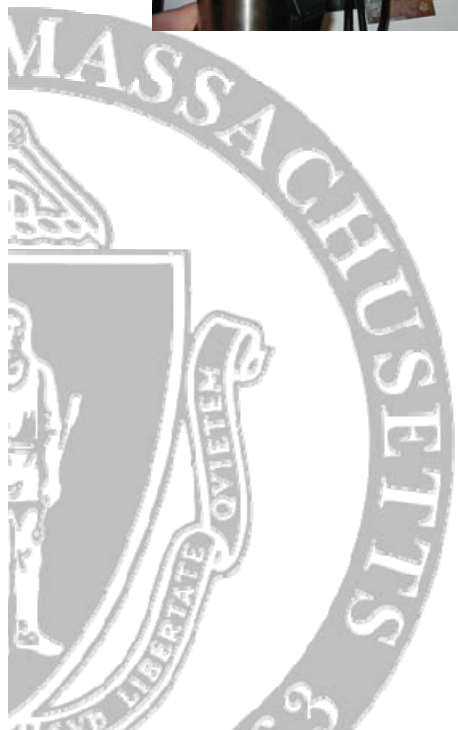


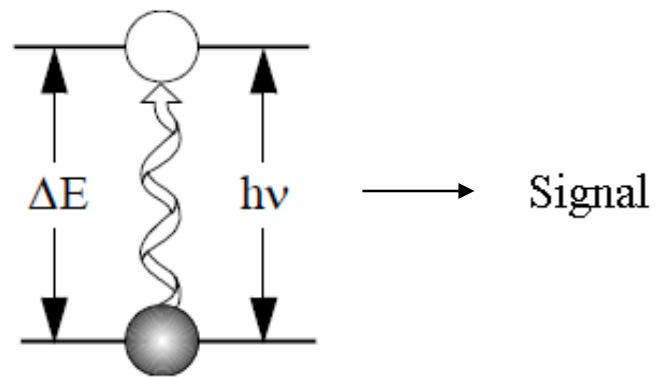
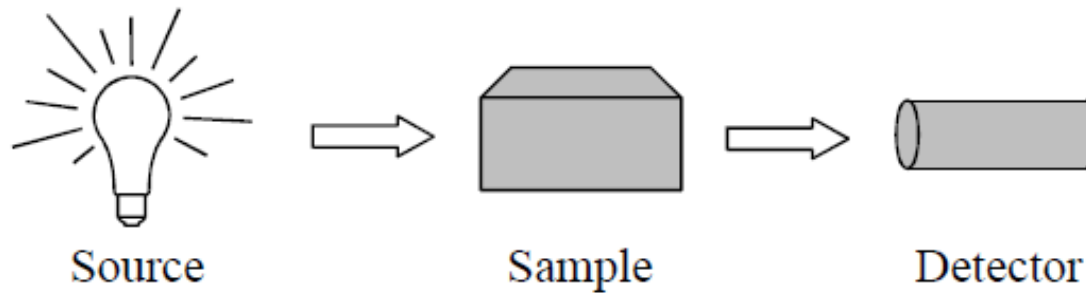
## EPR Spectroscopy



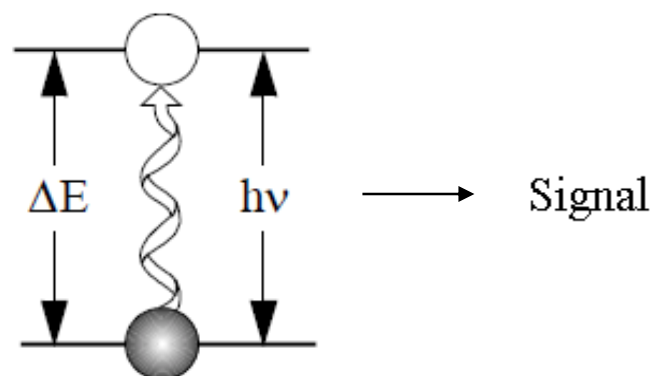
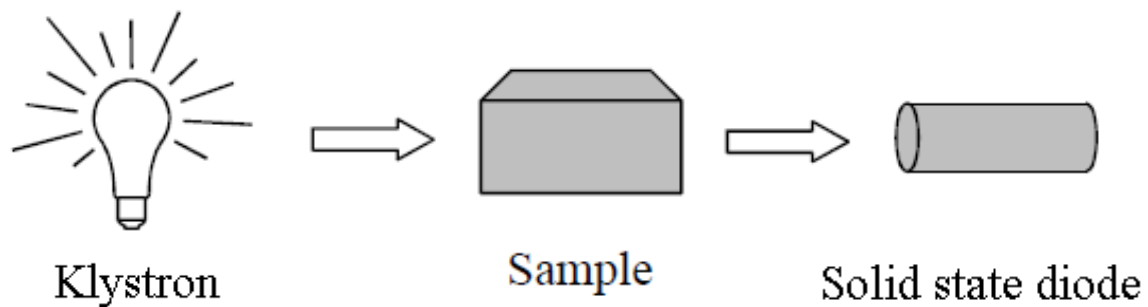
Gonca Seber (Lahti lab)



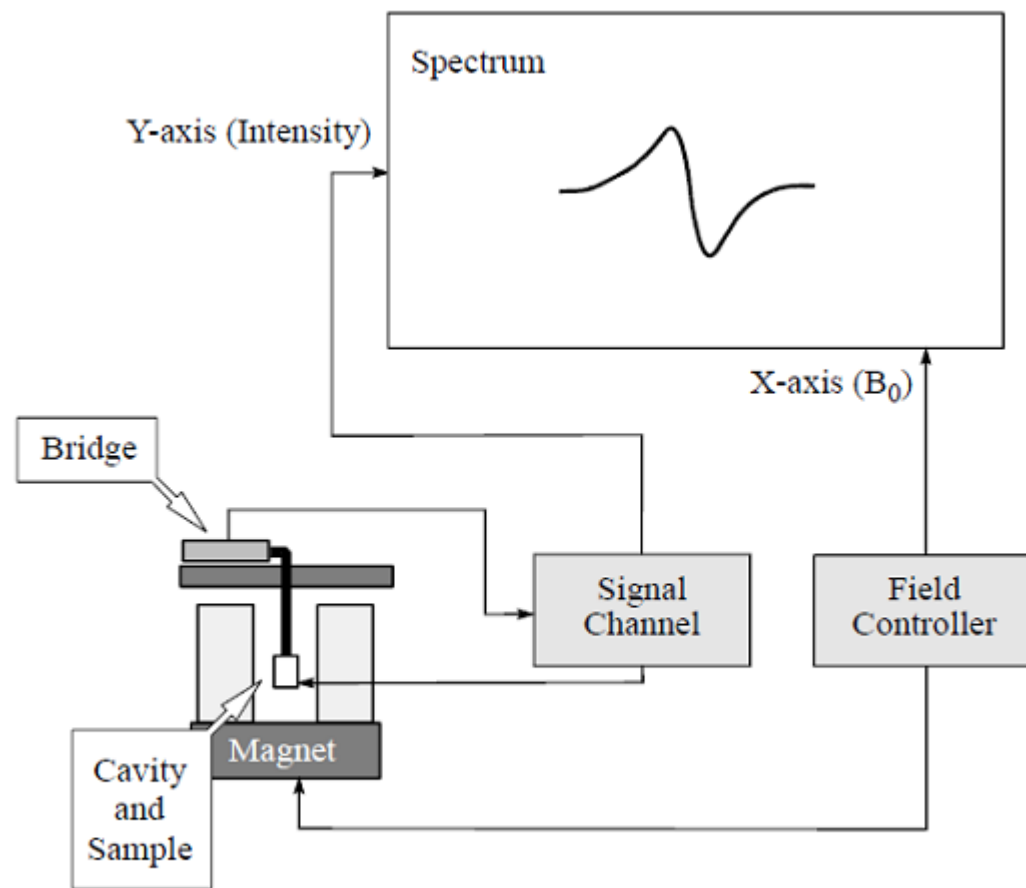
## *A simple spectrometer*



*EPR Spectrometer*

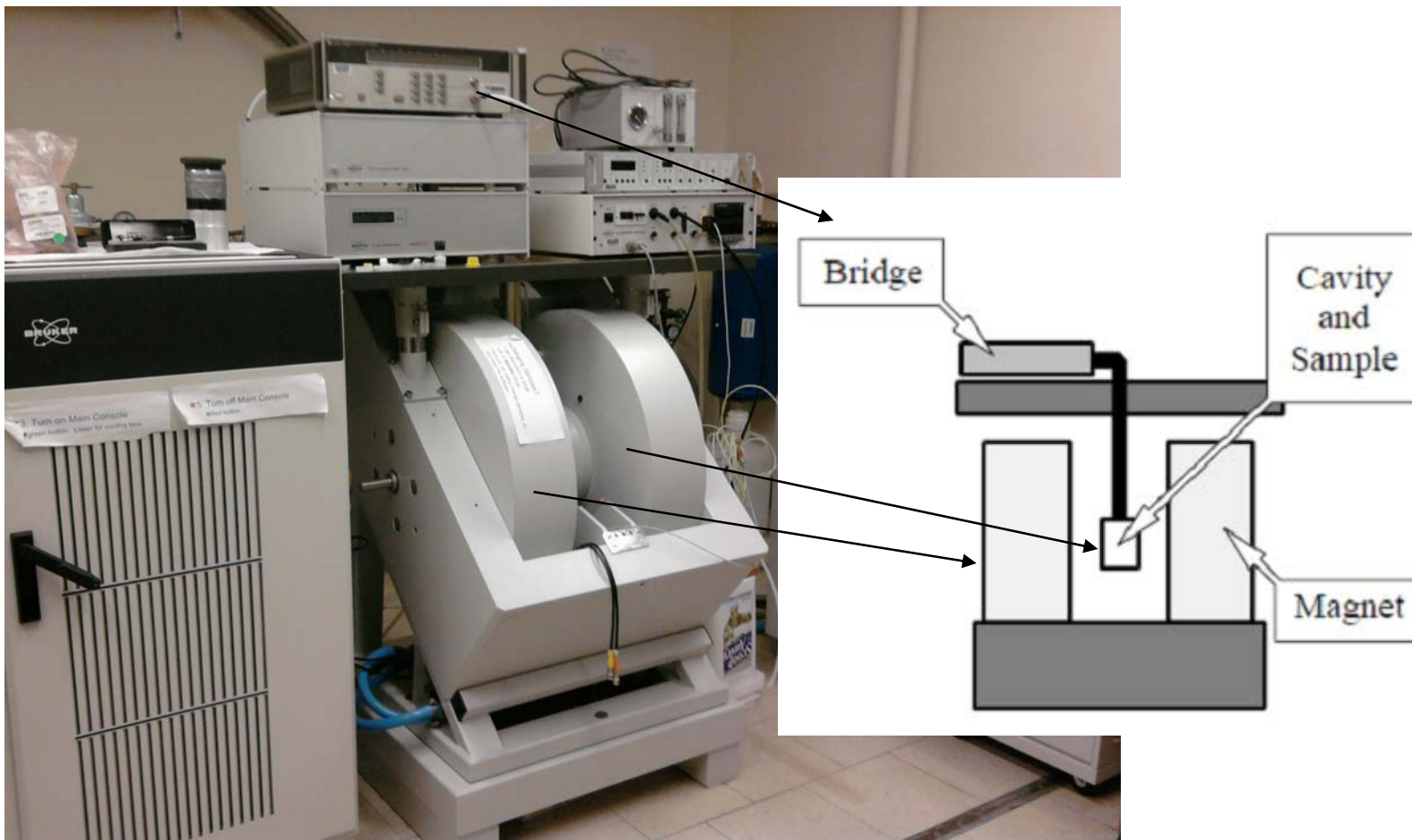


# *EPR Spectrometer*



Block diagram of an EPR spectrometer.

*EPR Spectrometer*



The general outlay of an EPR spectrometer.

## *EPR vs NMR*

---

- Both deal with the interaction of electromagnetic radiation with magnetic moments.
- EPR focuses on interaction of an external magnetic field with the unpaired electrons in a molecule rather than the nuclei of individual atoms.
- Radiation in MHz range (rf) is used for NMR whereas radiation in GHz range (mw) is used for EPR experiments.

## *Microwave Band*

---

Microwave Band	Frequency (GHz)	$B_{\text{res}}$ (G)
L	1.1	390
S	4.0	1430
X	9.75	3480
Q	34.0	12100
W	94.0	33500

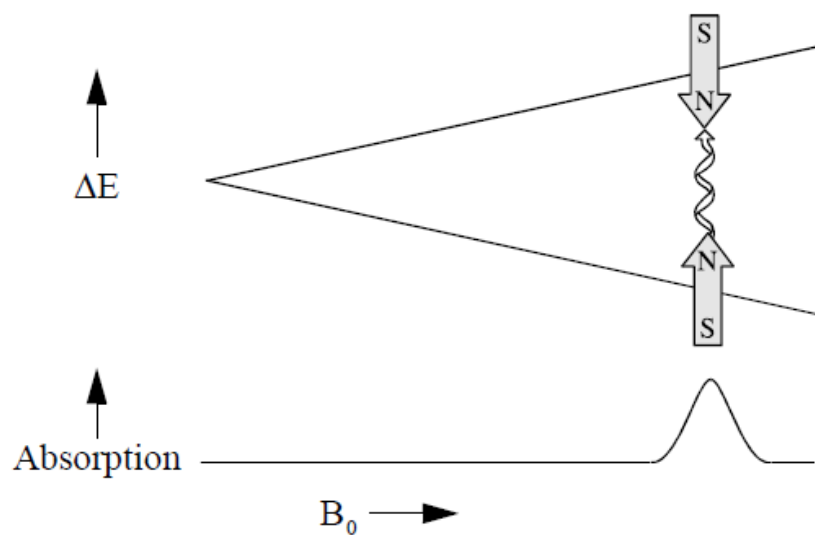
Field for resonance,  $B_{\text{res}}$ , for a  $g = 2$  signal at selected microwave frequencies.

## *Scope of the EPR technique*

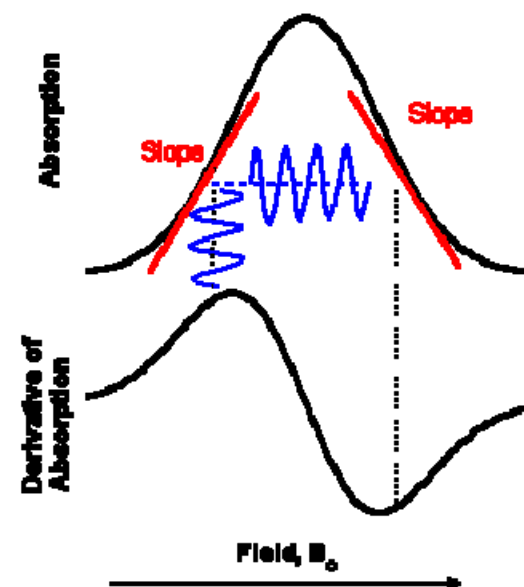
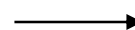
---

- EPR is a technique that is applicable to systems in a paramagnetic state or which can be placed in such a state.
- Examples
  1. Free radicals in the solid, liquid or gas phases.
  2. Transition ions including actinide ions
  3. Various point defects (eg. An electron trapped at a negative ion vacancy in crystals and glasses or deficiency of an electron, ie. a positive hole)
  4. Systems with more than one unpaired electron (eg. Triplet-state systems, biradicals, etc.)
  5. Systems with conducting electrons (eg. Semiconductors, metals.)

## *EPR Spectroscopy*

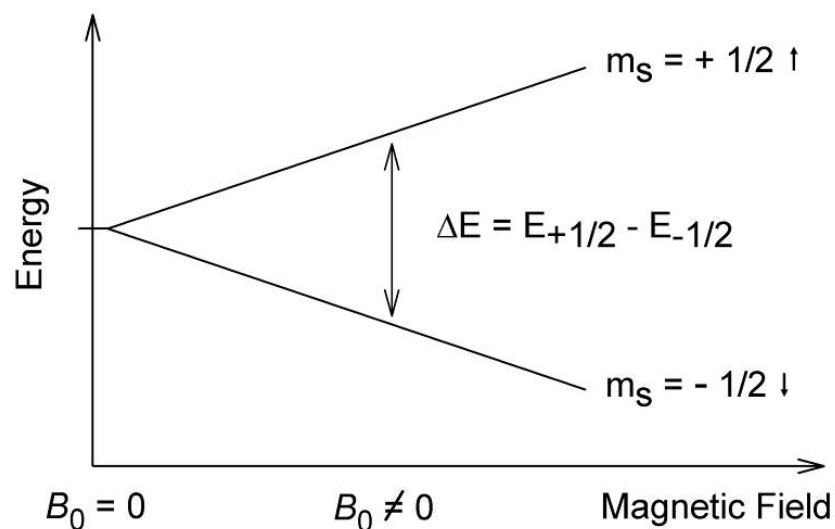


Transition associated with the absorption of electromagnetic energy.



Obtained spectra is the first derivative of the absorption spectra.

## *Zeeman Effect*



$$\uparrow_{B_0} \longrightarrow \Delta E = h\nu = g \mu_B B_0 \longrightarrow g = \frac{h\nu}{\mu_B H}$$

$\swarrow$        $\downarrow$        $\searrow$   
 g-value    Bohr magneton    External magnetic field

Variation of the spin state energies as a function of the applied magnetic field.

## *g-value*

---

- $g$ -value represents the response factor of a spin unit to external magnetic fields.
- It's a unit-less constant that is a characteristic of a spin unit. An isolated electron in a vacuum has  $g=2.002319$  and most electron spin based magnetic systems have  $1.9 < g < 2.1$  (especially organics)

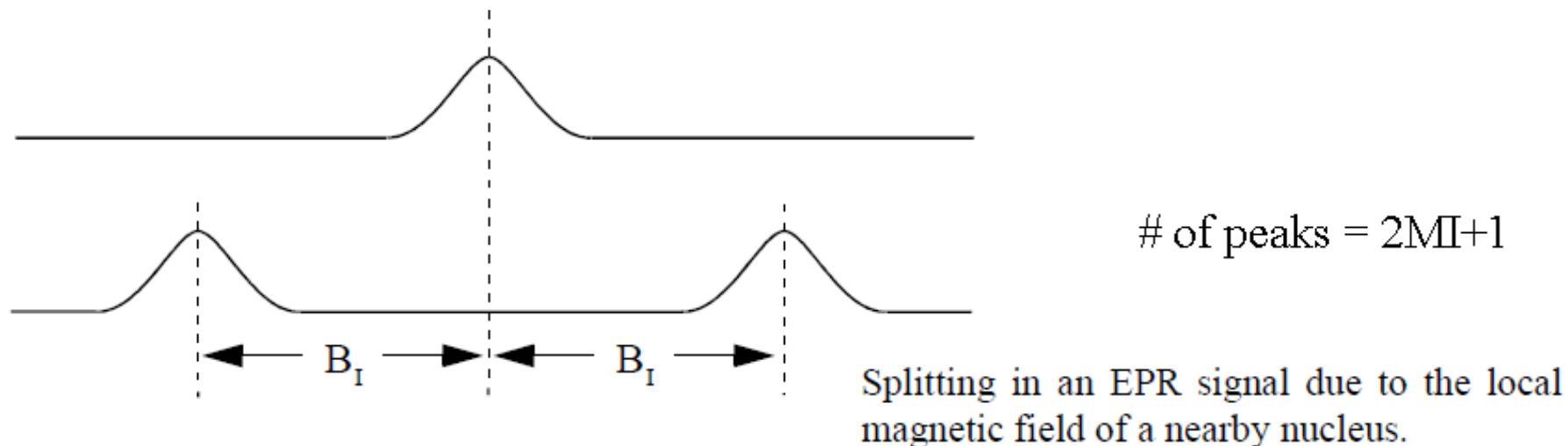
## *What can we learn from the g-value?*

---

- The species of the atom on which the unpaired  $e^-$  sits.
- The molecular orbitals in which the unpaired  $e^-$  resides.
- The nature of chemical bonds to which the unpaired  $e^-$  belongs.
- The surrounding molecular environments from which the unpaired  $e^-$  feels interactions.
- The materials possess their own proper magnitude of g-values which makes it possible to specify or predict the various situations of the unpaired electron.

## Hyperfine Coupling

- Similar to spin-spin coupling in NMR.
  1. Coupling of the electron magnetic moment to the magnetic moment of its own nucleus.
  2. Coupling of the electron magnetic moment to a magnetic moment of a different atom-called super hyperfine splitting.



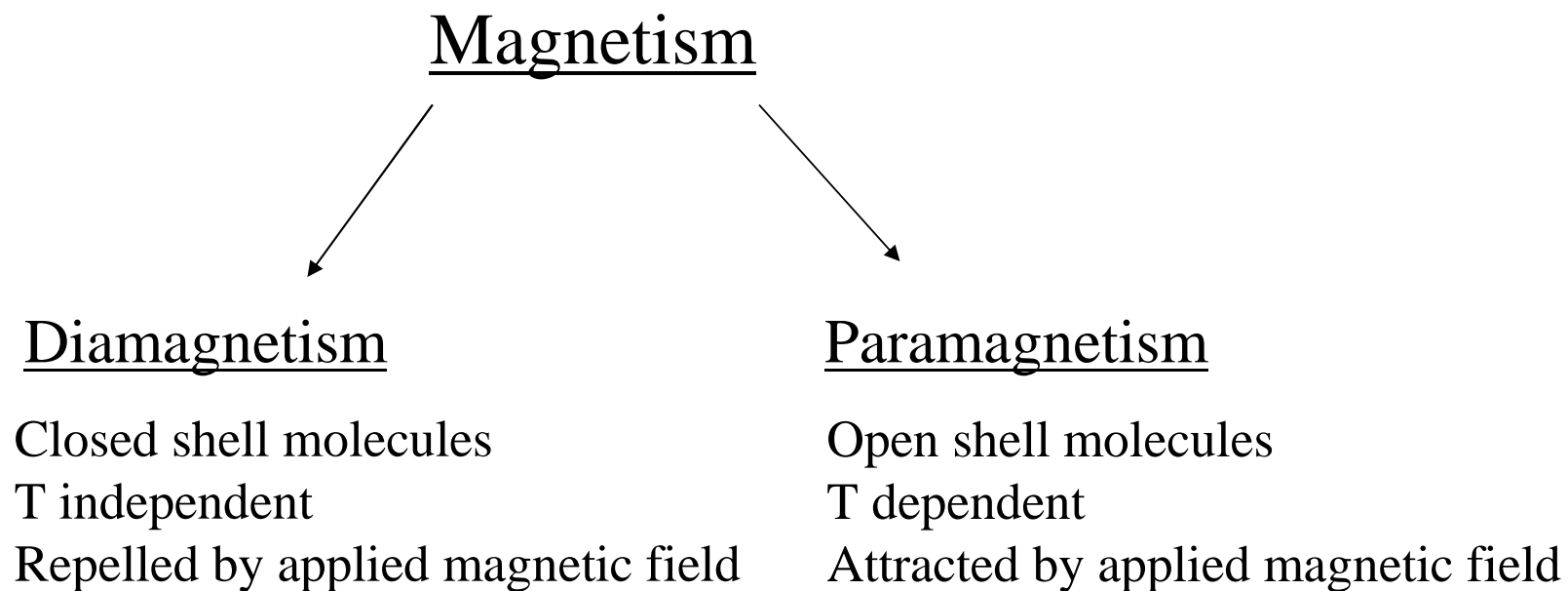
## *Why do I use EPR spectroscopy?*

---

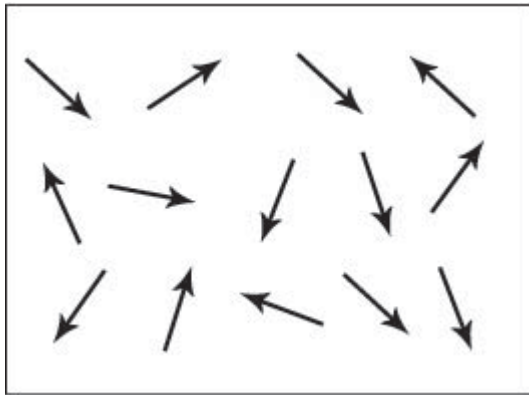
- For the identification of new, purely organic, persistent radicals capable of showing spontaneous magnetization below a certain critical temperature.
- For spin counting experiments
- To study the g-anisotropy of certain single crystals under different temperatures.

*Types of Magnetism*

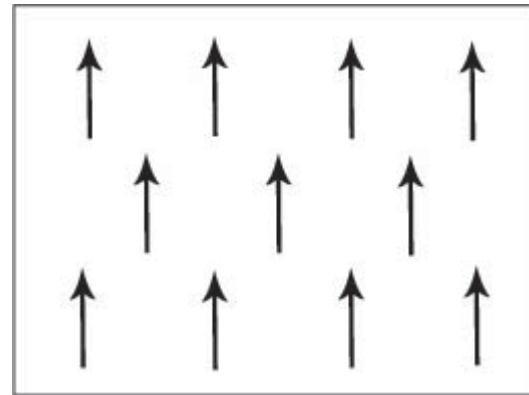
---



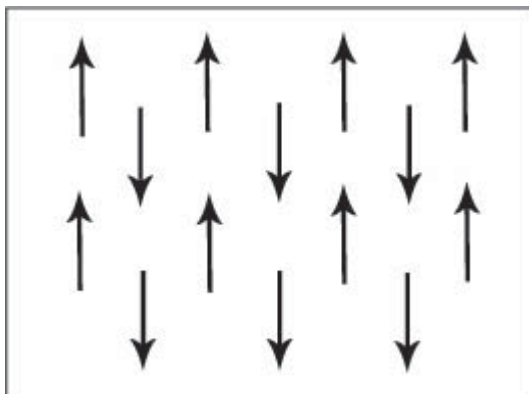
*Types of Magnetism*



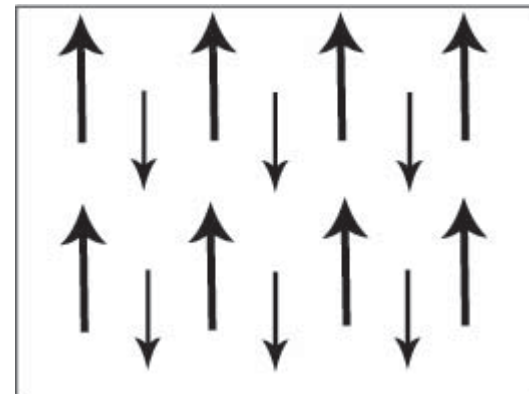
Paramagnetism



Ferromagnetism



Antiferromagnetism



Ferrimagnetism

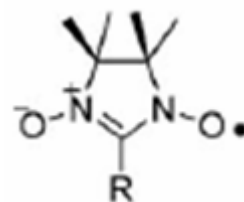
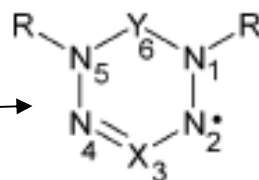
## *Molecular Magnetism*

---

- Traditional magnets
- Unpaired electron spins reside on d or f type of orbitals.
- Made up of atomic lattices
- High temperature preparation techniques
- Molecular magnets
- Unpaired electrons can reside on s and p orbitals as well (for the purely organic species)
- Building blocks are molecular in nature
- Low temperature preparation techniques

## *Stable Radicals*

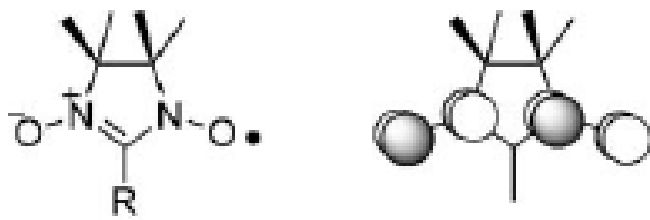
- ***Hydrocarbon-based radicals***
  - \* Triphenylmethyl
  - \* Phenalenyl
  - \* Cyclopentadienyl
  - \* Phenoxy
- ***Nitrogen and/or oxygen based radicals***
  - \* Aminyl
  - \* Hydrazyl
  - \* Tetraazapentadienyl, Tetrazolinyl
  - \* Verdazyl
  - \* Oxoaminyl
  - \* Nitroxide
  - \* Nitronyl Nitroxide
- ***Spin density on nitrogen and sulfur***
  - \* Thioaminyl
  - \* Dithiadiazolyl
  - \* Dithiazolyl
  - \* Thiazinyl



## *Nitronyl Nitroxide Radicals*

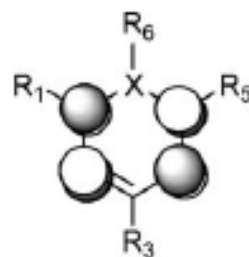
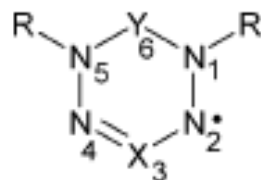
---

- Most stable example of nitroxides.
- Readily prepared from most aldehydes.
- Spin density is mainly on the nitrogen and oxygen atoms.
- They have chemically equivalent nitrogen atoms.



## *Verdazyl Radicals*

- Generally air and moisture-stable and their stability doesn't require bulky substituents.
- Typically don't dimerize in solution or in the solid state.
- Suitable for use in supramolecular chemistry involving H bond donors such as OH and NH<sub>2</sub>.
- They consist of planar rings



## *What makes the radical stable?*

---

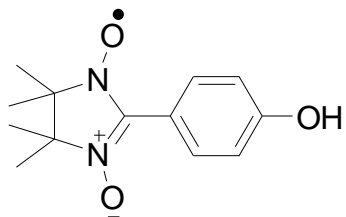
- Steric protection (incorporation of bulky substituents) to provide kinetic and thermodynamic stability.
- Delocalization of the spin density.(to dilute the amount of spin on any atom)
- Heteroatom based radicals (effective carriers of spin density)

## *Challenge!!*

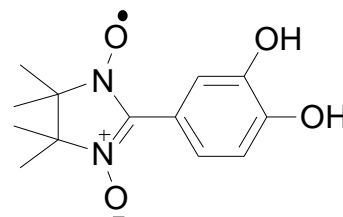
---

- In order to create stable paramagnetic materials one has to construct open shell structures.
- The stability of the organic radicals has to be increased through chemical modifications.
- Introduction of ferromagnetic intermolecular interactions is desirable.
- To achieve magnetic spin ordering in a bulk solid one must first achieve appropriate crystal ordering.
- One of the promising strategies for controlling the solid state packing behavior is hydrogen bonding.

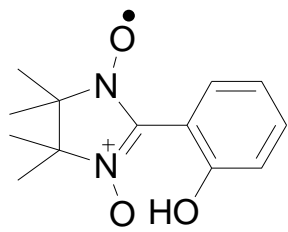
## The Effect of Hydrogen Bonding



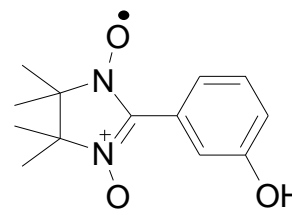
FM interactions



AFM and FM interactions



FM interactions

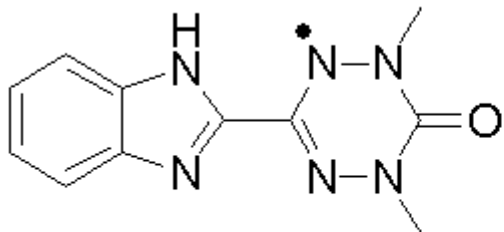


AFM interactions

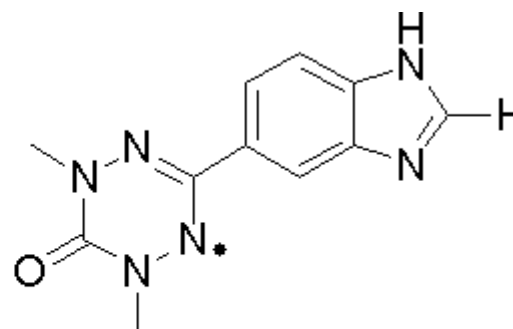
Cirujeda, J.; Gasio, E.; Rovira, C.; Stanger, J. L.; Turek, P.; Veciana, J. *J. Mater. Chem.* **1995**, 5(2), 243-252.

## 1. Use of EPR for the identification of radicals

- Verdazyl radicals

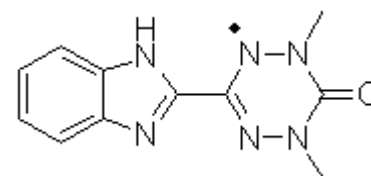
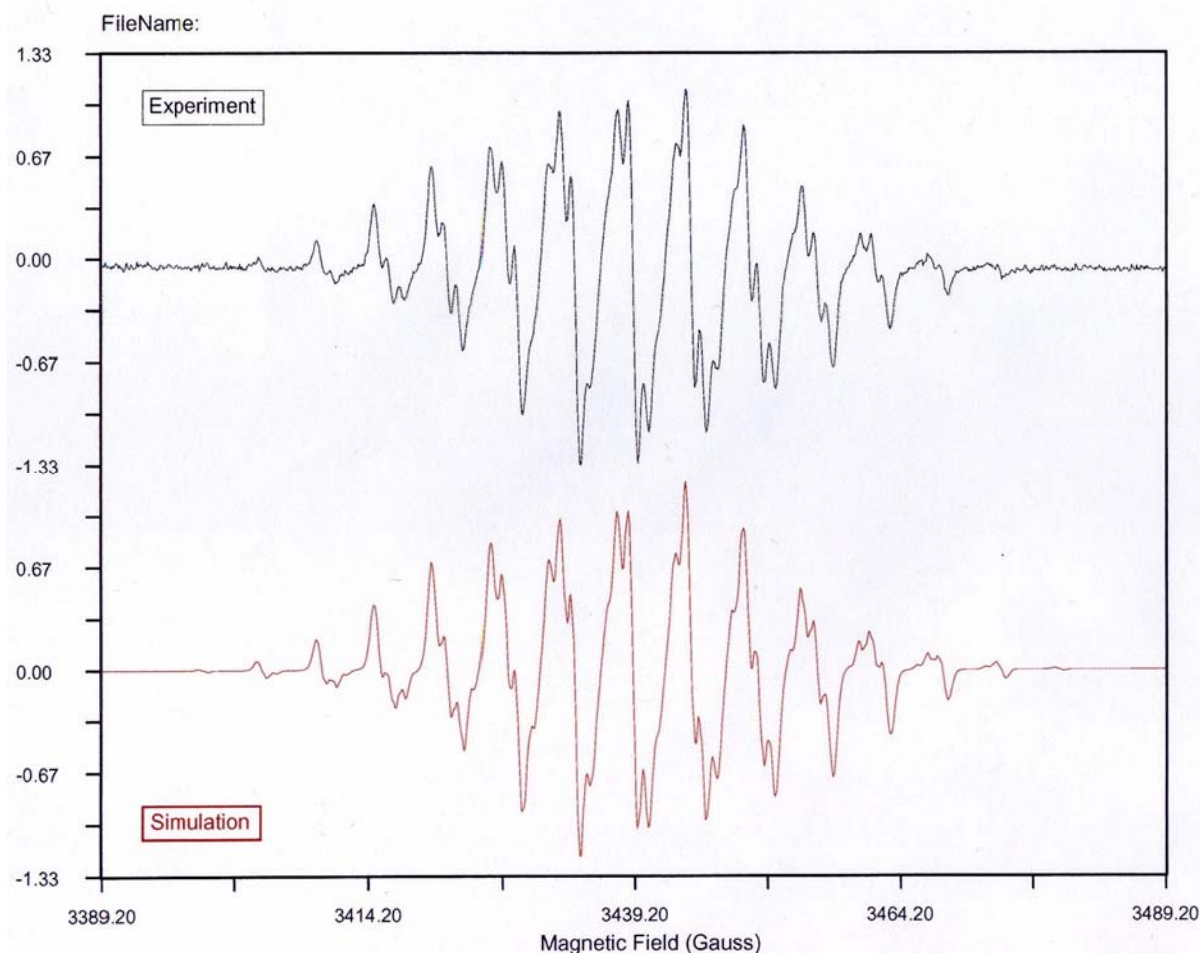


2-BIm-verdazyl



5-BIm-verdazyl

## Experimental vs Simulation



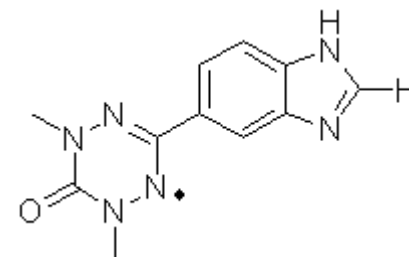
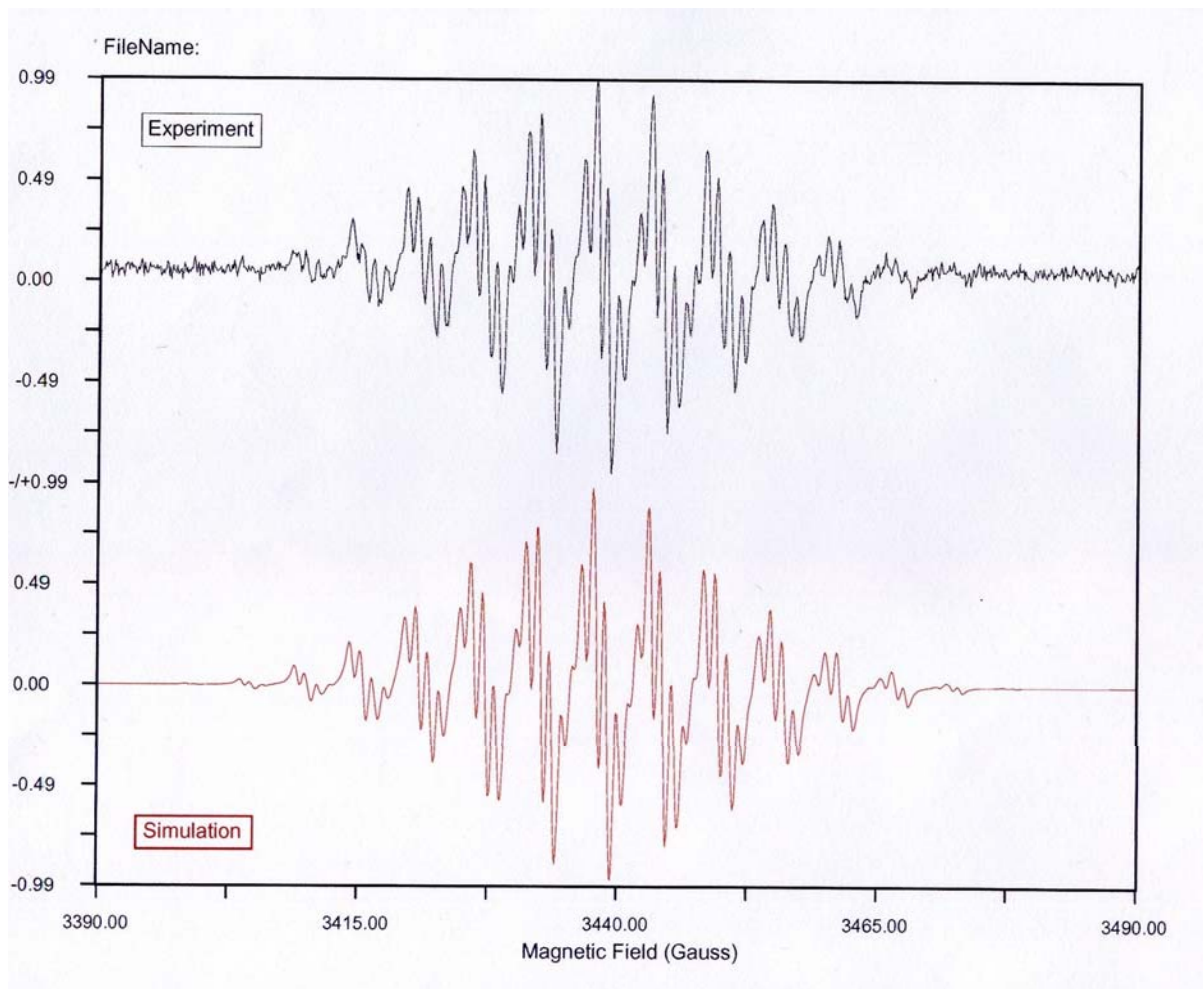
**Species number: 1**

Rel. conc. : 100.000      Lorentzian : 39.828

Line width : 0.316      G-shift : -0.278

Nuclei	Coupling	Spin	Number
1	6.462	1.0	2
2	5.271	1.0	2
3	5.564	0.5	6
4	0.472	0.5	1

## Experimental vs Simulation



**Species number: 1**

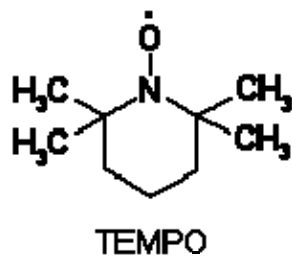
Rel. conc. : 100.000      Lorentzian : 94.042

Line width : 0.447      G-shift : -1.582

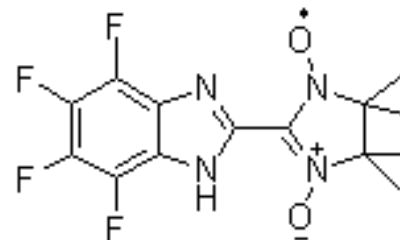
Nuclei	Coupling	Spin	Number
1	6.456	1.0	2
2	5.410	1.0	2
3	5.205	0.5	6
4	0.852	0.5	1

## 2. Spin counting experiments

- To find the amount of spin in a molecule by comparison to a standard, which is considered a 100% spin.
- With the help of these experiments one can understand the purity of the synthesized compound.

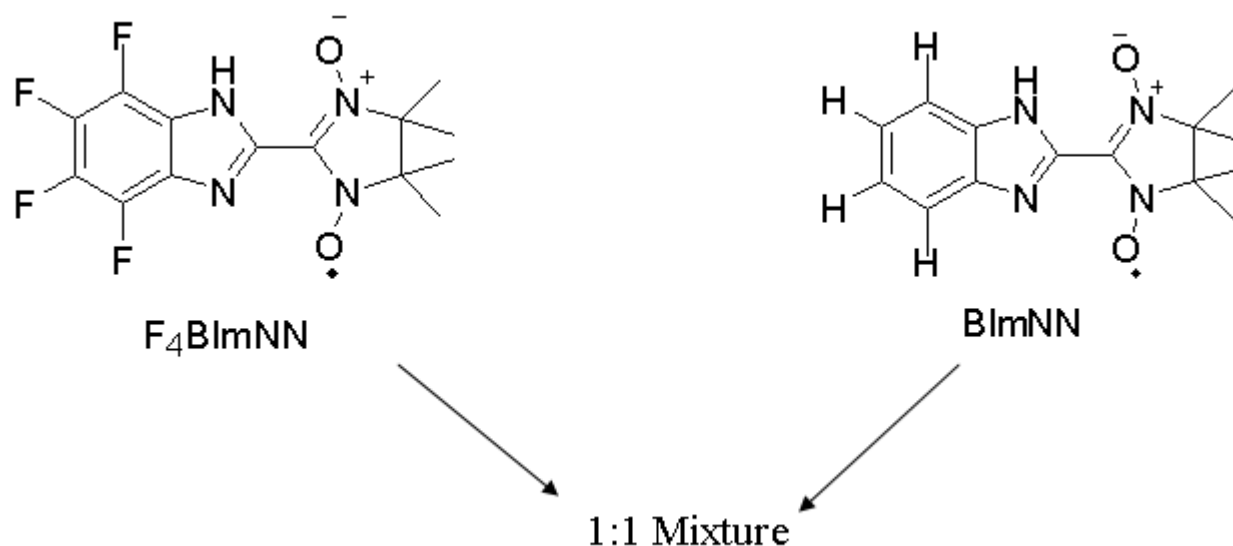


vs

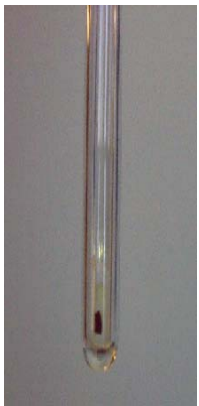


### 3. *g*-anisotropy

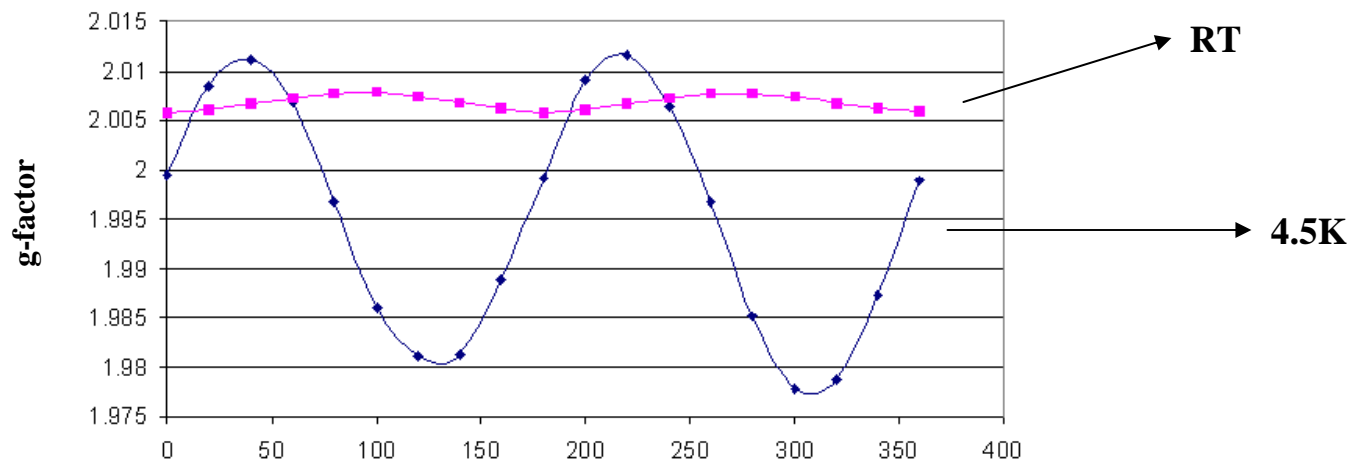
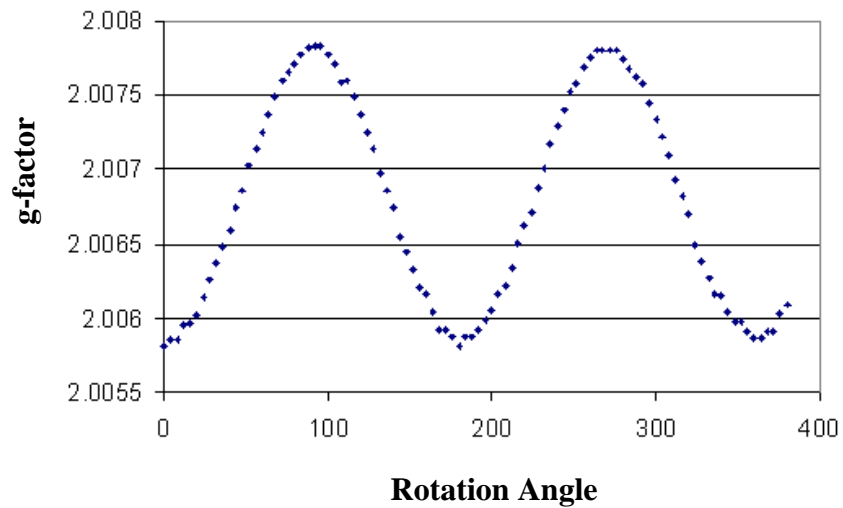
- Single crystal studies of  $F_4\text{BImNN}$  and  $F_4\text{BImNN} + H_4\text{BImNN}$
- Preparing new organic alloys from  $F_4\text{BImNN}$  and  $\text{BImNN}$



*Goniometer*



## Mixed Crystal-ez



*Questions?*

---

