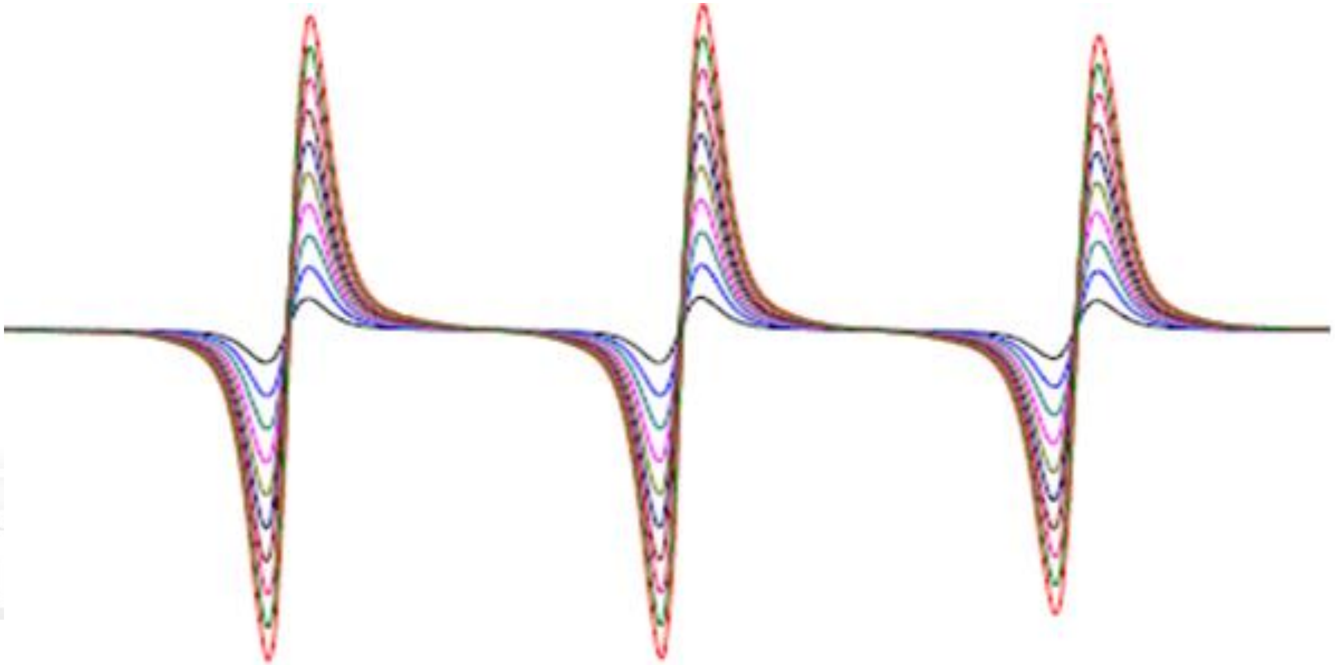
Electron Spin Resonance Spectroscopy



Rodah C. Soy & Otto Joseph

Outline

- Background of EPR
- Basic principle
- Instrumentation
- Applications

Background

- **Electron Spin Resonance (ESR) or Electron paramagnetic resonance Spectroscopy (EPR):**
    - powerful non-destructive magnetic resonance spectroscopic technique
- **Used to analyse substance with one or more unpaired electrons and radicals**
- **Invented by Zavoiskii in 1944**
- **Similar to Nuclear magnetic resonance (NMR)**
    - EPR is three times more sensitive than NMR

Background

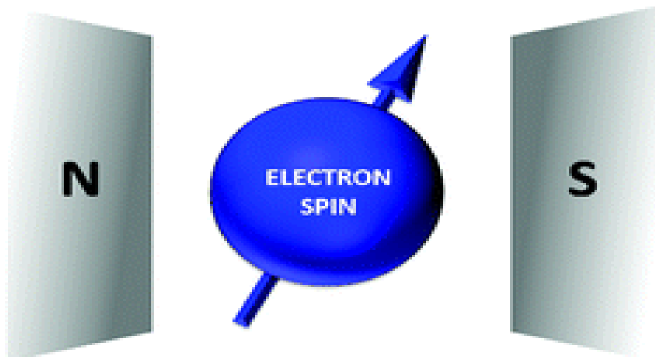
➢ **Compounds analysed using EPR**

❖ **Stable paramagnetic substances e.g.**

- **transition metal ions, their complexes, and molecules like NO, O_2 and NO_2**

❖ **Unstable paramagnetic substances e.g. free radicals or radical ions**

- **formed as intermediates in chemical reactions or by irradiation e.g. from**
  - **photolysis, thermolysis, radiolysis, electrolysis e.t.c**

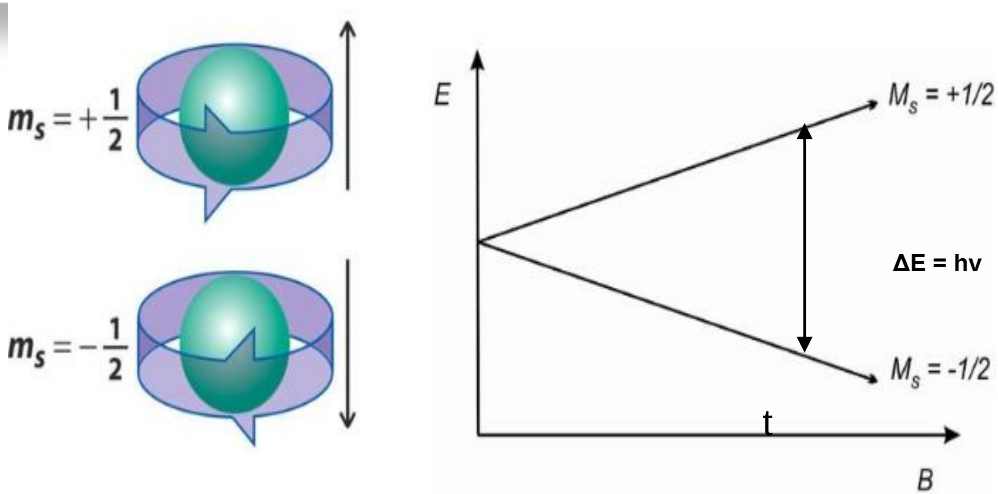


✓ Structure
✓ Reactivity
✓ Mechanisms
✓ Bonding
✓ Intermediates
✓ Distances

Roessler & Salvadori. *Chemical Society Reviews*. **2018**;47(8):2534-53.

Basic principle

- **EPR measures the transition between electron spin energy levels**
  - transition between the two different electron spin energy states takes place by absorption of a quantum of radiation of an appropriate frequency in the microwave region



Resulting energy levels of an electron in a magnetic field

$$\Delta E = hv = g\beta H_0$$

g=Bohr magneton

- **Required frequency of radiation dependent upon strength of magnetic field**
  - Common field strength 0.34 and 1.24T
  - 9.5 (X-band) and 35 GHz (Q-Band)

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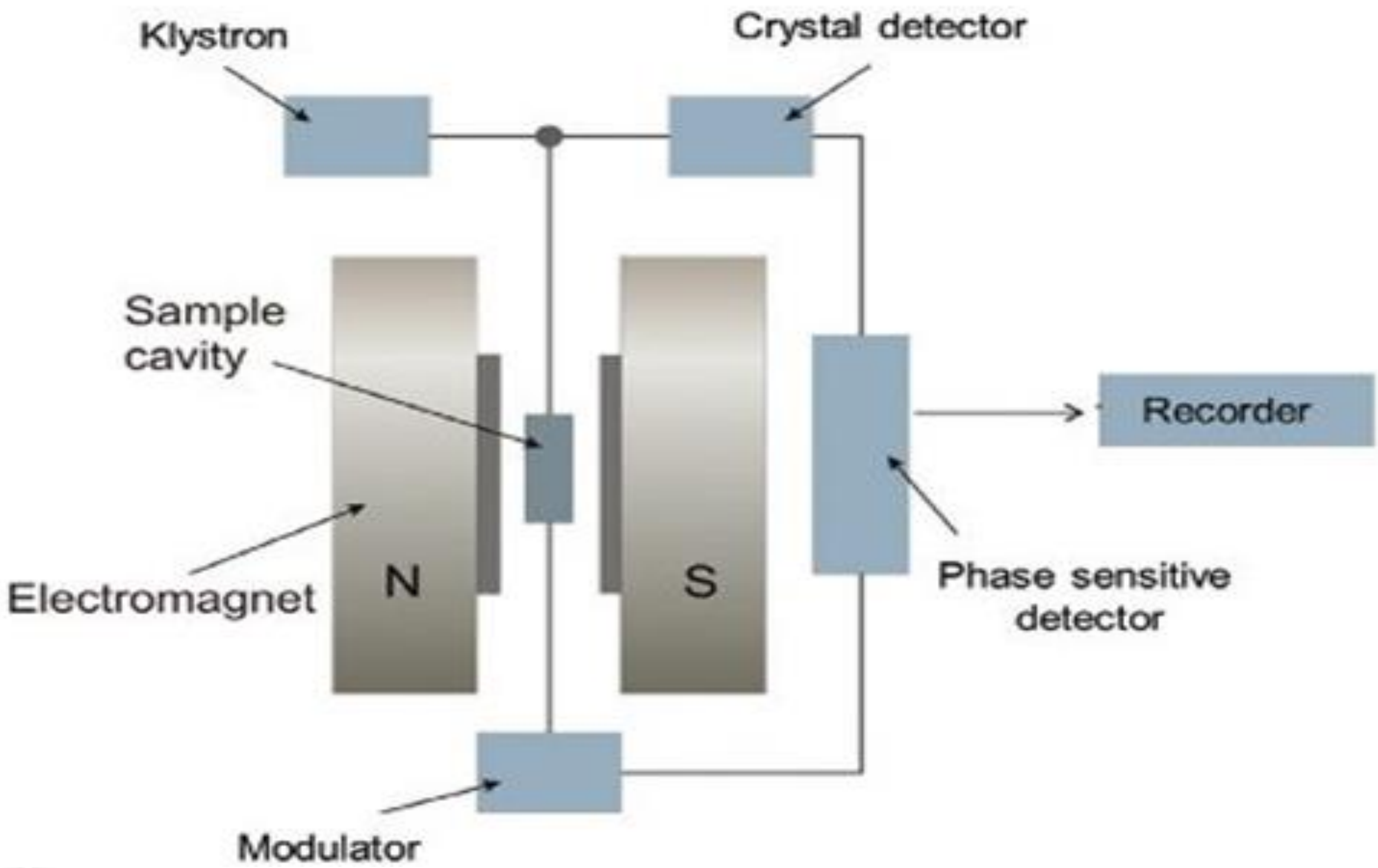
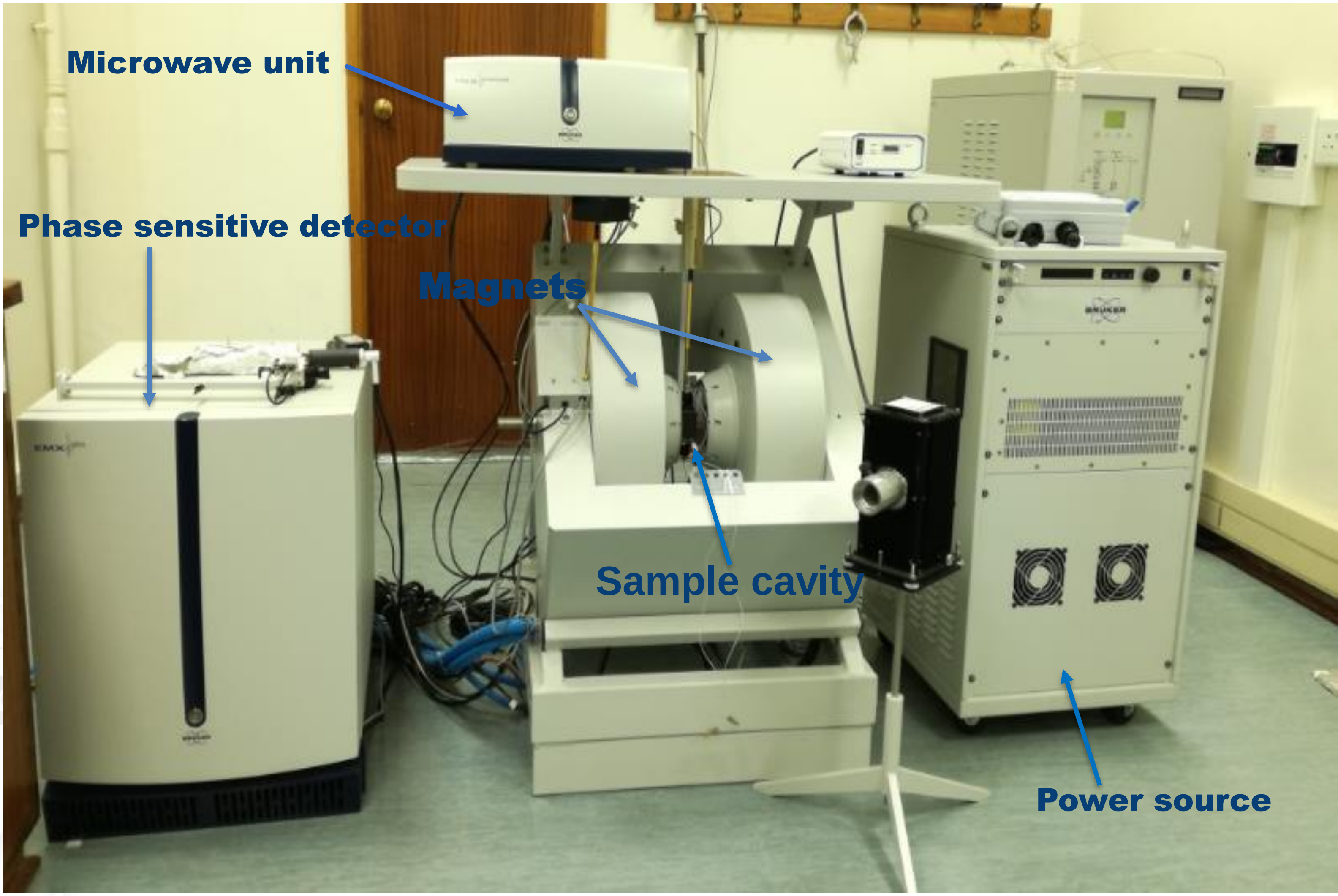
EPR instrument schematic diagram



- **EPR samples:**
  - single crystal, solid powder, liquid, solution or frozen solutions and is usually contained in a tube of about 5 mm diameter

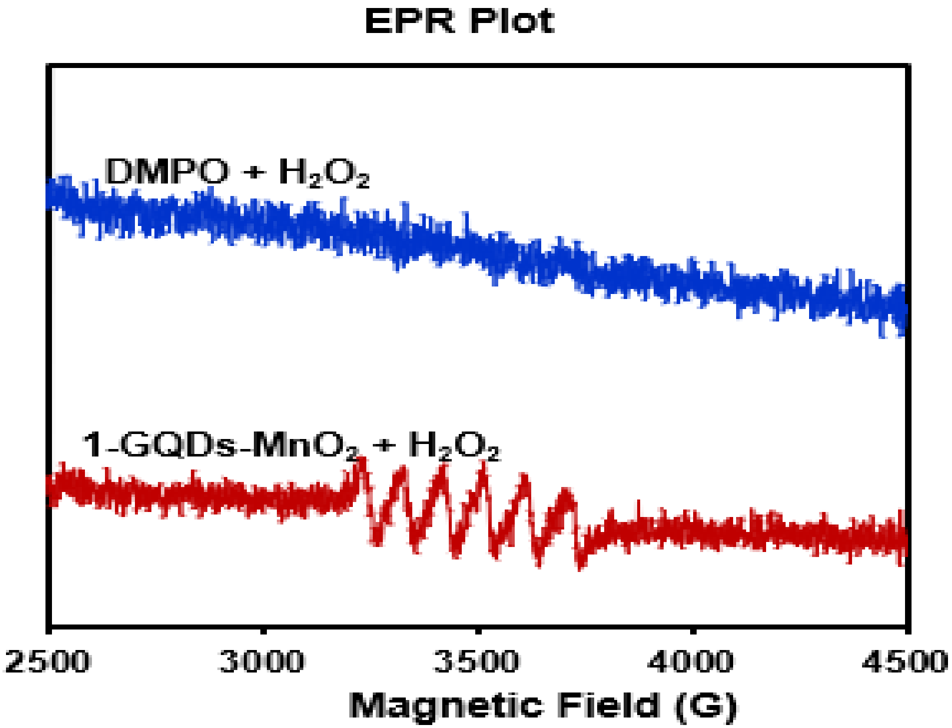
www.tech-faq.com/esr-spectroscopy.html

EPR instrument in the NIC



Applications of EPR

➢ **Catalytic mechanism of 1-GQDs-MnO_2**



*DMPO reacts with OH• radicals to generate an active DMPO/OH• abduct.

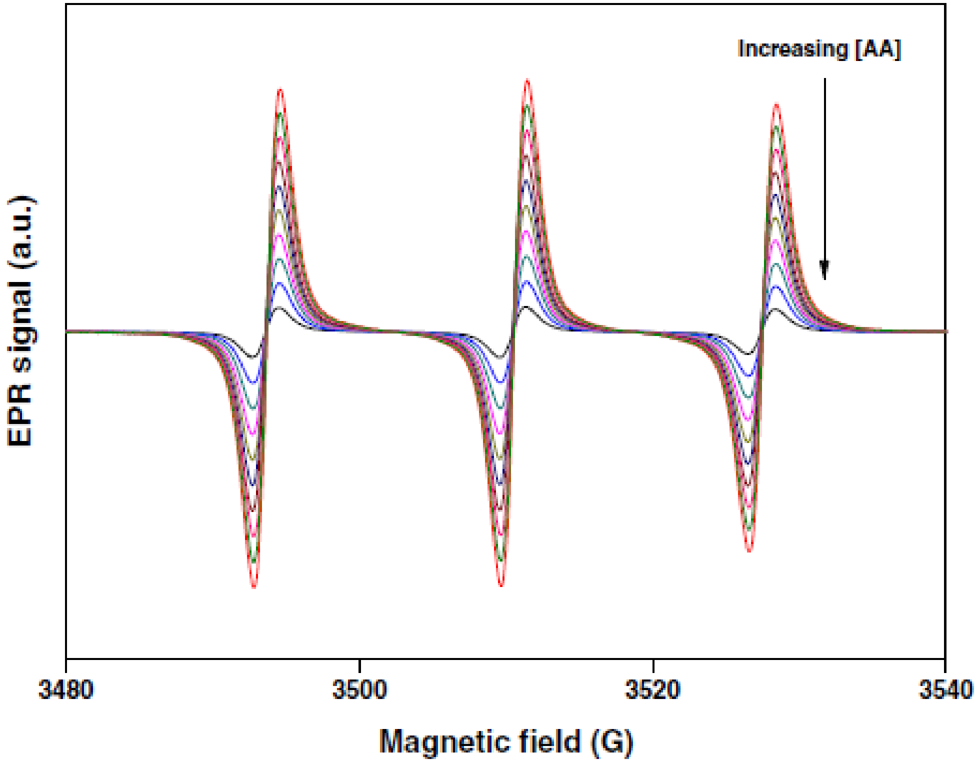
Shows the presence of Mn in the Mn^{+4} state (MnO_2)

Catalase-like properties

***DMPO: 5,5-Dimethyl-1-pyrroline N-oxide**

➢ **GQDs-4-Amino-TEMPO/SN-GQDs-4-amino-TEMPO nanoconjugates**

- selective sensing ascorbic acid (AA)



Quencher: 6-Tetramethylpiperidine-N-Oxide (TEMPO)

EPR signals of the TEMPO conjugates target analyte (AA).

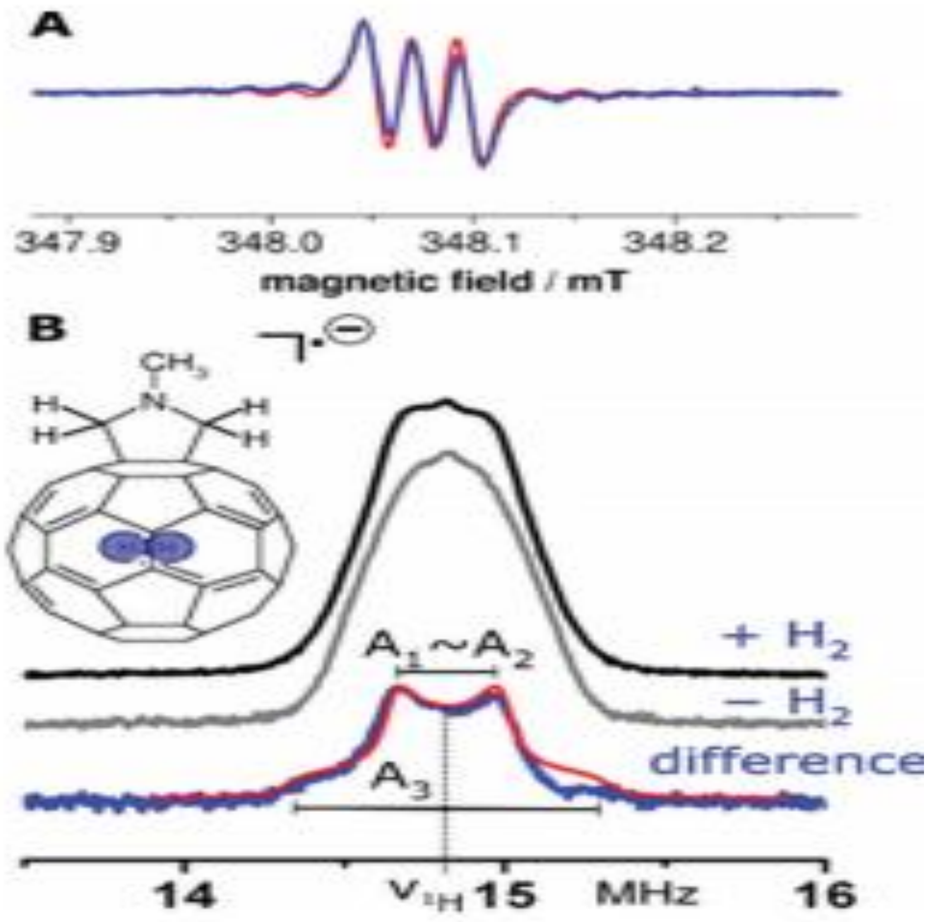
Achadu , Britton & Nyokong . *Journal of fluorescence*. **2016,** 1;26(6):2199-212.

Experiments

A. Continuous Wave EPR (CW)
B. Pulsed EPR
    - Electron nuclear double resonance spectroscopy (ENDOR)
    - ESEEM
    - HYSCORE

Host Guest Interactions

ENDO
R



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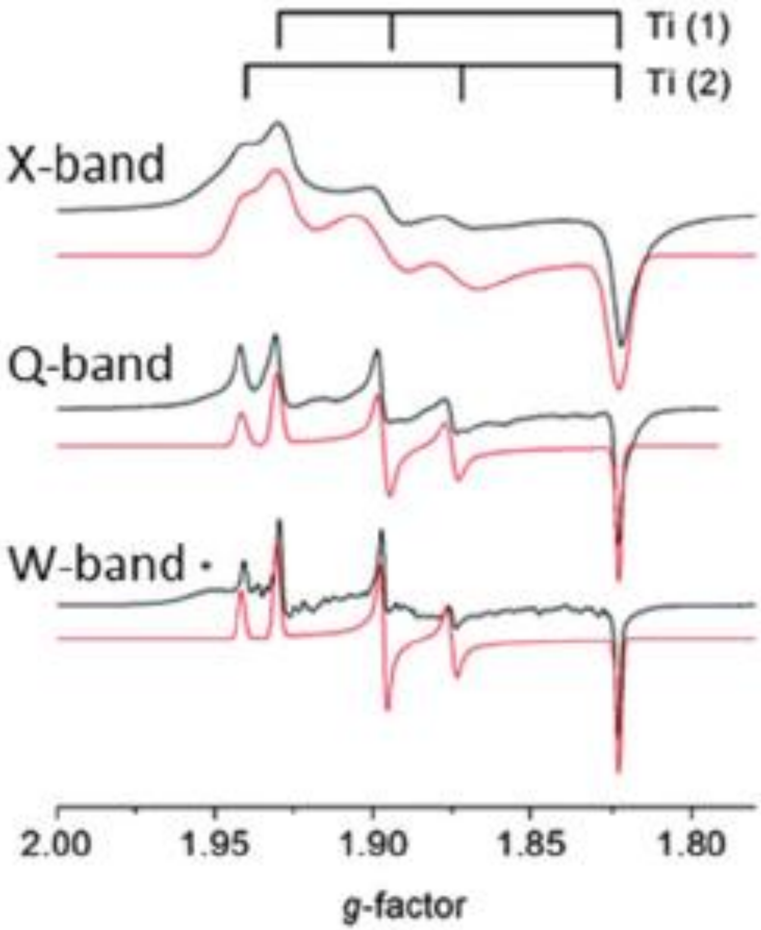
Transition Metals



$TiCl_3(Py)_3$

Continuous Wave (CW) EPR

No shift in signals despite frequency change

Experimental

Simulated

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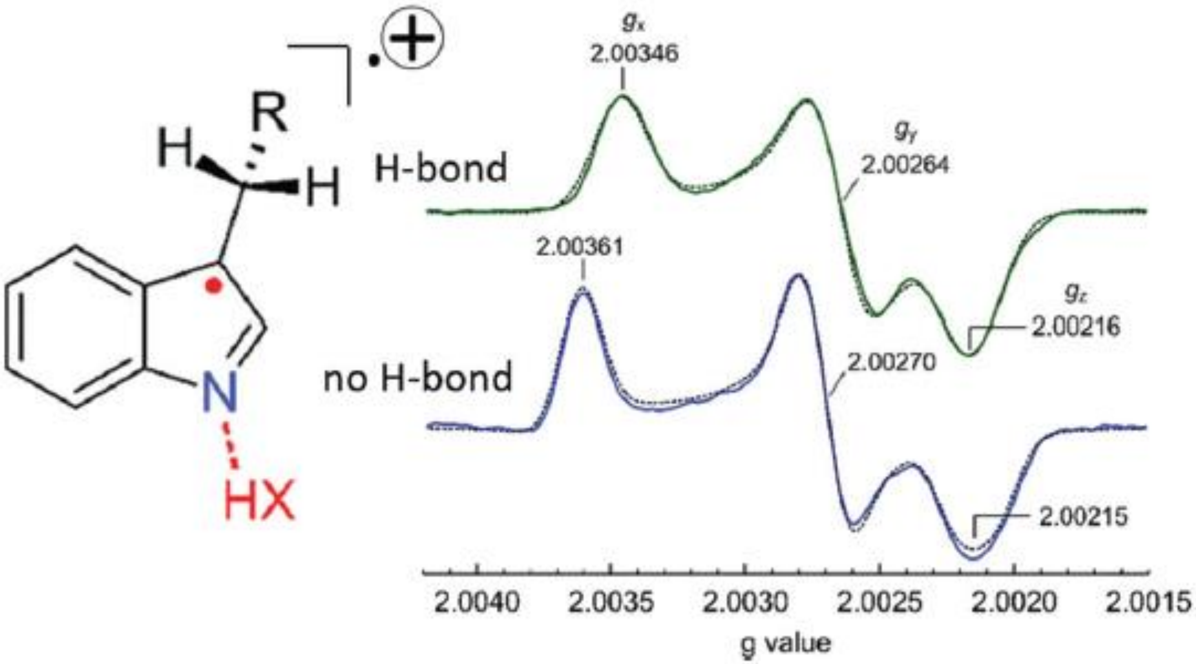
Aminoacids

Tryptophan radical cation



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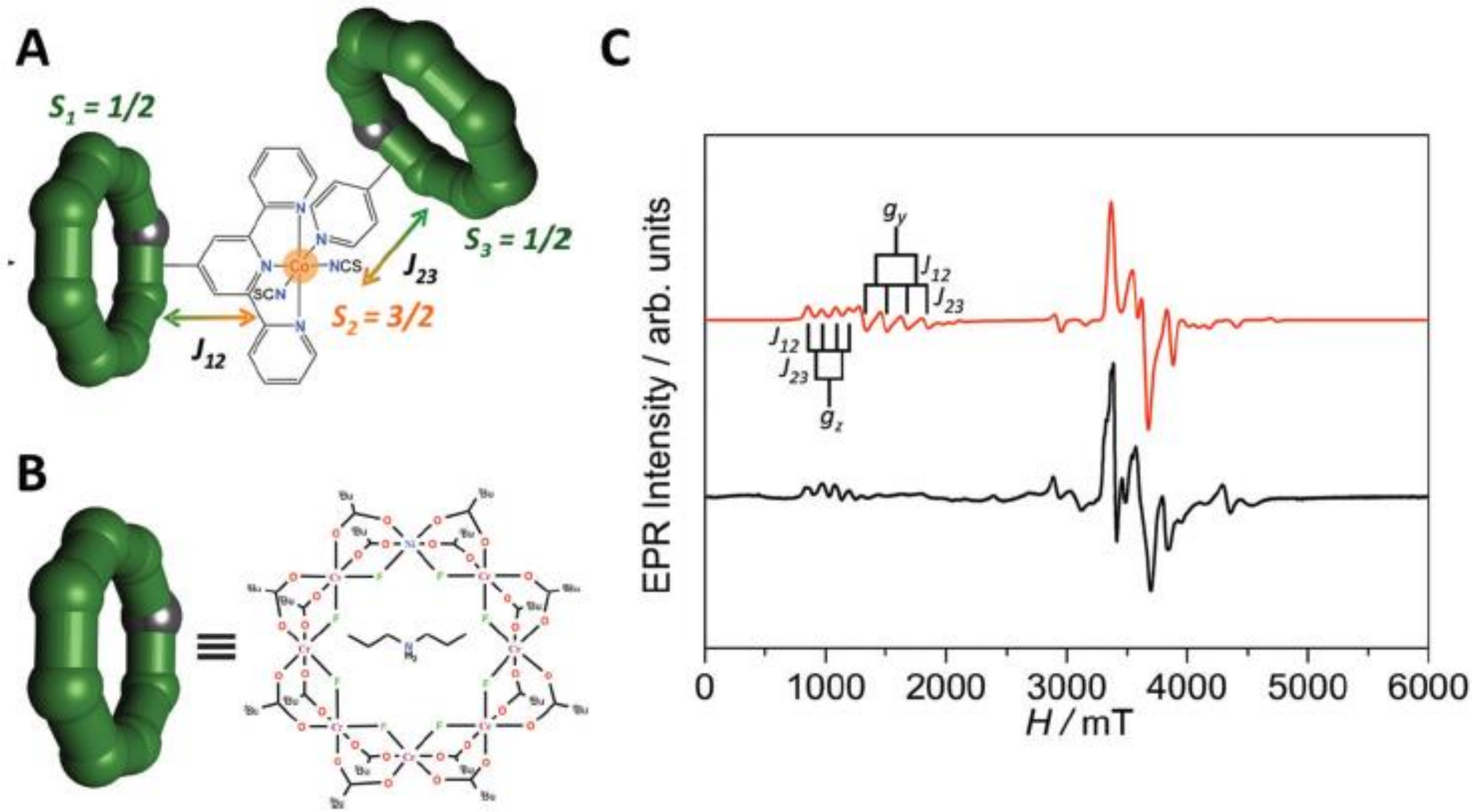
Nanomagnets



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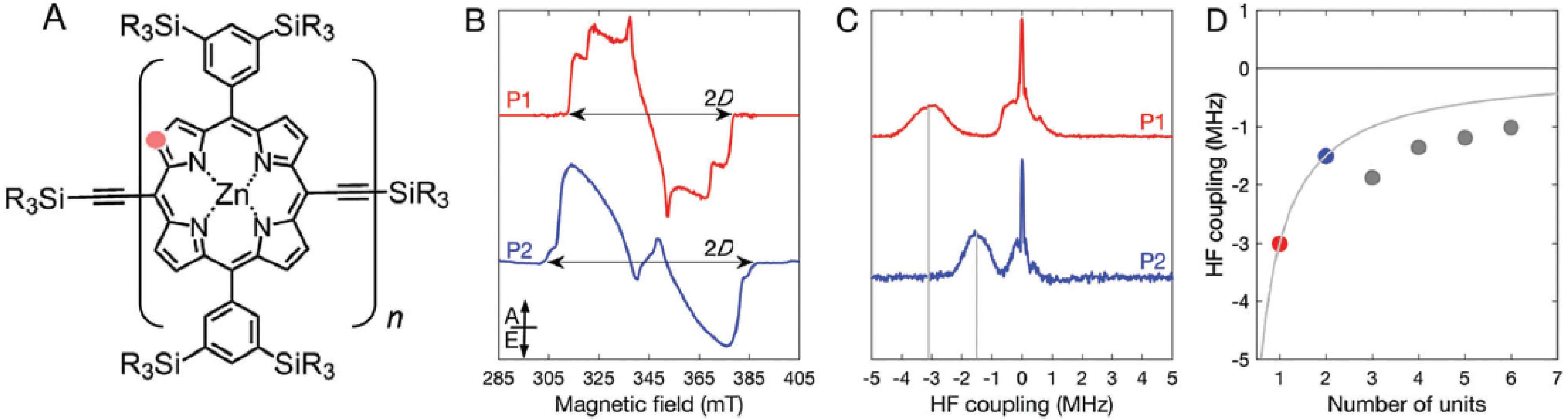
Molecular Wire Distance Measurements

Spin Polarization change due to # of porphyrin units



Time Resolved

ENDOR

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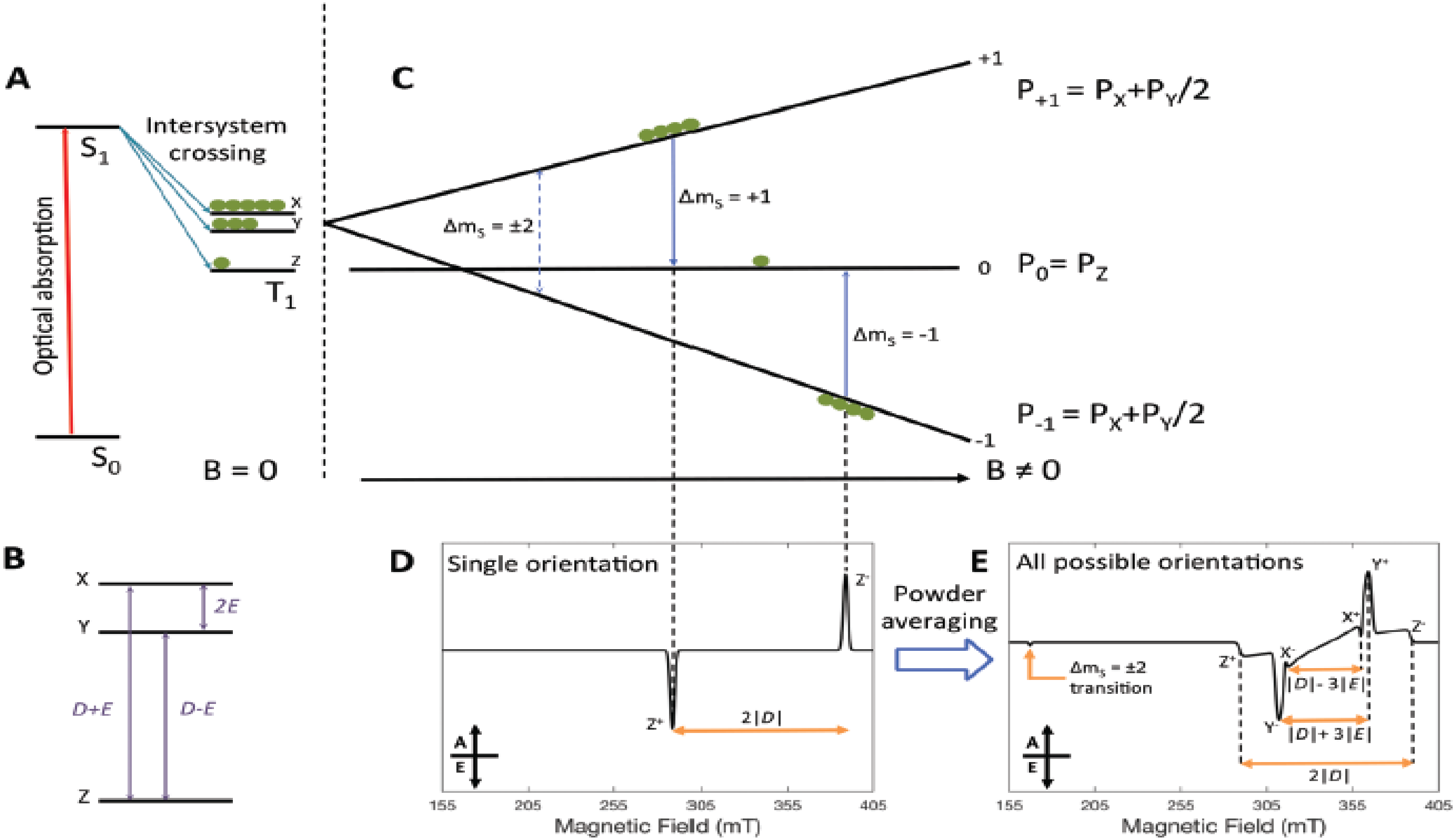
Time Resolved – Triplet State EPR



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Thank you