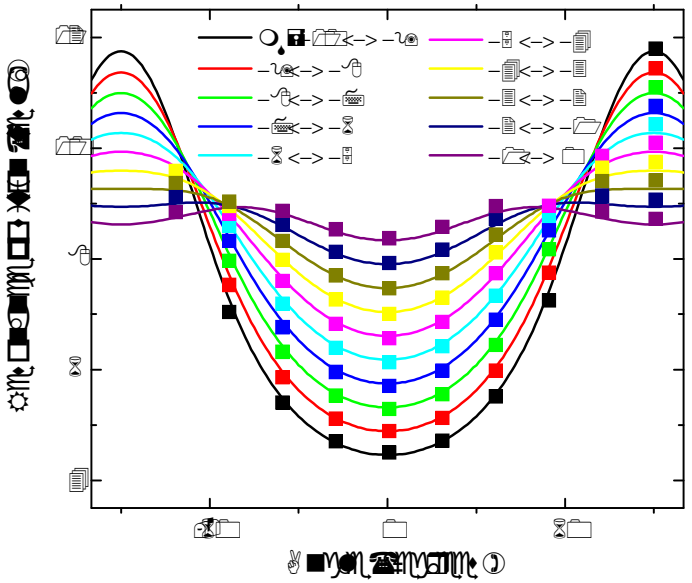
$$H = \mu_B g \mathbf{S} \cdot \mathbf{B_0} + DS_z^2 + E(S_x^2 - S_y^2)$$

g=2.00, D=-6.15 GHz, E=1.14 GHz

- A single crystal was rotated as function of a magnetic field.

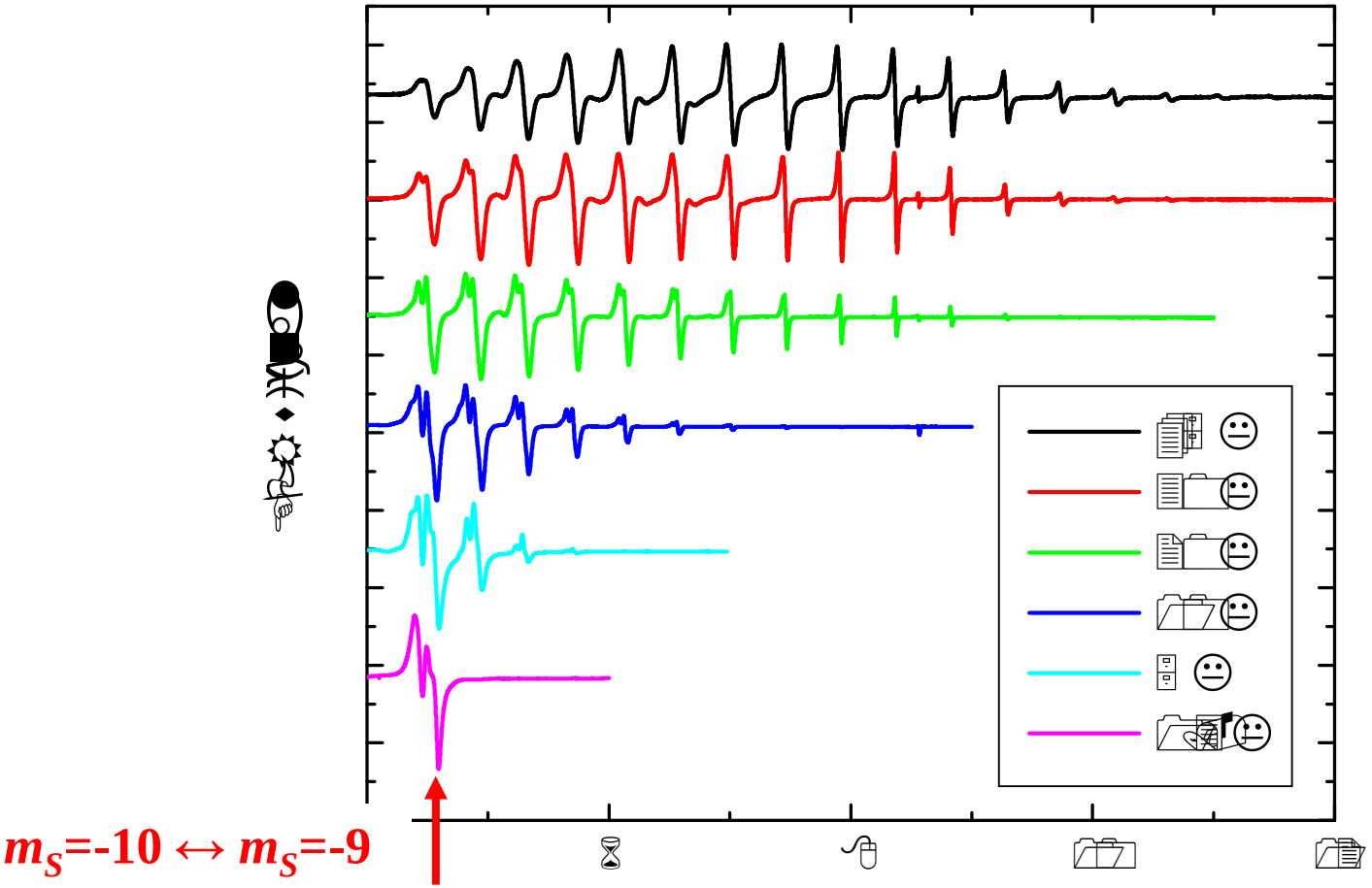






cw EPR – temperature dependence

- B ~ easy axis
- Indicates the ground state peak at 4.6 T.



Spin decoherence of SMMs

- No publication of spin echo from single-crystal SMMs.
- T_2 will be very short because of strong fluctuations of SMM spin bath.
- There are some observations of spin echo from highly diluted molecular magnets.

  C. Schlegel *et al.*, *Phys. Rev. Lett.* **101**, 147203 (2008).

  A. Ardavan *et al.*, *Phys. Rev. Lett.* **98**, 057201 (2007).

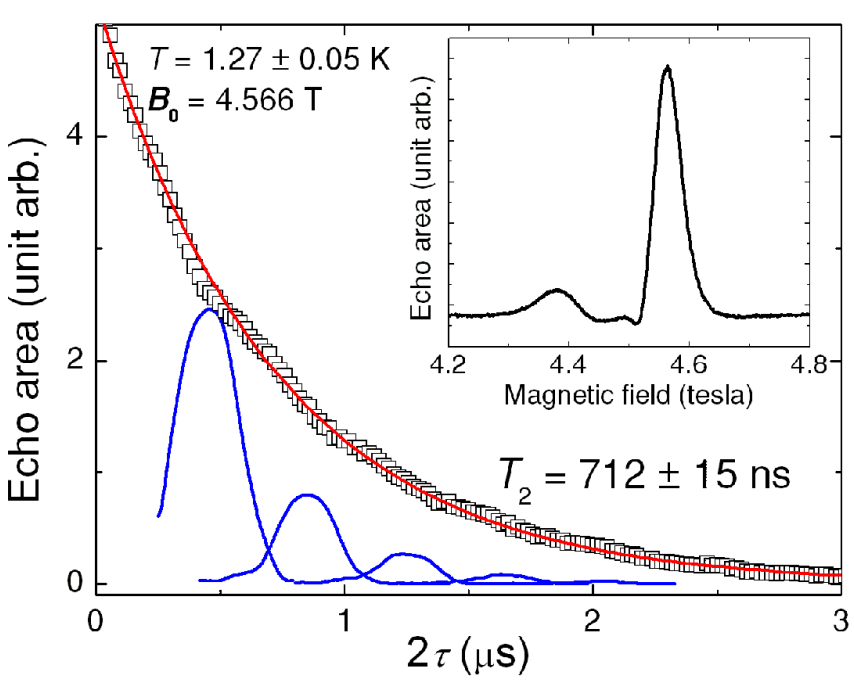
  S. Bertaina *et al.*, *Nature* **453**, 203 (2008).
- Fluctuations of electron spin bath can also be reduced by polarizing the spin bath.

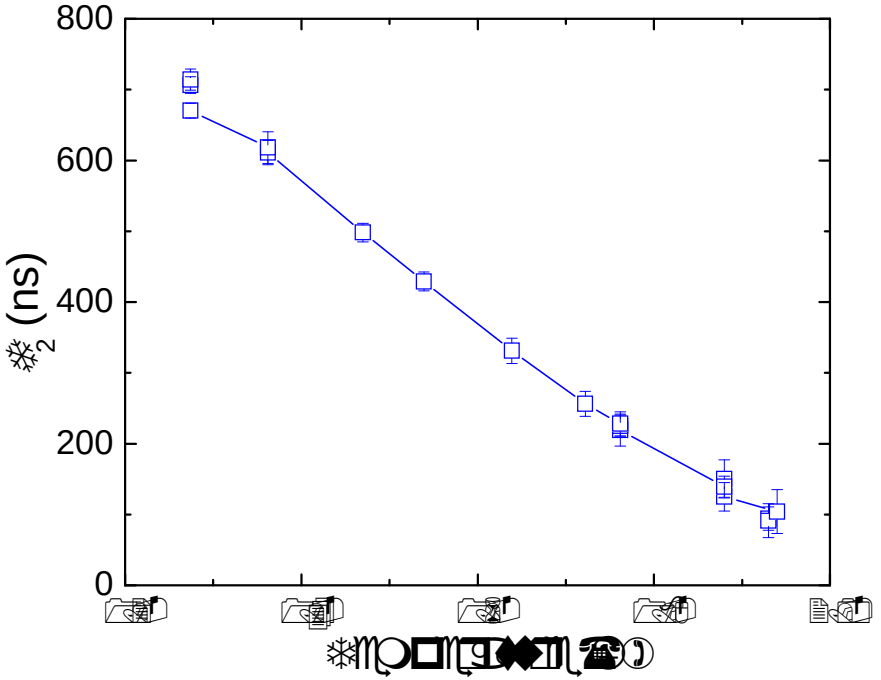
First spin echo measurement

- Strong temperature dependence indicates electron spin bath fluctuations.

- T_1 ~ 1 ms >> T_2

T_2 measurement





S=10 Fe_8 spin bath fluctuations

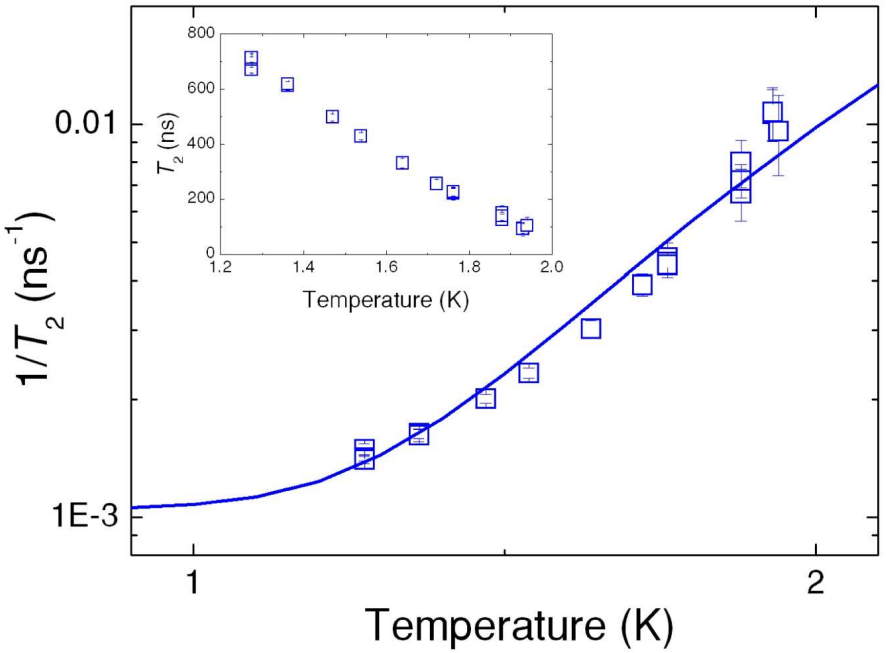
- S=10 spin flip-flop process:

$$\frac{1}{T_2} = A \sum_{m_S=-10}^{9} W(m_S)\, P_{m_S} P_{m_S+1} + \Gamma_{res}$$

$$P_{m_S} = \frac{e^{-\beta E(m_S)}}{Z}$$

$$W(m_S) = \left|\left\langle m_S+1, m_S \left| S_1^+ S_2^- \right| m_S, m_S+1 \right\rangle\right|^2$$

$$+ \left|\left\langle m_S, m_S+1 \left| S_1^- S_2^+ \right| m_S+1, m_S \right\rangle\right|^2$$



- Spin decoherence is significantly suppressed by spin polarization.

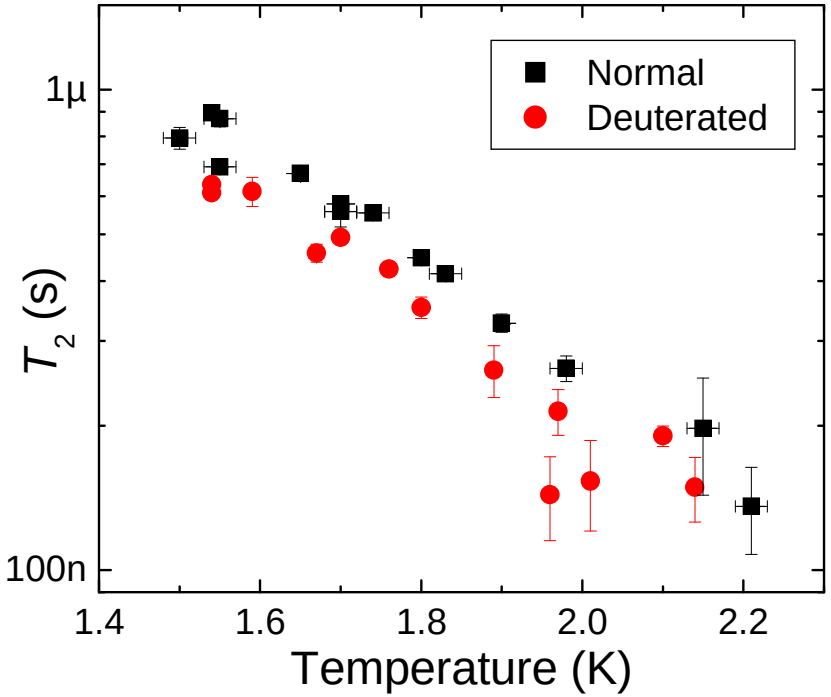
- Γ_{res} may be caused by couplings to nuclear moments (Proton & ^{57}Fe) and phonon.

S. Takahashi *et al.*, *Phys. Rev. Lett.*, in-press (2009) [arXiv:0810.1254]

No ^{1}H spin bath decoherence?

- Deuterated Fe_8 SMM was recently studied.
- Deuterium has much smaller magnetic moments than Hydrogen.
- Temperature dependence of T_2 is about same.
- A theory predicts that phonon decoherence >> nuclear decoherence.

  A. Morello *et al.*, *Phys. Rev. Lett.* **97**, 207206 (2006)



T_1 relaxation time

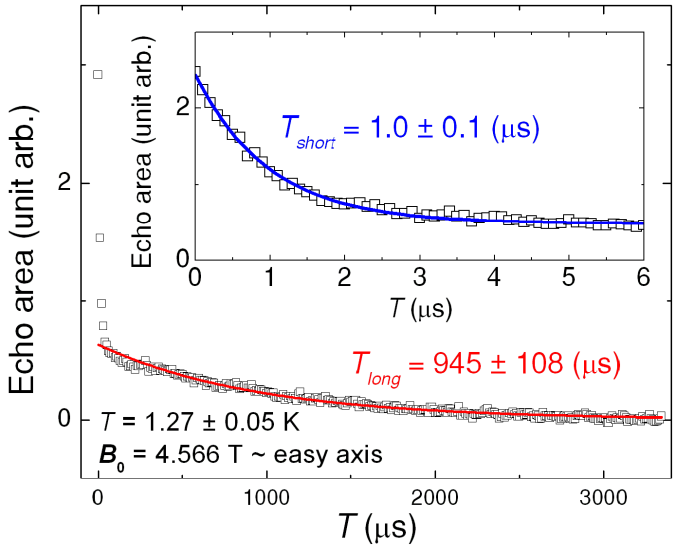
- Two decay curves have been measured.
- T_{long}: temperature-dependent (T_1)

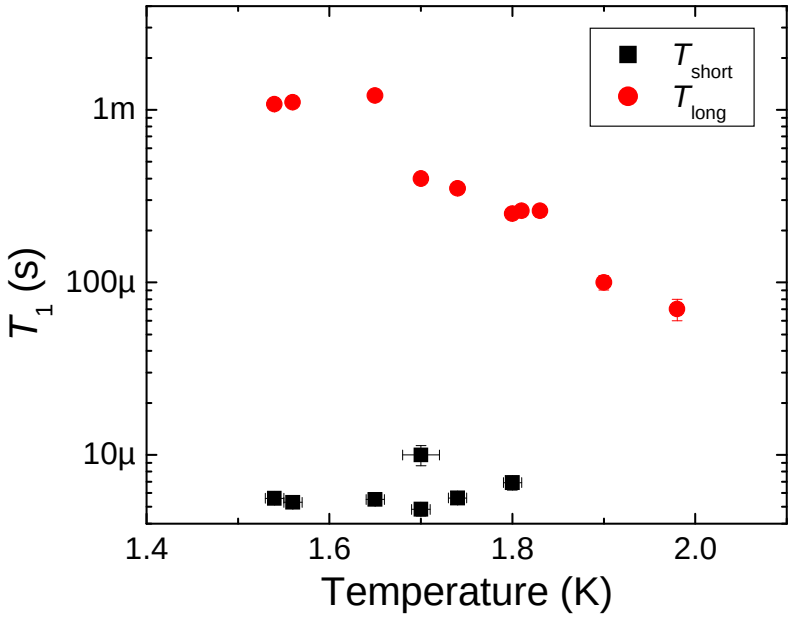
  Similar relaxation is reported by K. Petukhov *et al.*, Phys. Rev. B **75**, 064408 (2007).
- T_{short}: temperature-independent (Spectral diffusion?)
- Other T_1 measurements

~2 us: S. Bahr *et al.*, *Phys. Rev. Lett.* **99**, 147205 (2007)

~ 40 ns: M. Bal *et al.*, *Europhys. Lett.* **71**, 110 (2008)

T_1 measurement





S. Takahashi *et al.*, unpublished.

Summary – SMMs

- We observed spin echo in Fe_8 single crystals for the first time by suppressing spin decoherence.
- Low temperature T_2 is limited ~1μs.
- We are investigating the other decoherence sources and the origin of T_1.

Outline

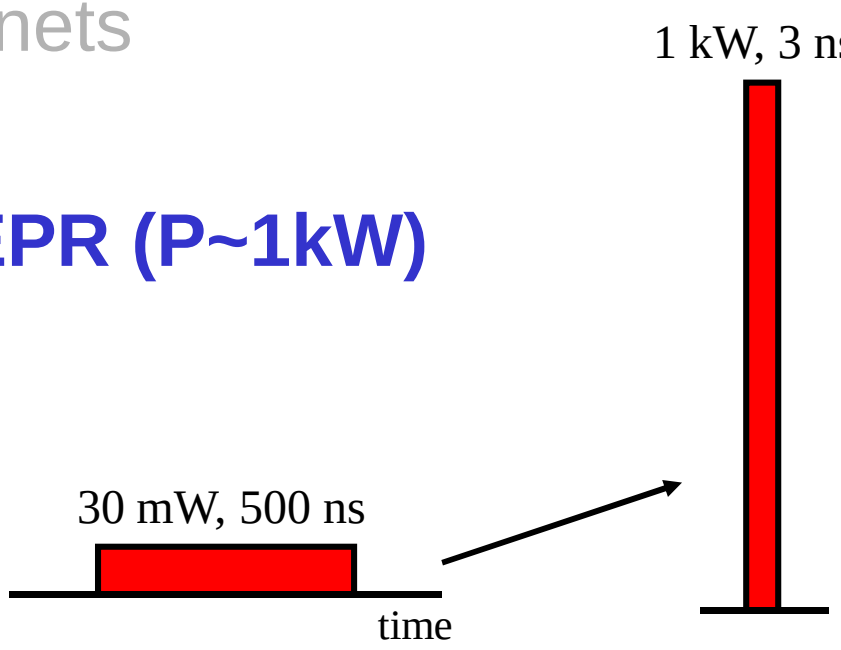
1. EPR with VDI source (P~30 mW)

- NV centers in diamond

- Single-molecule magnets

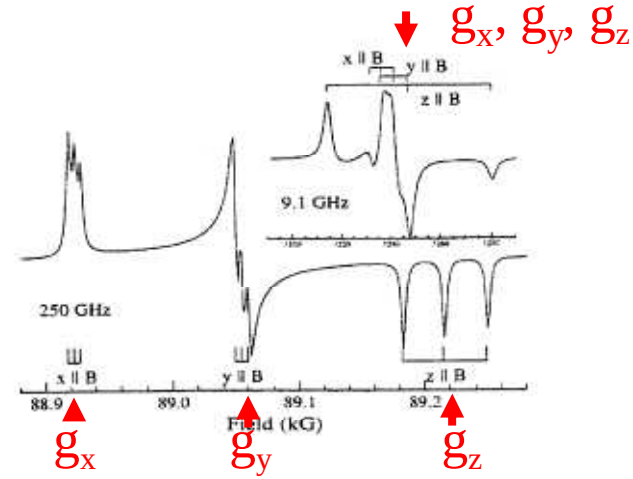
2. FEL-based pulsed EPR (P~1kW)

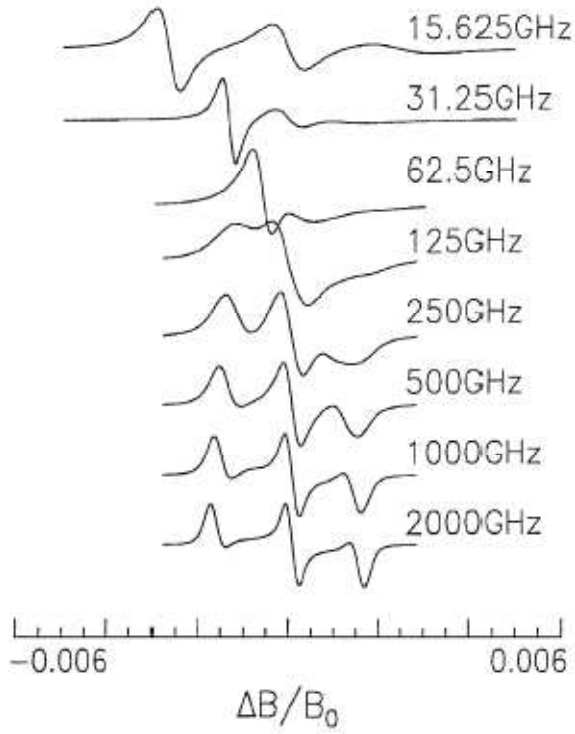
Tip angle of spins: $\alpha \propto B_{MW} \cdot t$



High-frequency EPR

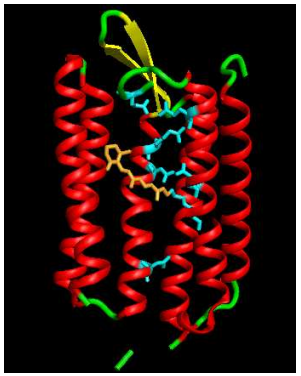
- Finer spectral resolution
- Less motional averaging
- Higher spin polarization
- Low-power/High-frequency pulsed EPR spectrometers (>150 GHz)
  - NHMFL (120, 240, 336 GHz)
  - Leiden (275 GHz)
  - Frankfurt (180 GHz)
  - Freie U. Berlin (360 GHz)
  - UCSB (240 GHz)
- High-power/High-frequency (P ~ 100 - 1kW)
- Better time resolution

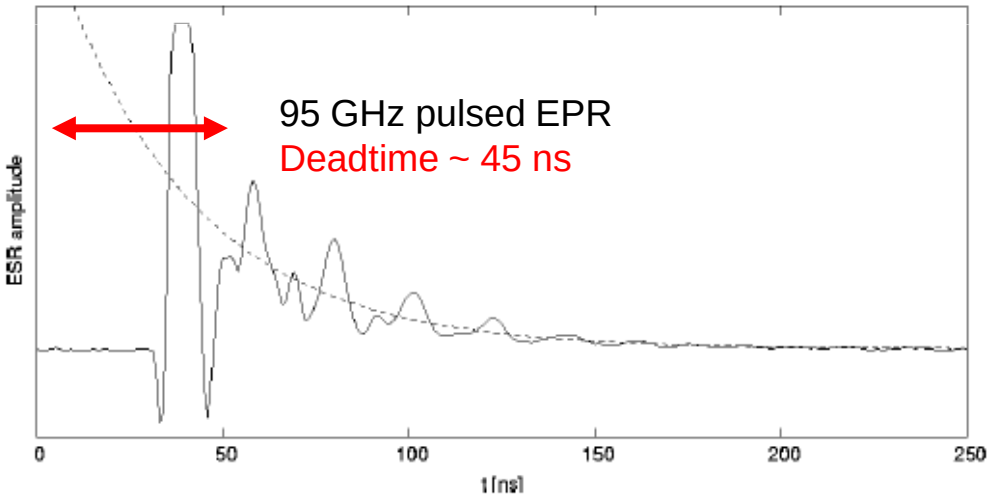




High-power pulsed EPR

- Short spin relaxation time (T_1 and T_2), *e.g.* SMMs & proteins in aqueous solution.
- Fast structure change, *e.g.* “film” proteins in action
- 10 GHz and 35 GHz pulsed EPR systems with 100 ns time resolution
- High frequency EPR for better time resolution
  - Shorter deadtime (✪ Q/ω)
- A few 95 GHz systems.
  - Freed group (Cornell)
  - Smith group (St. Andrews, UK)
- No commercial high power THz source.
- UCSB FEL covers up to 4.7 THz (1.26 THz = 45 tesla for g=2 EPR)

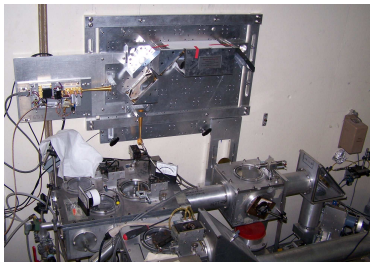




W. Haufbauer *et al., Rev. Sci. Instrum.* **75**, 1202 (2004)

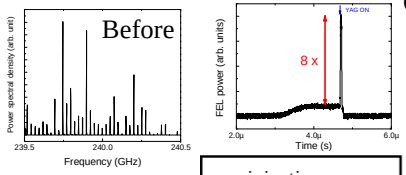
Setup overview

1. Free-electron lasers with injection-locking



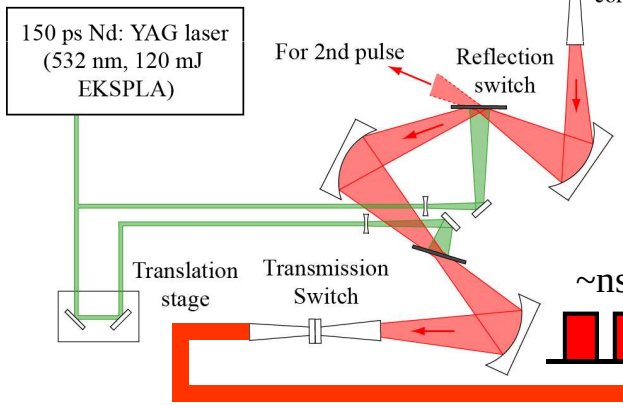
Injection-locking system

Cavity dump coupler

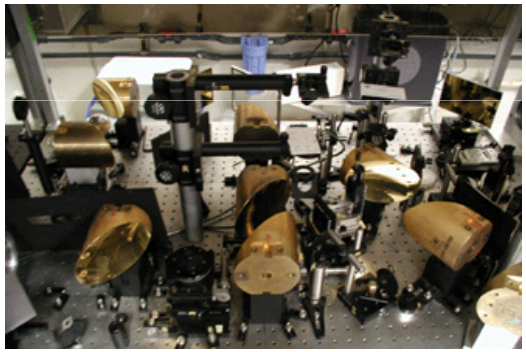


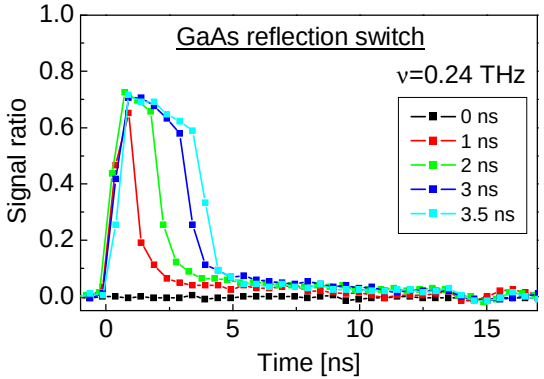
UCSB FELs (120 GHz – 4.7 THz)

2. Pulse Slicer



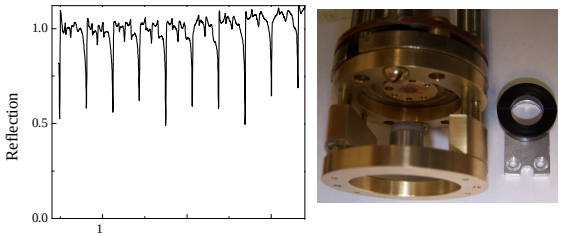
Back-to-back corrugated horn



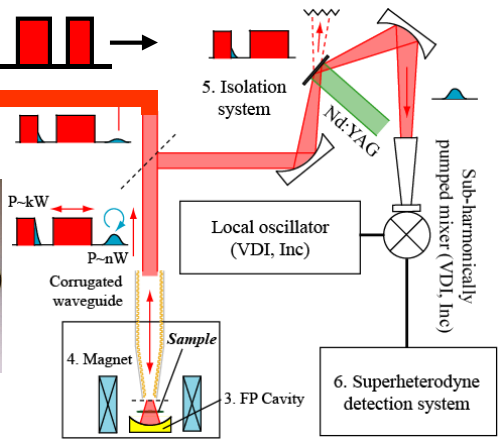


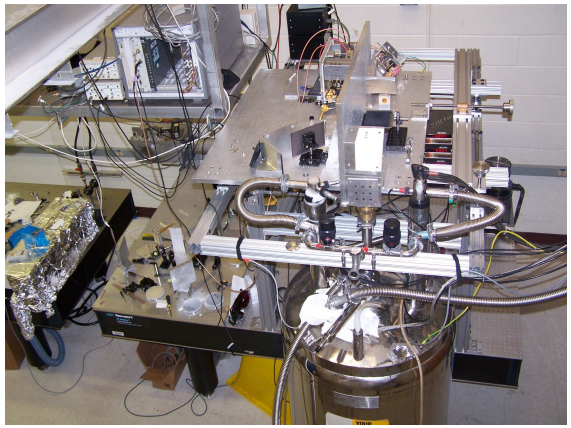
~ns

3. EPR spectrometer



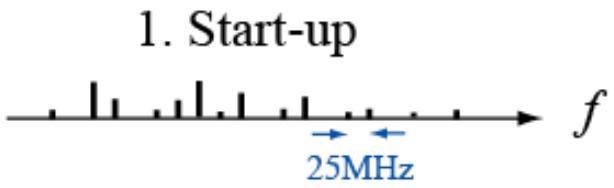
Fabry-Perot cavity

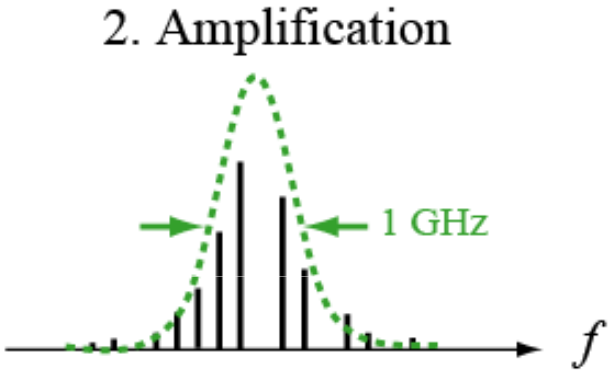


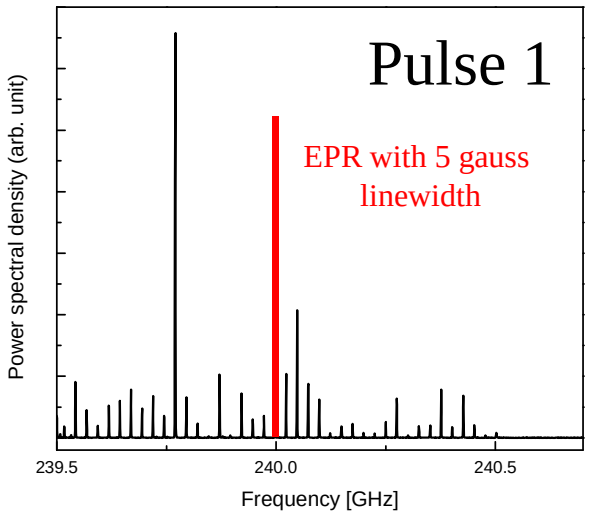


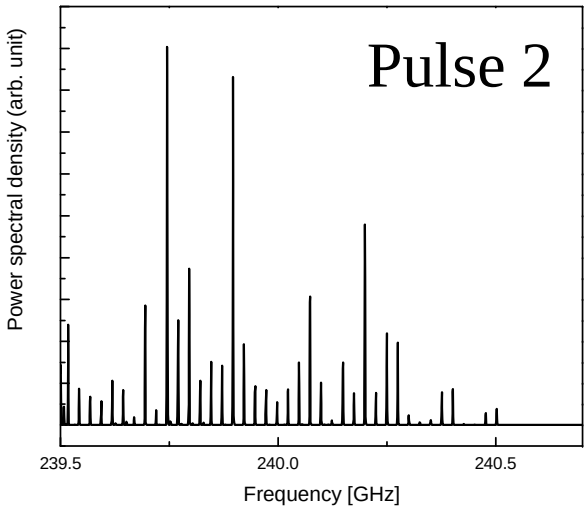
FEL - multimode radiation

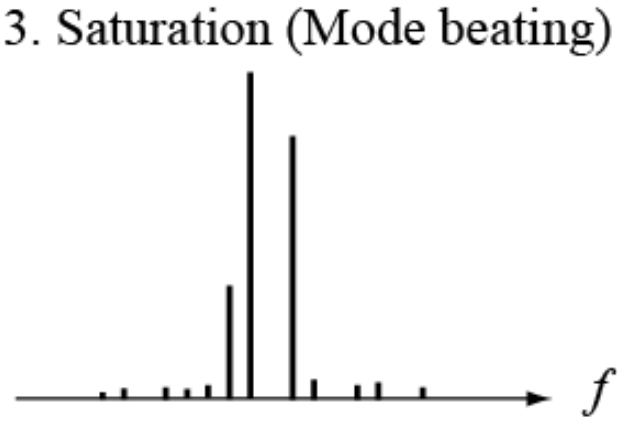
- We built 240 GHz spectrum analyzer to observe FEL spectrum.
- UCSB FEL employs a 6 m (20feet) long Fabry-Perot cavity (25 MHz mode spacing) in the undulator.
- Radiation modes of the FEL depend on stochastic start-up process and FEL gain bandwidth ~1 GHz.
- Multimode lasing and pulse-to-pulse frequency





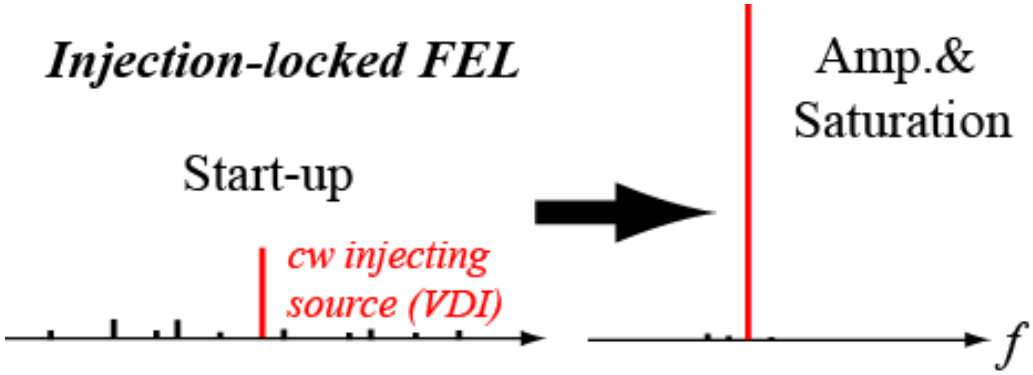


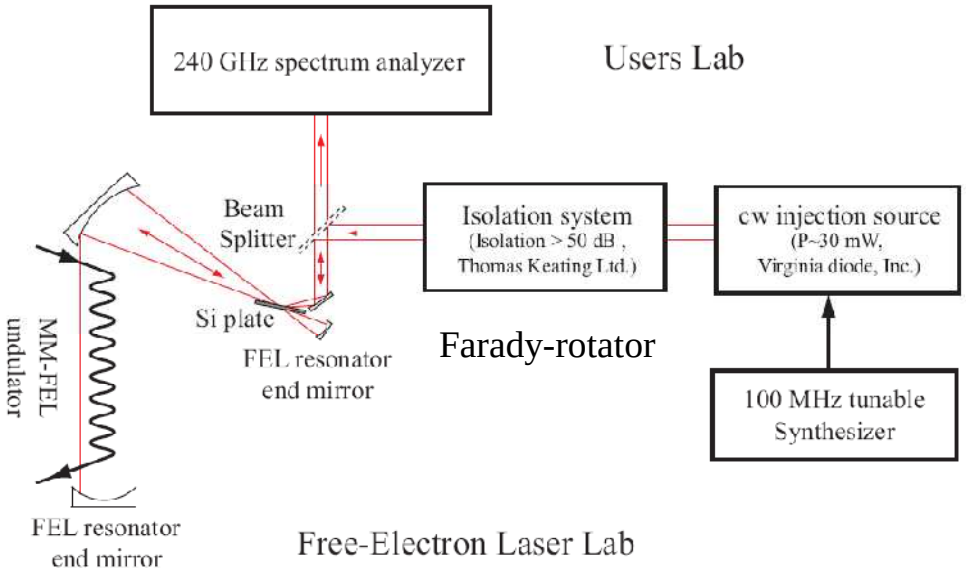


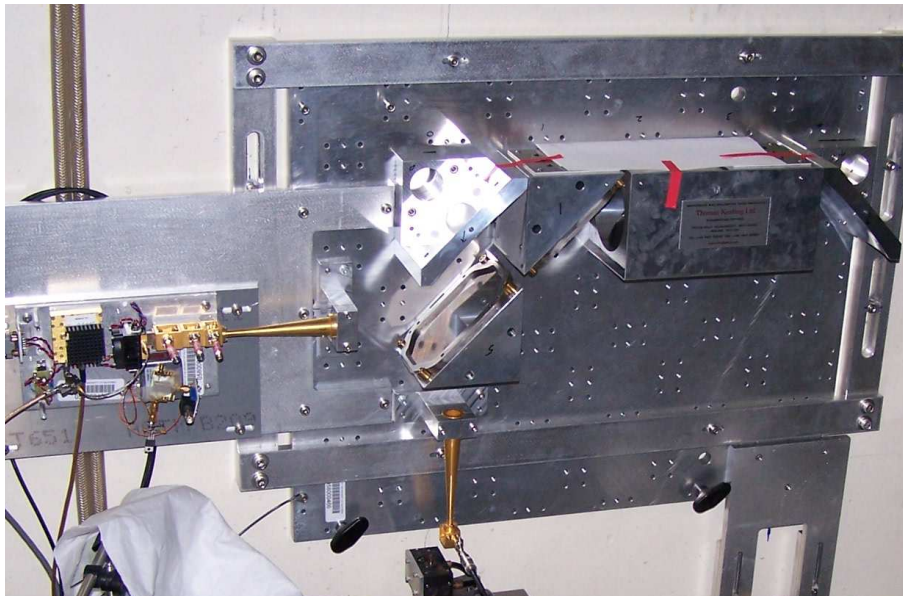


Injection-locking

- Two state-of-the-art instruments
  - VDI tunable ultra-stable injection source (~30 mW)
  - Thomas-Keating isolator
- Si plate coupler
- 240 GHz spectrum analyzer
- 240 GHz isolator (TK)

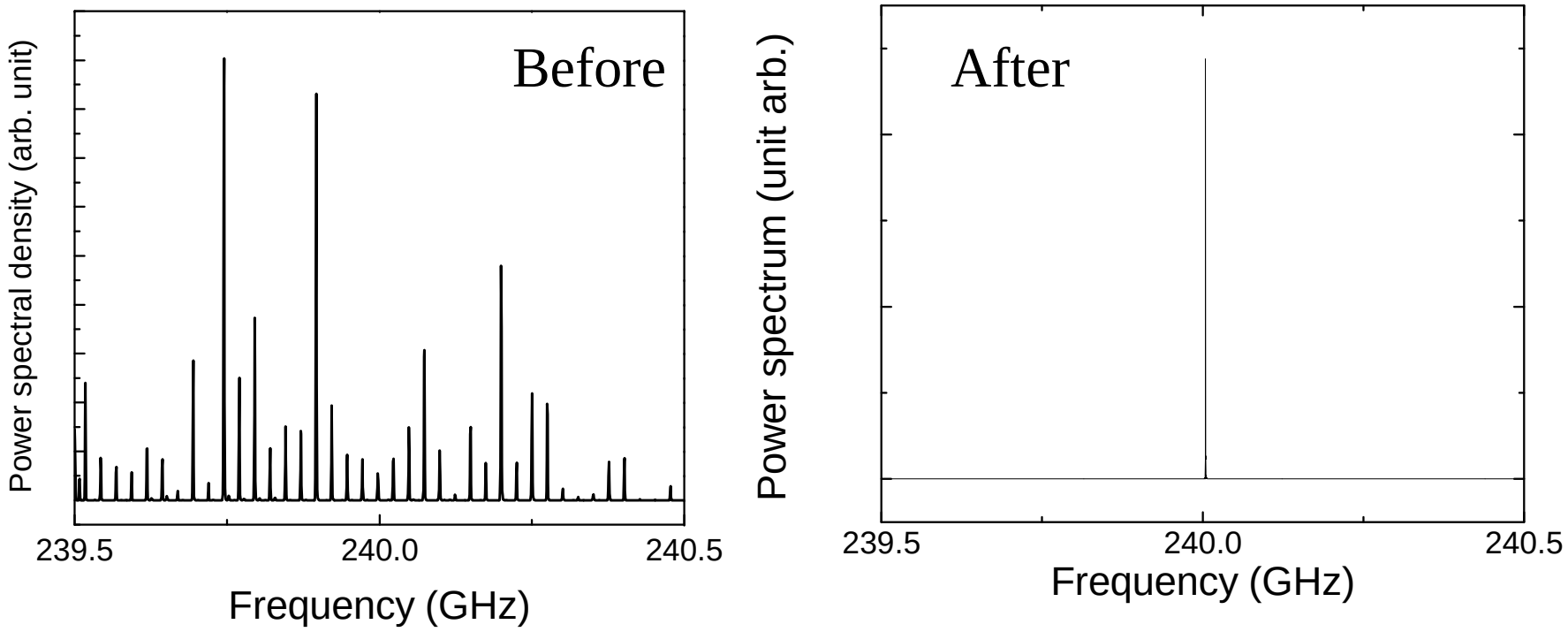






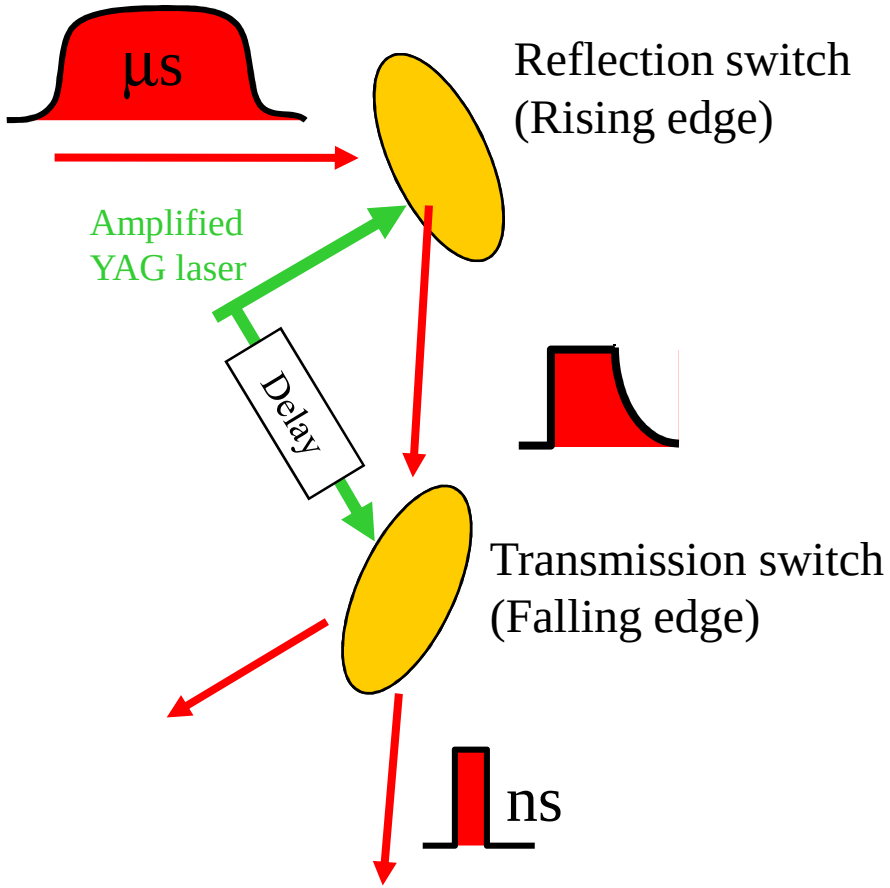
Single-mode lasing

- No pulse-to-pulse frequency fluctuation
- Sub-MHz linewidth (~500 kHz@2 μs pulse duration)



S. Takahashi *et al.*, *Appl. Phys. Lett.* **91**, 174102 (2007).

Pulse slicer

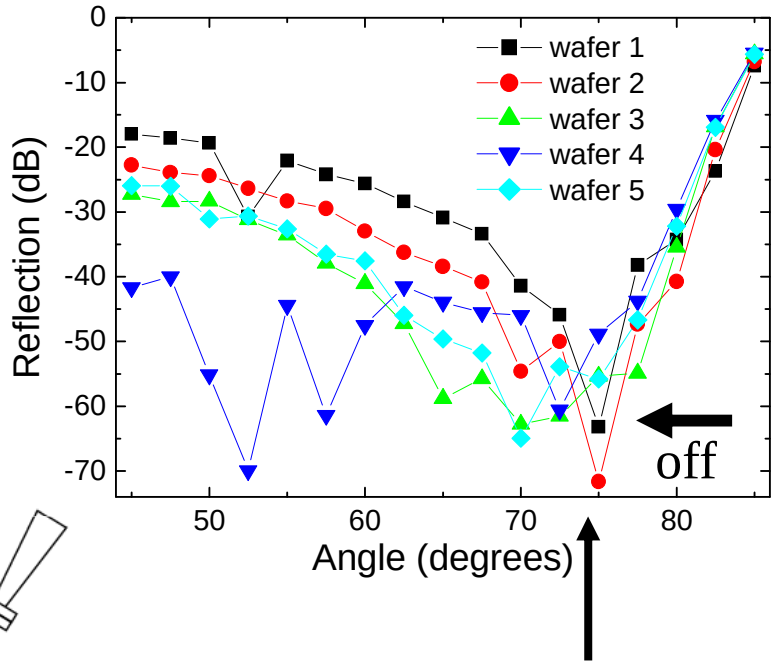


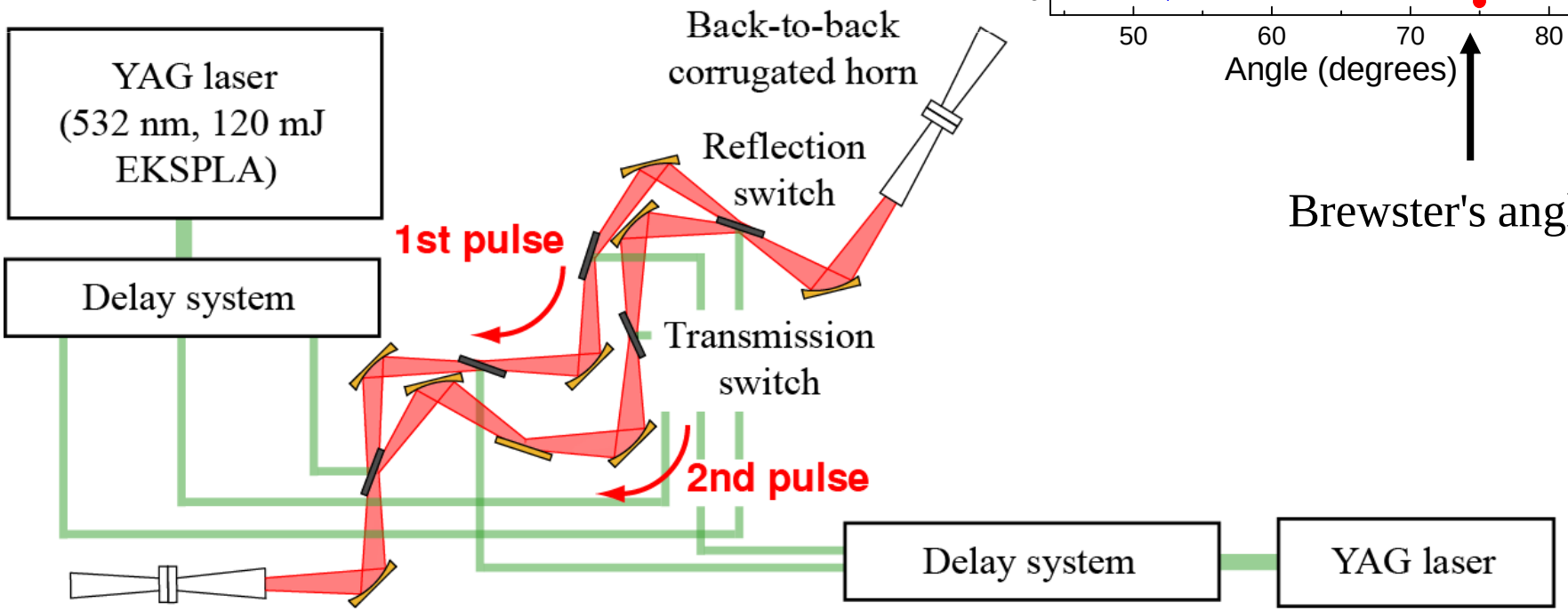
- Pulse slicer is made by photo-activated Si or GaAs switches.
- Rising and falling times are < 150 ps.
- Pulsewidth is varied by a delay line of YAGlaser.

- F. A. Hegmann *et al.*, *Appl. Phys. Lett.* **76**, 262 (2000).
- M. F. Doty *et al.*, *Rev. Sci. Instrum.* **75**, 2921 (2004).

New pulse slicer

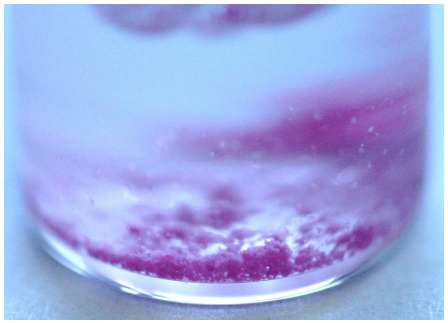
- Contrast is a key!
- Tune Si wafer thickness
- > 60 dB contrast ratio

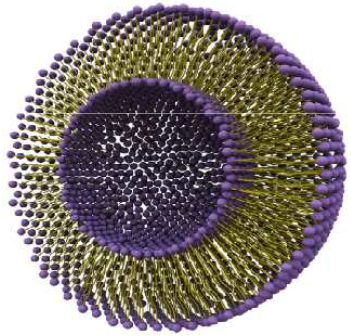




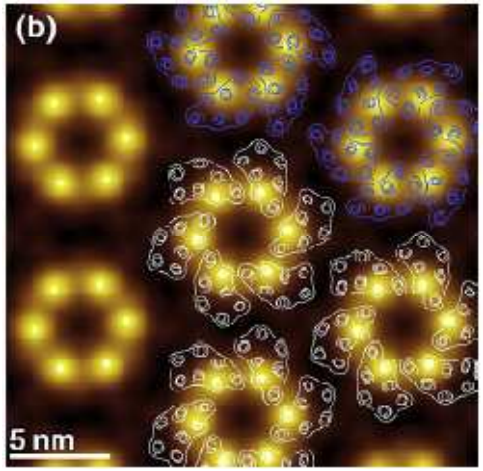
T_2-based distance measurement

1. Concentration dependence of nitroxide and spin-labeled lipid vesicles
2. DNP of protons.
3. Assembly of proteorhodopsin





Lipid vesciles in solution



proteorhodhopsin

A. L. Klyszejko *et al.*, *J. Mol. Biol.* **376**, 35 (2008)

Conclusion

- High-frequency EPR can quench electron spin decoherence with low-temperatures.
- High-frequency EPR can access nuclear spin decoherence.
- FEL-based EPR for ns spin dynamics
- Possible T_2-based distance measurement

Acknowledgement

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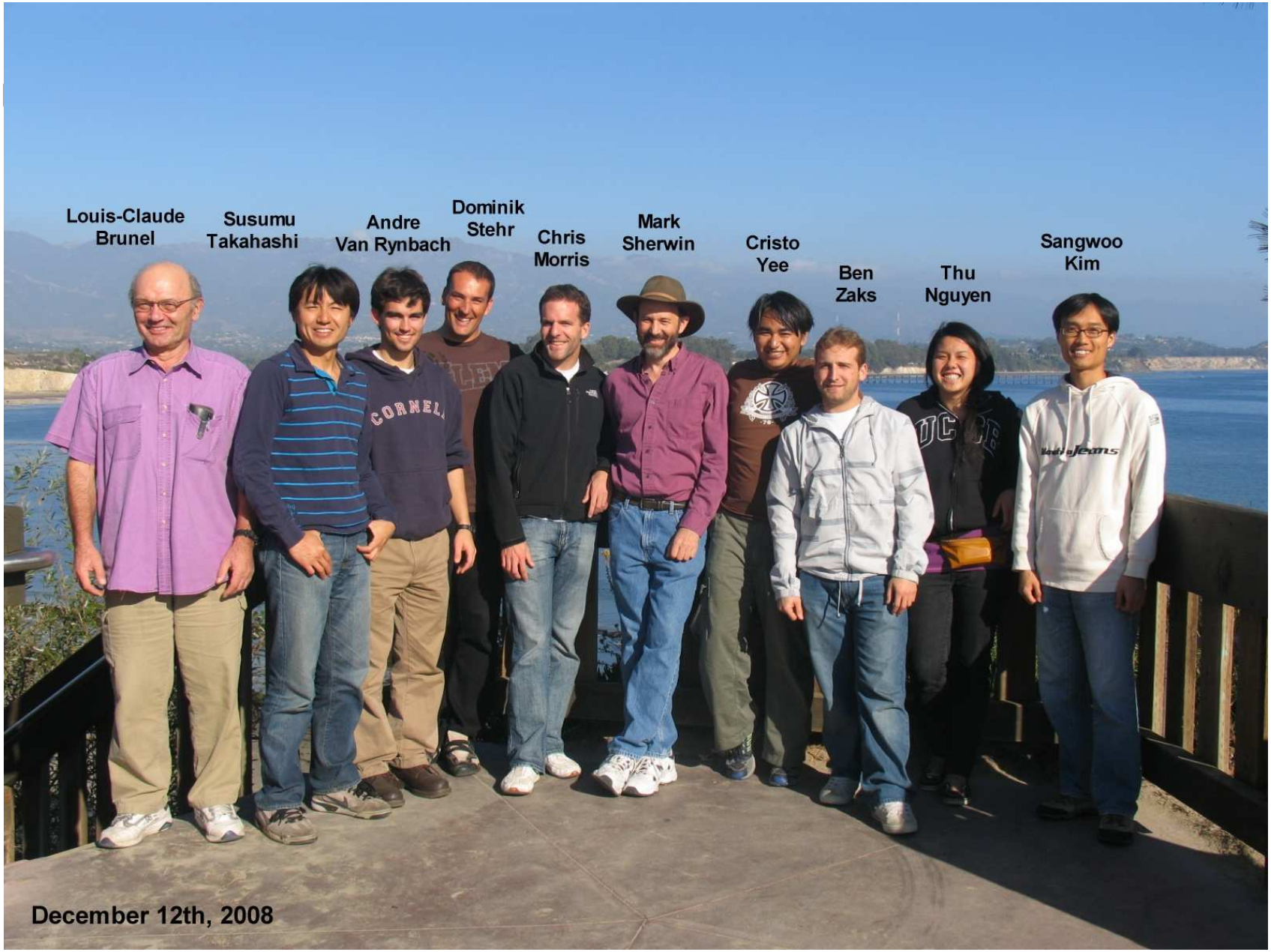
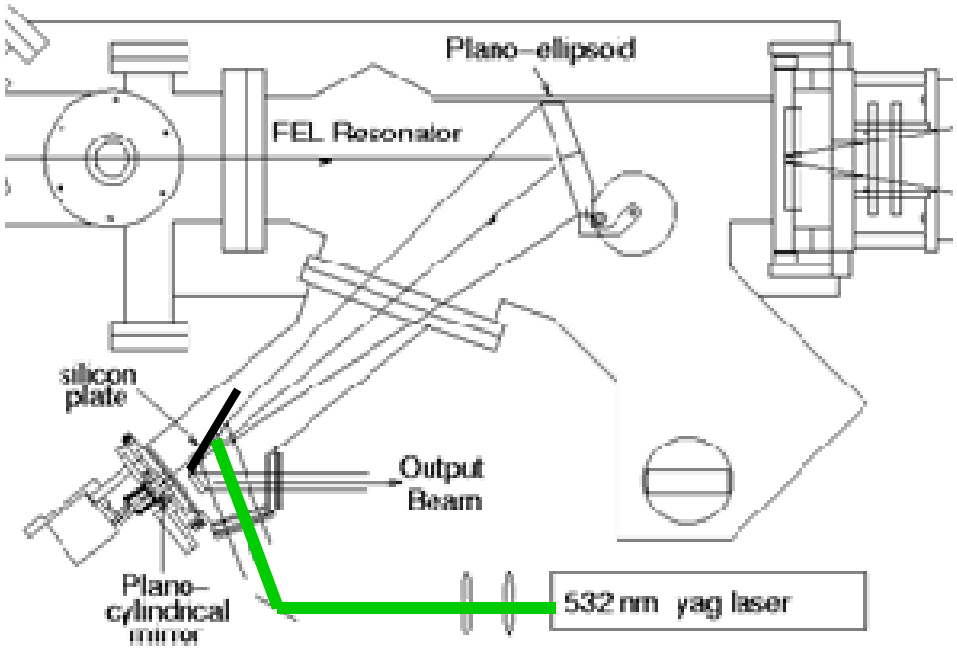
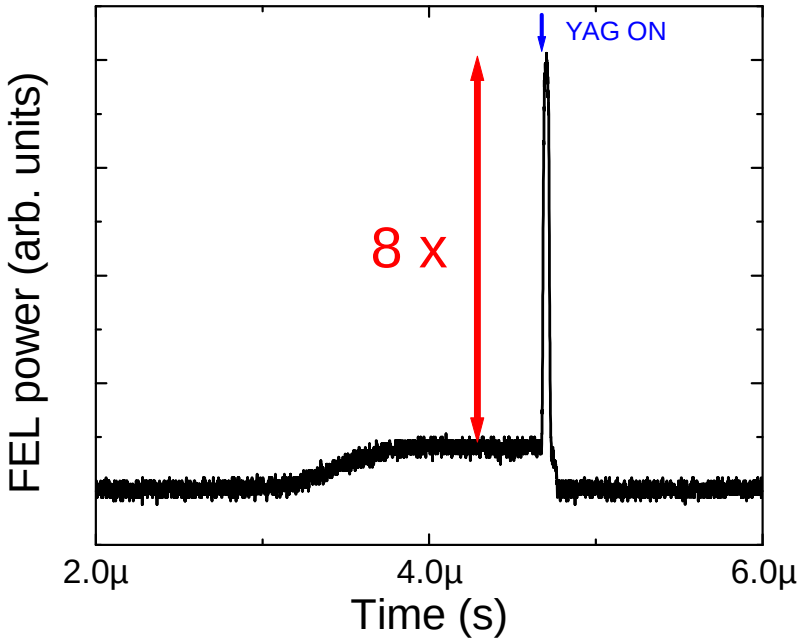
Acknowledgement

- 

Cavity dump coupler

- Amplification of FEL output for sub-ns time resolution.
- Normal FEL coupler has 5~20 % coupling, so only 5~20 % of intracavity power couples out.
- Cavity dump coupler (CDC) couples out the entire intracavity power.



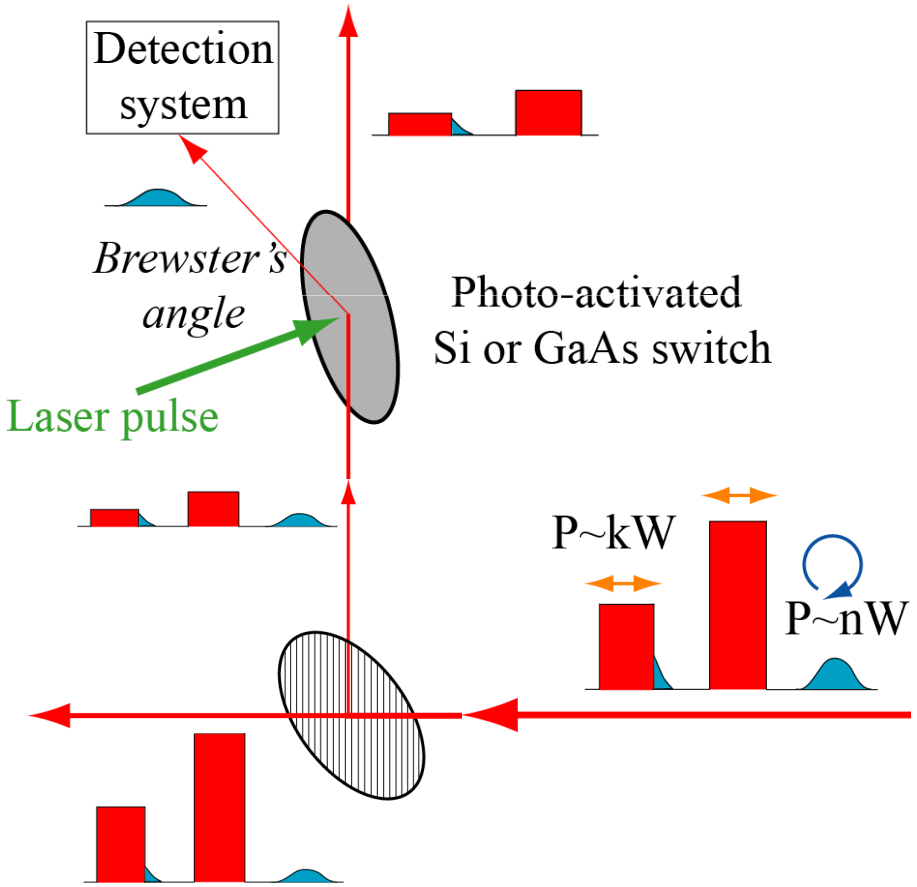


FEL cavity

S. Takahashi *et al.*, *manuscript in preparation* (2009).
J. P. Kaminski *et al.*, *Appl. Phys. Lett.* **57** 2270 (1990)

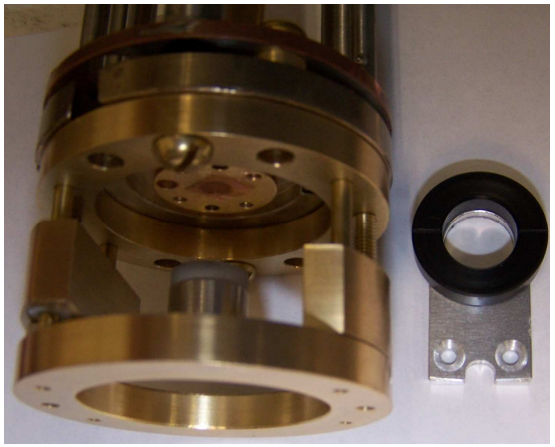
Isolator

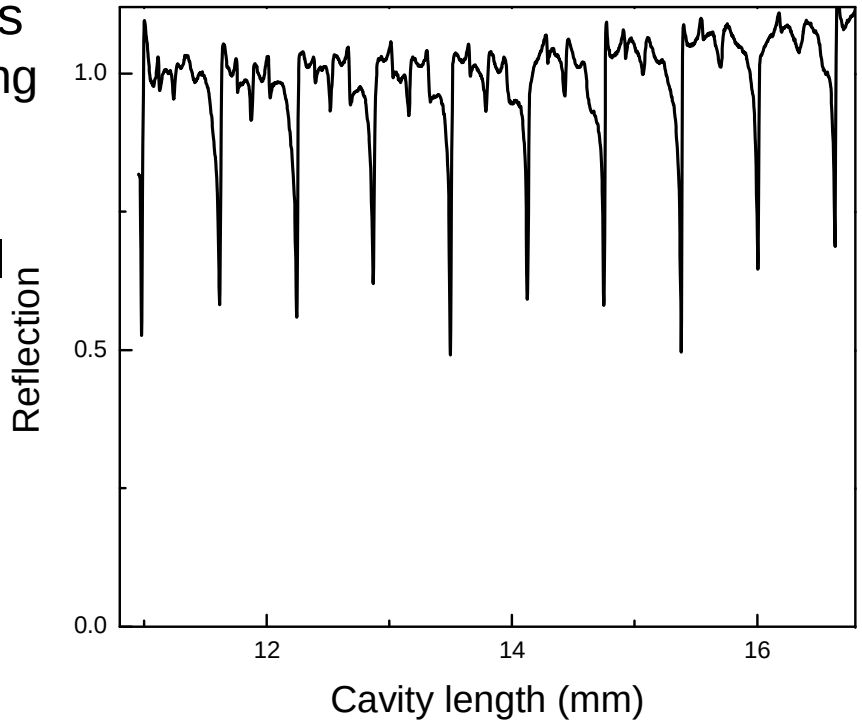
- Huge reflection and tiny sample signal.
- Inputs ~ kW, EPR < nW →ΔP>120dB
- 1st isolation: wire-grid polarizer (EPR is circularly polarized.)
- 2nd isolation: Photo-activated Si or GaAs switch
- Short switching (<100 ps)



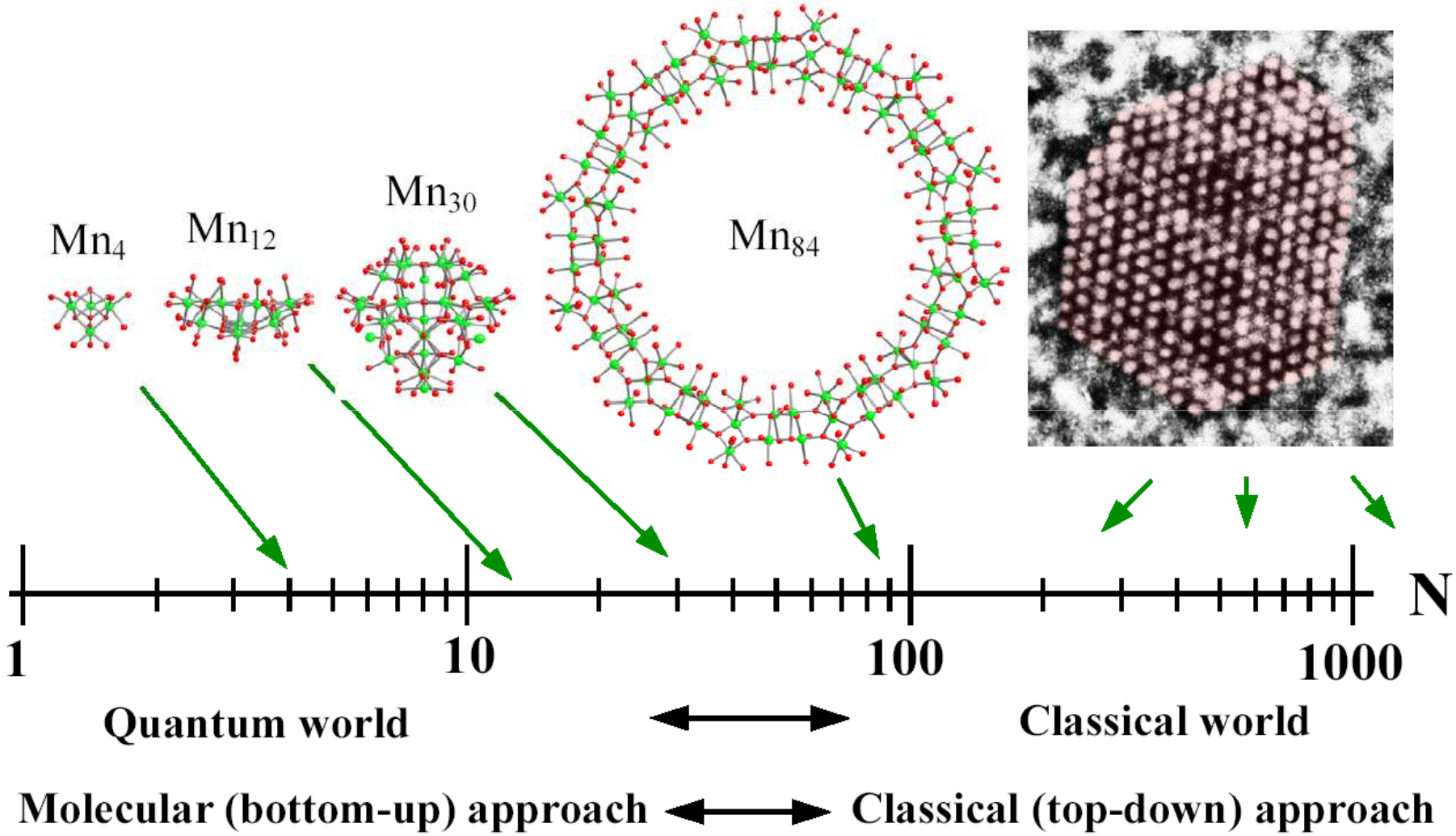
Fabry-Perot cavity

- Semi-confocal cavity
- EPR couples to H-field; water couples to E-field
- Aqueous sample is mounted at H-field maximum and E-field minimum.
- Two translation stages
  1. End-mirror positioning
  2. Sample positioning
- *In-situ* T-stage control
- Finesse ($\Delta l/l$)~ 50





“Bottom-up” approach



A. J. Tasiopoulos *et al.*, *Angew. Chem. Int. Ed.* **43**, 2117 (2004).