

**Introduction
to
Electron Spin Resonance
Spectroscopy**

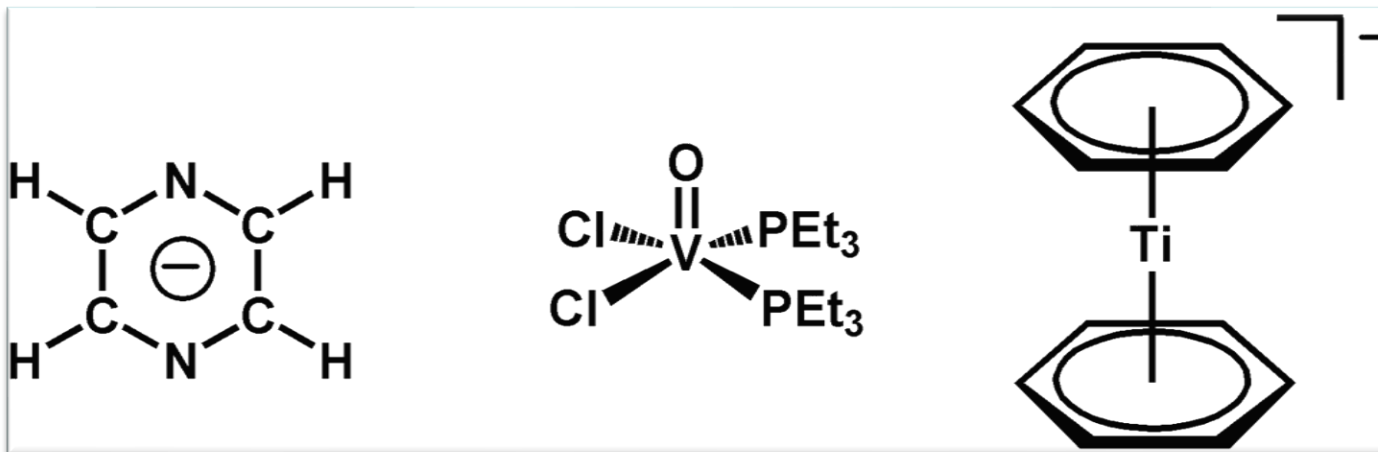
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Introduction

- Electron Spin Resonance Spectroscopy is also called EPR Spectroscopy (Electron Paramagnetic Resonance Spectroscopy)
- Non-destructive technique
- Applicable for species with one or more unpaired electrons, *e. g.* Free radicals, Transition metal compounds
Stable species: O₂, NO, [Fe(CN)₆]³⁻

- Useful for unstable paramagnetic compounds generated *in situ*, e. g. Electrochemical oxidation or reduction

Transients: CH_3 , C_6H_6^- , $\text{Ge}[\text{N}\{\text{Si}(\text{CH}_3)_3\}_2]_3$



Applications:

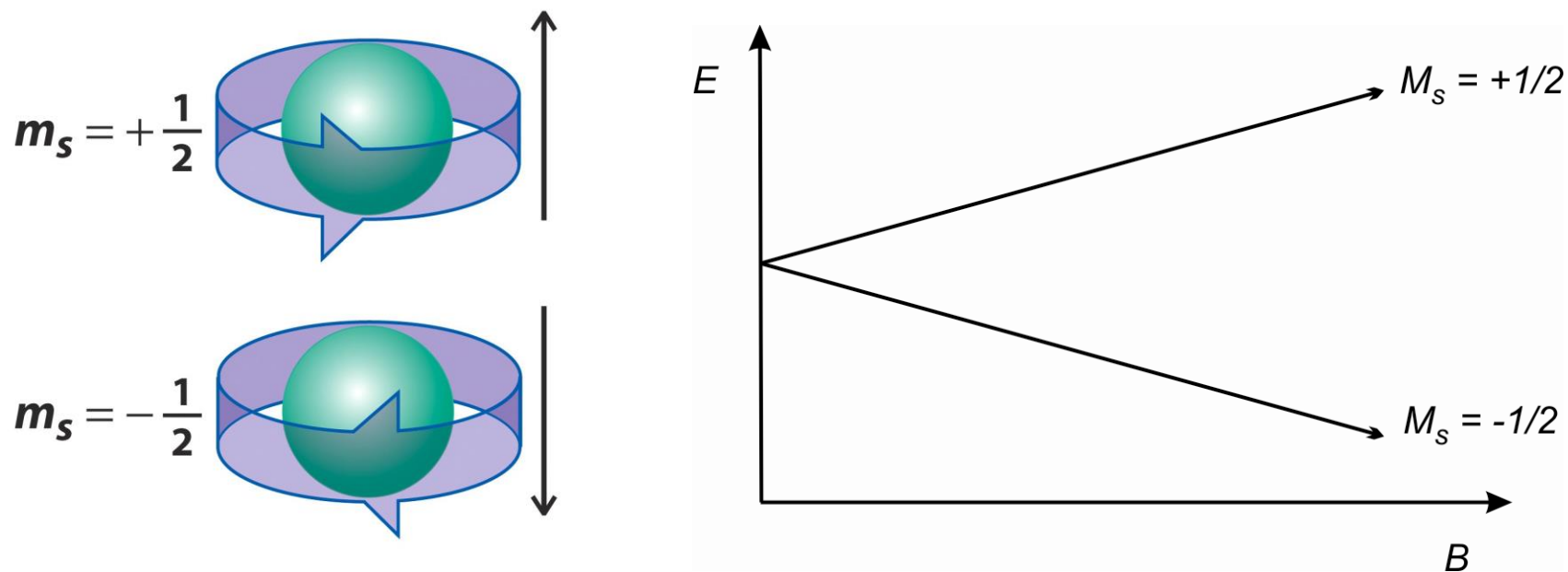
- Oxidation and reduction processes
- Reaction kinetics
- Examining the active sites of metalloproteins

Salient features:

- ESR measures the transition between the electron spin energy levels which are induced by the appropriate frequency radiation.
- Required frequency of radiation depends on strength of applied magnetic field and generally falls in Microwave region
- Common field strength employed are 0.34 and 1.24 T

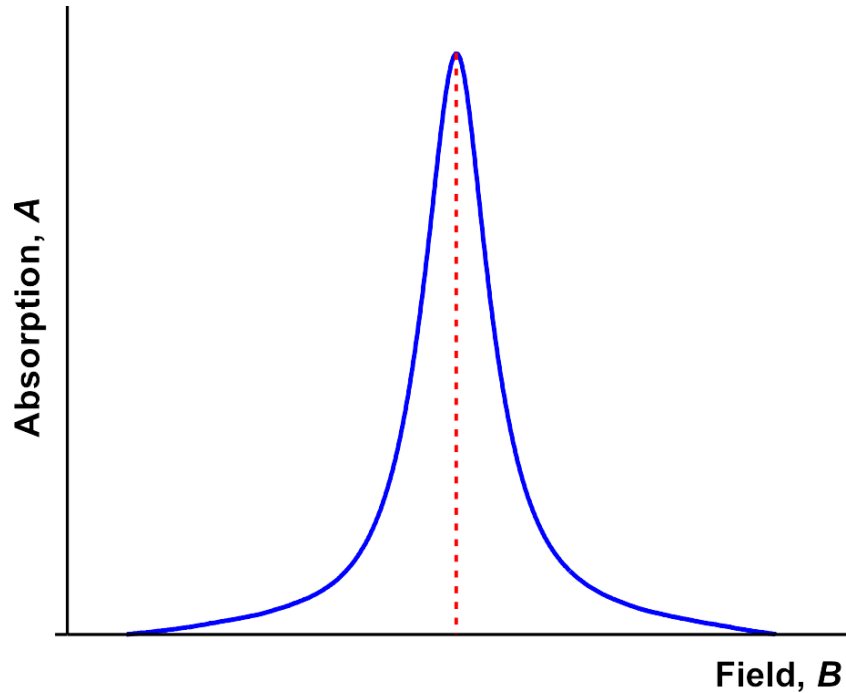
Principles of ESR spectroscopy

- Electron spin moment interacts with applied electromagnetic radiation

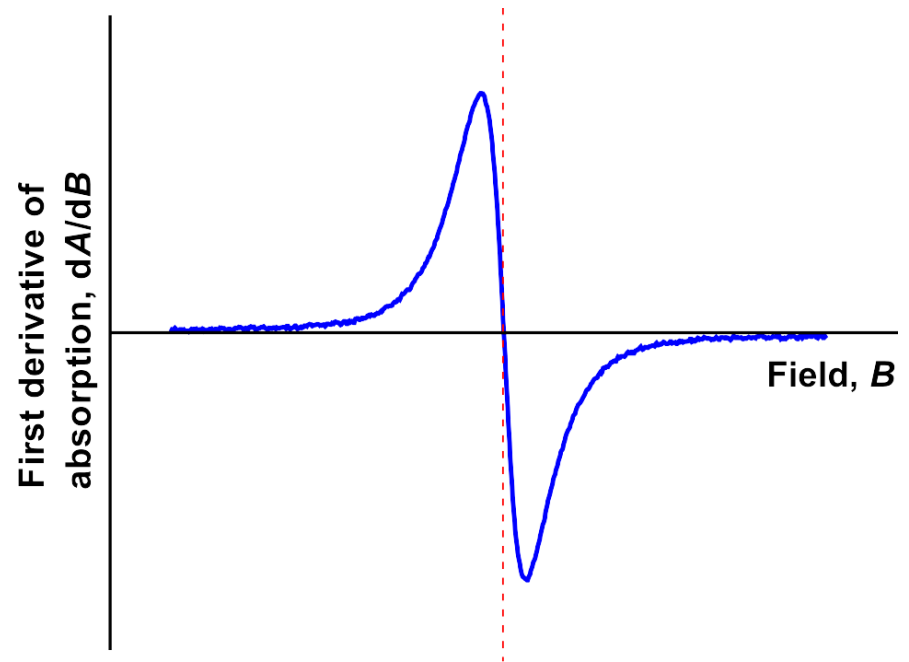


Resulting energy levels of an electron in a magnetic field

Types of Spectra in ESR:



Absorption Spectrum



Derivative Spectrum

Derivative Spectra are more easy to interpret for as maxima is clearly visible

Energy of electron spin levels:

➤ Based on the spin of an electron and its associated magnetic moment, for a molecule with one unpaired electron, the energy can be described as:

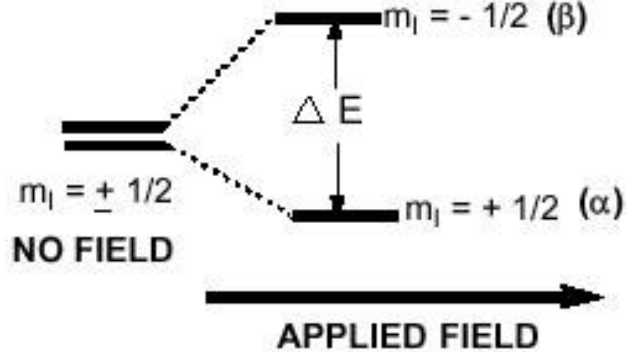
In the presence of a magnetic field, the two electron spin energy levels are:

$$E = gm_B B_0 M_S$$

g = proportionality factor m_B = Bohr magneton

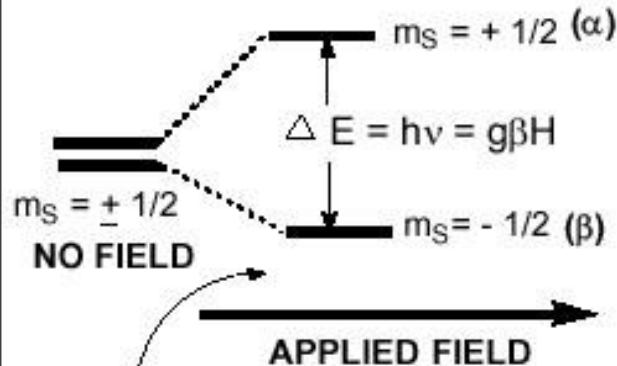
M_S = electron spin quantum number (+1/2 or -1/2) B_0 = Magnetic field

NUCLEAR SPIN STATES



TWO ENERGY STATES ARISE FROM THE ALIGNMENT OF NUCLEAR MOMENTS RELATIVE TO A FIELD ΔE IS IN THE ENERGY RANGE OF RADIOFREQUENCIES

ELECTRON SPIN STATES



DIFFERENT ENERGY STATES ARISE FROM THE INTERACTION OF THE UNPAIRED ELECTRON SPIN MOMENT (GIVEN BY $m_S = \pm 1/2$ FOR A FREE ELECTRON) WITH THE MAGNETIC FIELD ΔE IS IN THE ENERGY RANGE OF MICROWAVE FREQUENCIES

THIS IS KNOWN AS THE ZEEMAN INTERACTION

Hyperfine splitting

EPR signal splitting by neighboring spin active nuclei is called hyperfine interactions/splitting; which can provide information about:

- Number and identity of nuclei
- Distance from unpaired electron

Interactions with neighboring nuclei has the energy:

$$E = gm_B B_0 M_S + AM_S m_I$$

A = hyperfine coupling constant

(Measured as the distance between the centers of two signals)

m_I = nuclear spin quantum number

Selection rules for ESR

- Selection rules are same as for NMR
- Every isotope of every element has a ground state nuclear spin quantum number, I has value of $n/2$, n is an integer
- Isotopes with even atomic number and even mass number have $I = 0$, and have no EPR spectra (^{12}C , ^{28}Si , ^{56}Fe , ...)
- Isotopes with odd atomic number and even mass number have n even (^2H , ^{10}B , ^{14}N , ...)
- Isotopes with odd mass number have n odd (^1H , ^{13}C , ^{19}F , ^{55}Mn , ...)

The magnitude of the splitting and the number of lines in ESR spectrum depend upon:

- The nuclear spin of the interacting nucleus

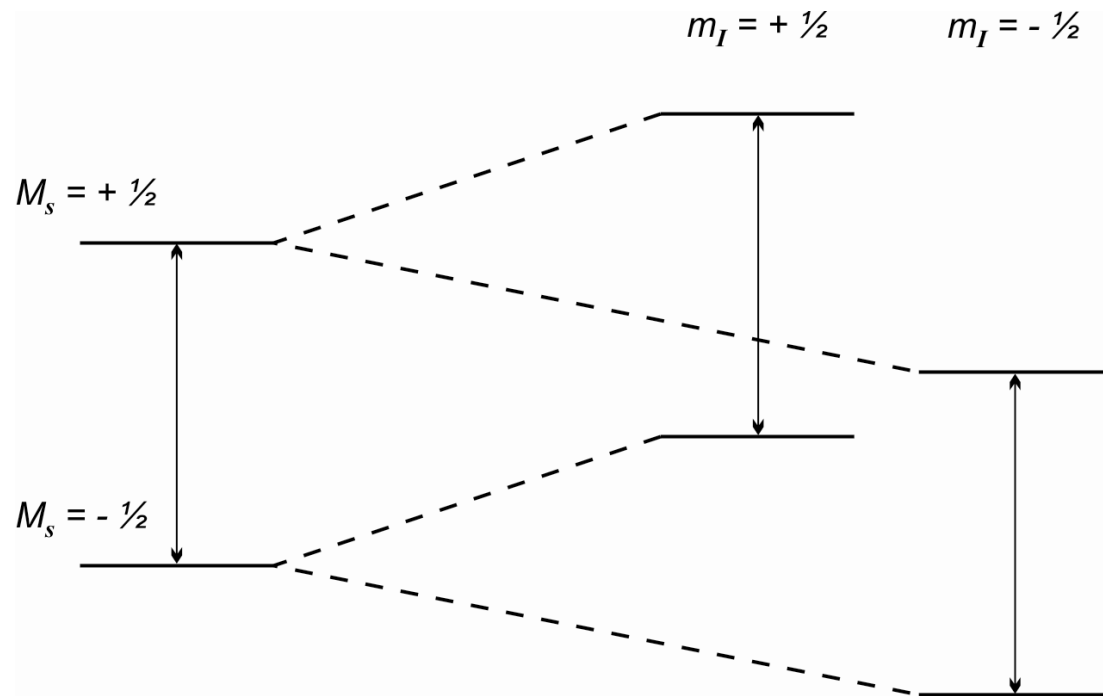
No. of lines = $2nI + 1$) so $I = \frac{1}{2}$ (for spin active nucleus) gives 2 lines, etc.

Herein, n = no. of spin active nucleus.

- The nuclear gyromagnetic ratio
- The magnitude of the interaction between the electronic spin and the nuclear spin
Magnitude of the splitting typically decreases greatly with increasing numbers of bonds between the nucleus and unpaired electron.

The hyperfine effect

- The magnetic field experienced by the unpaired electron is affected by nearby nuclei with non-zero nuclear spin



Selection Rules:

$$\Delta M_s = \pm 1$$

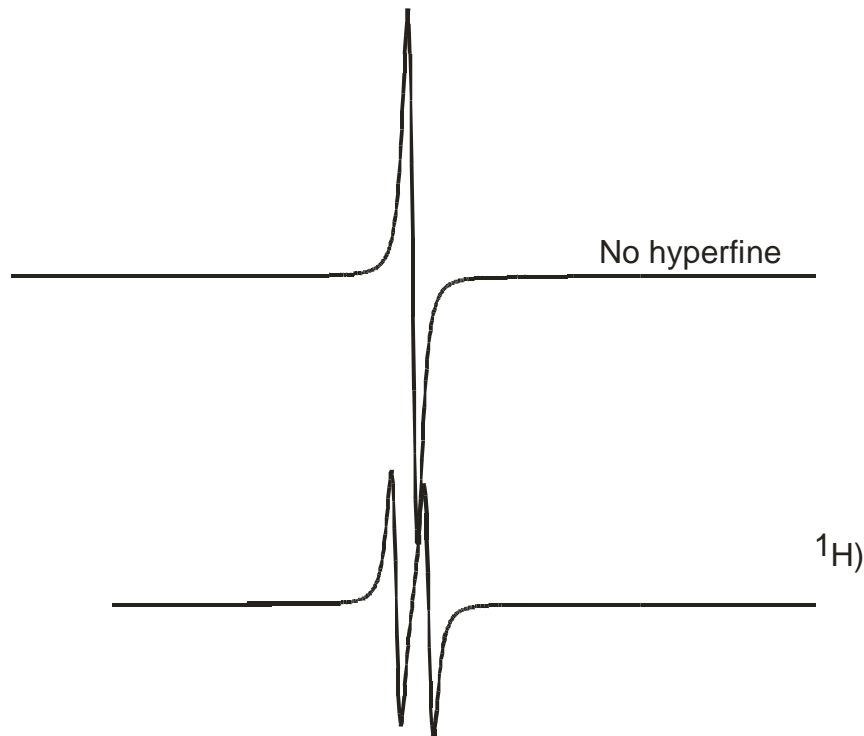
$$\Delta M_I = 0$$

Interaction with a single nucleus of spin $\frac{1}{2}$

Hyperfine coupling

If the electron is surrounded by n spin-active nuclei with a spin quantum number of I , then a $(2nI+1)$ line pattern will be observed in a similar way to NMR.

In the case of the hydrogen atom ($I=1/2$), this would be $2(1)(1/2) + 1 = 2$ lines.



List of some spin active nuclei with spins

Element	Isotope	Nuclear spin	No of lines	% abundance
Hydrogen	^1H	$\frac{1}{2}$	2	99.985
Nitrogen	^{14}N	1	3	99.63
	^{15}N	$\frac{1}{2}$	2	0.37
Vanadium	^{51}V	$\frac{7}{2}$	8	99.76
Manganese	^{55}Mn	$\frac{5}{2}$	6	100
Iron	^{57}Fe	$\frac{1}{2}$	2	2.19
Cobalt	^{59}Co	$\frac{7}{2}$	8	100
Nickel	^{61}Ni	$\frac{3}{2}$	4	1.134
Copper	^{63}Cu	$\frac{3}{2}$	4	69.1
	^{65}Cu	$\frac{3}{2}$	4	30.9
Molybdenum	^{95}Mo	$\frac{5}{2}$	6	15.7
	^{97}Mo	$\frac{5}{2}$	6	9.46

Intensity of ESR signals

- ❑ Relative intensities determined by the number of interacting nuclei
 - *If only one nucleus interacting (All lines have equal intensity)*
- ❑ If multiple nuclei interacting, distributions are derived based upon spin
 - *For spin $1/2$ (most common), intensities follow binomial distribution*

Hyperfine splitting multiply with the number of nuclear spins

Benzoquinone anion radical:

1 H = splits into 2 lines 1:1

2 H = split into 3 lines 1:2:1

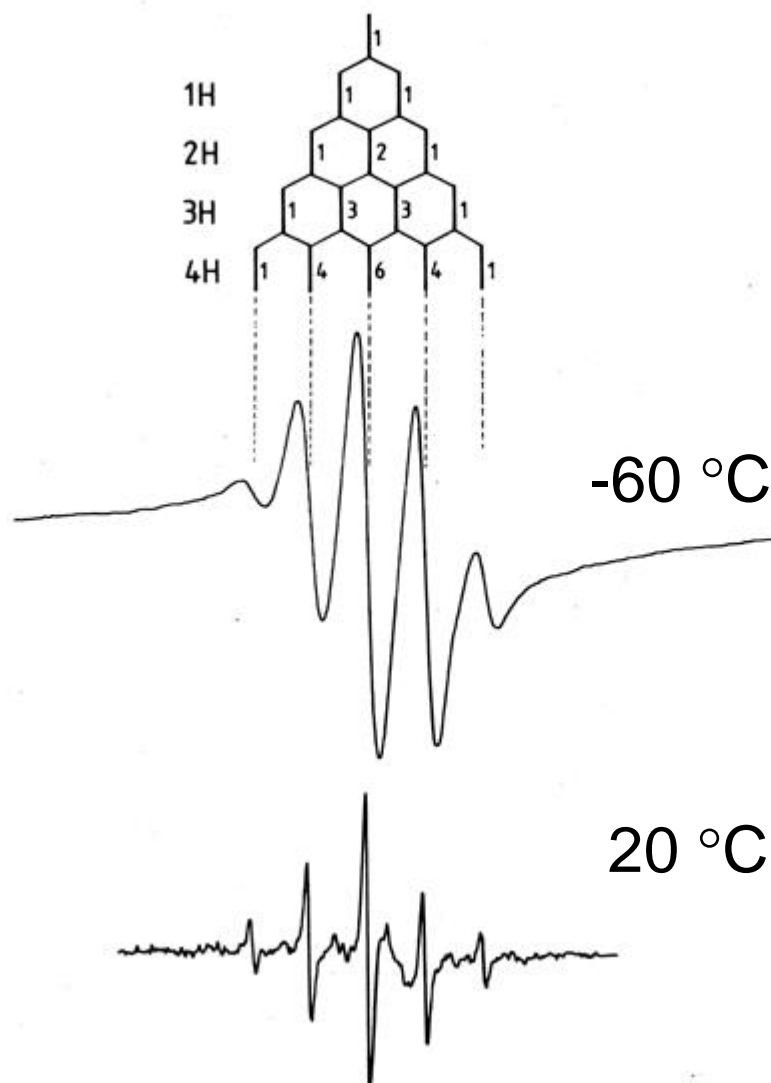
3 H = split into 4 lines 1:3:3:1

4 H = split into 5 lines 1:4:6:4:1

At higher temperature:

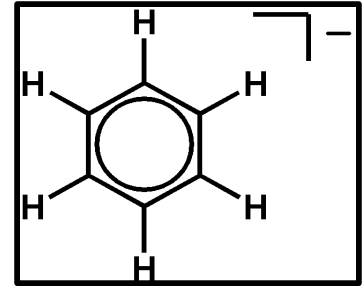
faster motion - sharper lines

shorter lifetime - smaller signal



Example of hyperfine splitting:

- Radical anion of benzene $[\text{C}_6\text{H}_6]^-$

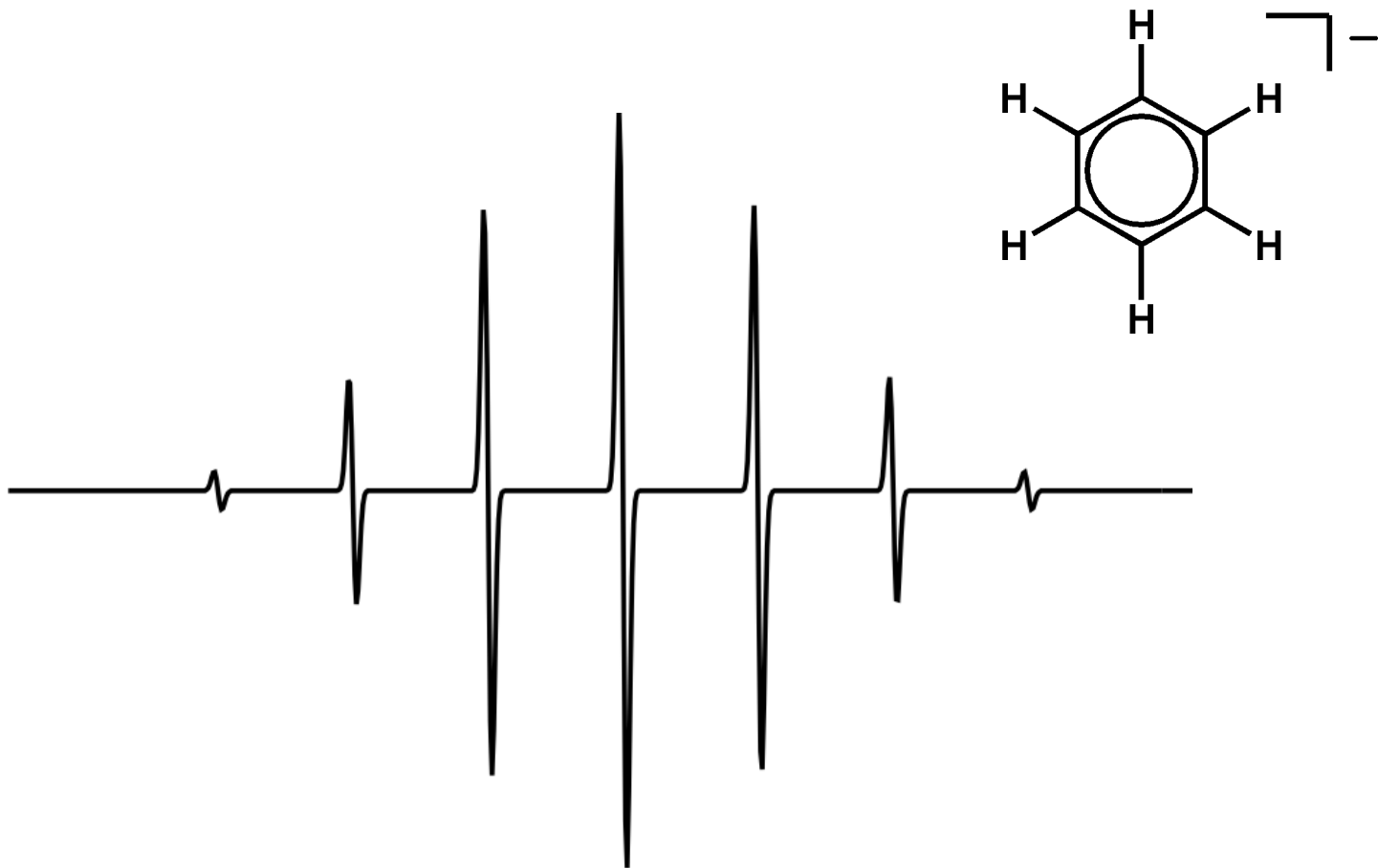


- Electron is delocalized over all six carbon atoms
 - Exhibits coupling to six equivalent hydrogen atoms
- So,

$$2NI + 1 = 2(6)(1/2) + 1 = 7$$

- So spectrum should be seven lines with relative intensities 1:6:15:20:15:6:1

EPR spectrum of benzene radical anion



VO(acac)₂: Interaction with vanadium nucleus

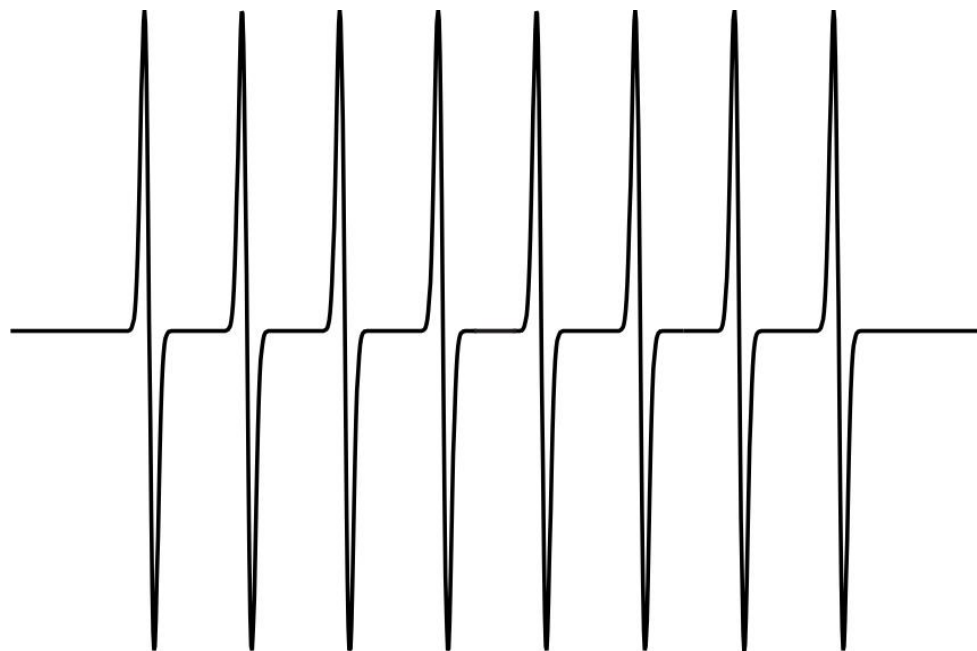
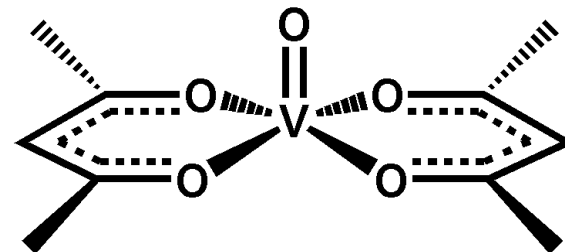
For vanadium, $I = 7/2$

– So,

$$2NI + 1 = 2(1)(7/2) + 1 = 8$$

– You would expect to see 8 lines of equal intensity

ESR spectrum of vanadyl acetylacetonate



Questions!!!