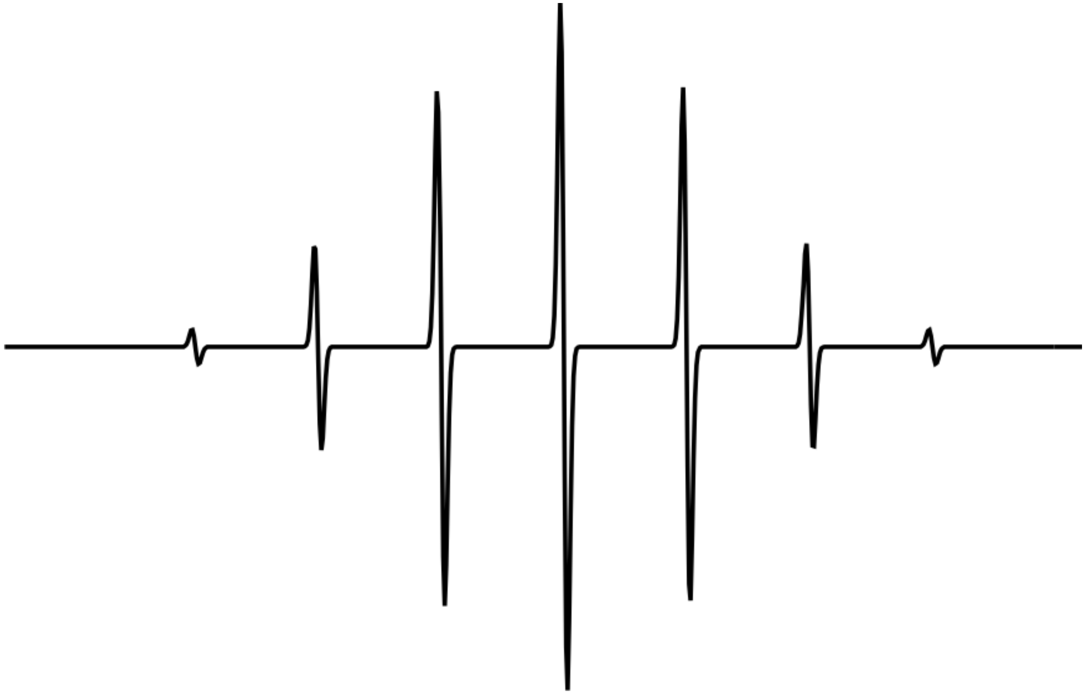
Electron Spin Resonance Spectroscopy



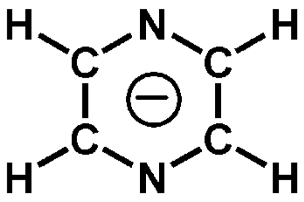
ESR Spectroscopy

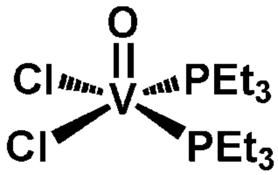
- Electron Spin Resonance Spectroscopy
- Also called EPR Spectroscopy
  - Electron Paramagnetic Resonance Spectroscopy
- Non-destructive technique

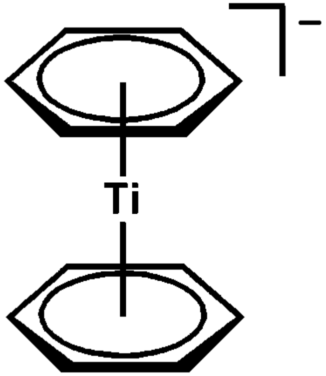
- Applications
  - Oxidation and reduction processes
  - Reaction kinetics
  - Examining the active sites of metalloproteins

What compounds can you analyze?

- Applicable for species with one or more unpaired electrons
  - Free radicals
  - Transition metal compounds
- Useful for unstable paramagnetic compounds generated *in situ*
  - Electrochemical oxidation or reduction



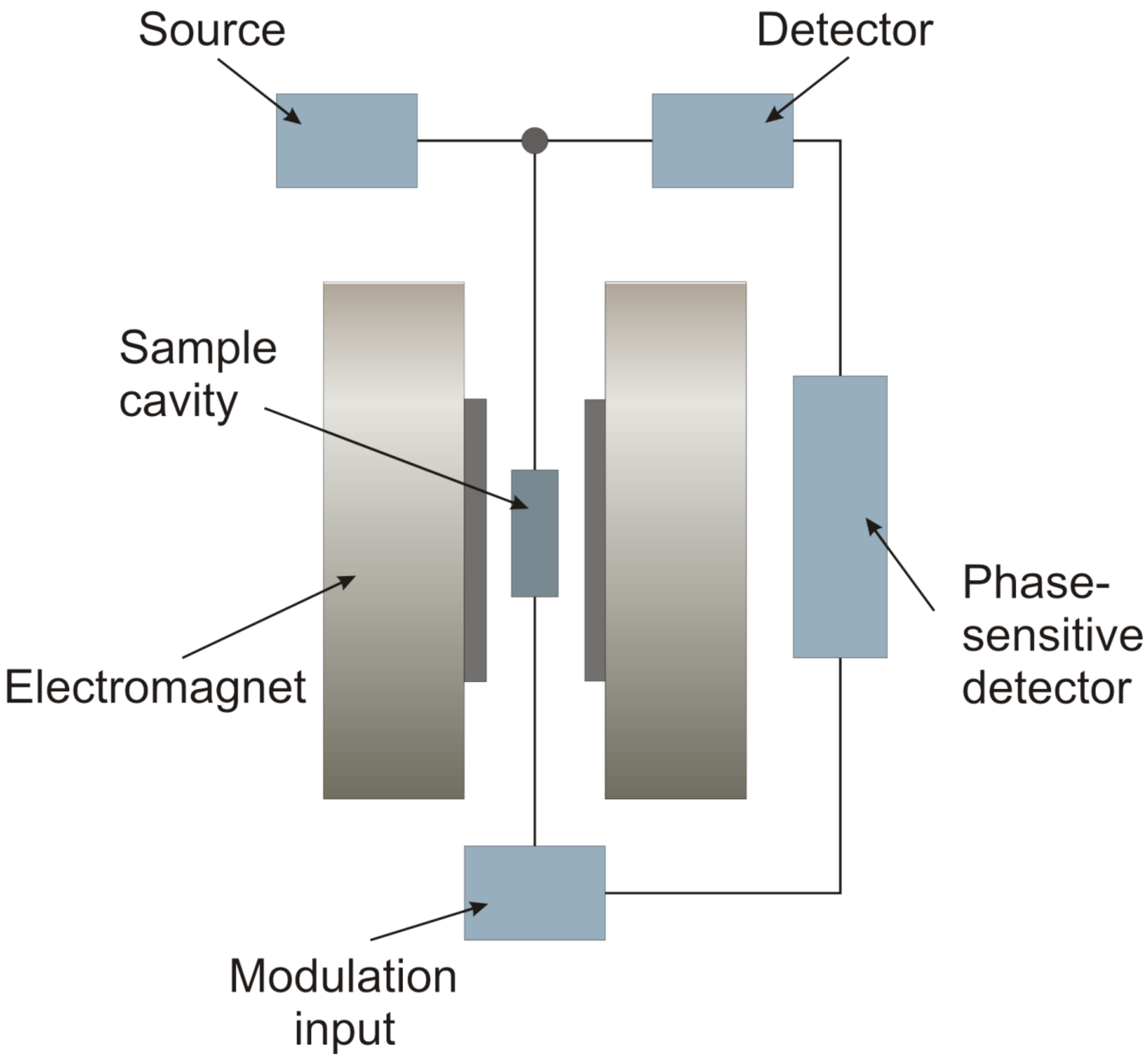




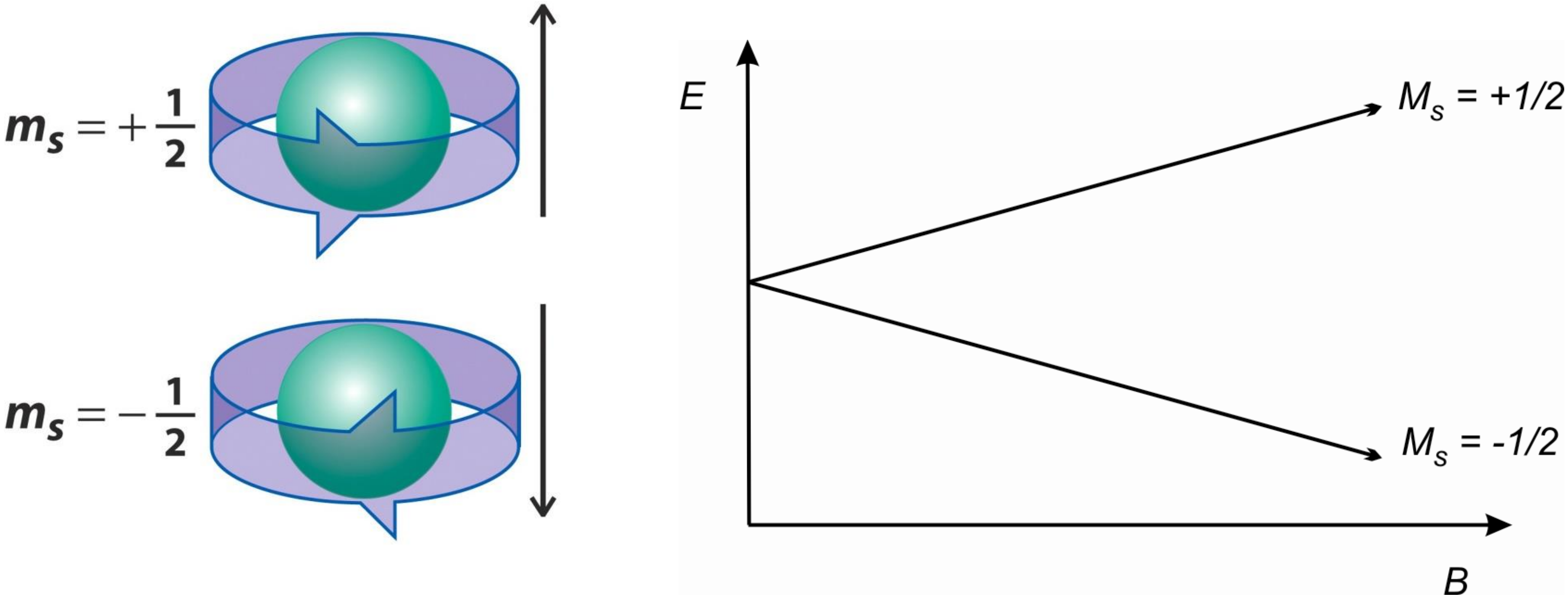
Energy Transitions

- ESR measures the transition between the electron spin energy levels
  - Transition induced by the appropriate frequency radiation
- Required frequency of radiation dependent upon strength of magnetic field
  - Common field strength 0.34 and 1.24 T
  - 9.5 and 35 GHz
  - Microwave region

How does the spectrometer work?



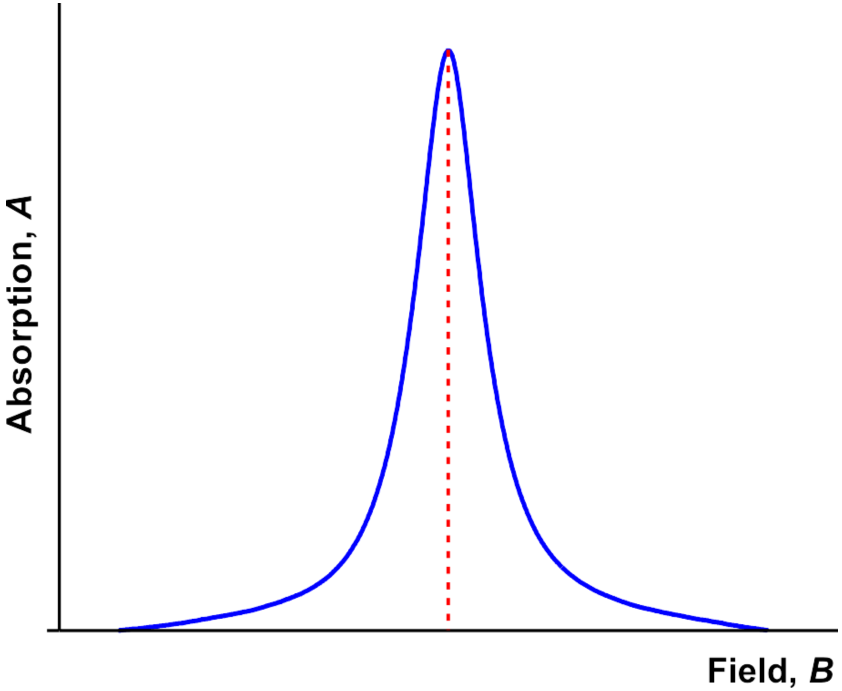
What causes the energy levels?

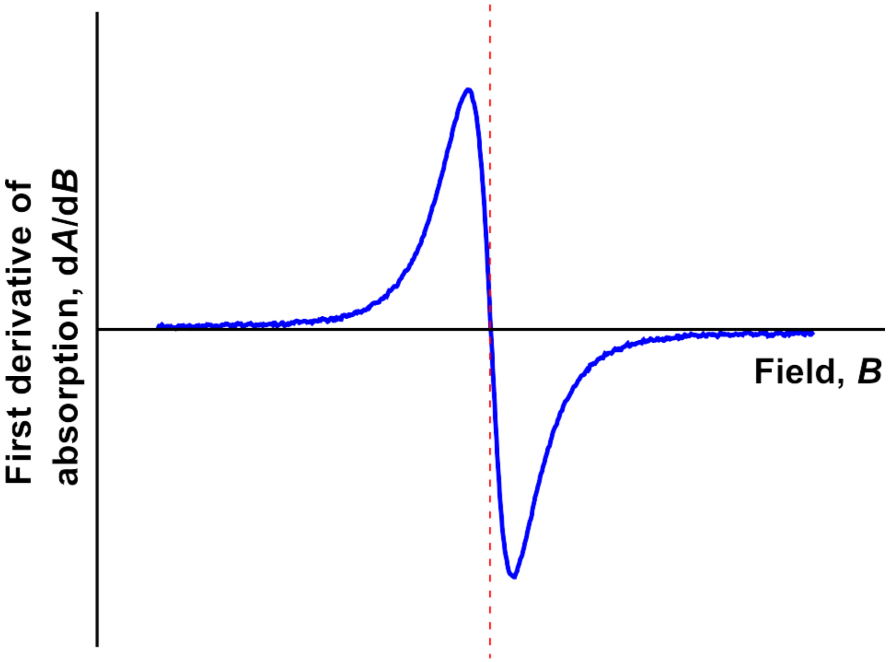


Resulting energy levels of an electron in a magnetic field

Ebsworth, E. A. V.; Rankin, David W. H.; Cradock, Stephen *Structural Methods in Inorganic Chemistry*; CRC Press: Boca Raton, 1987.

Spectra





When phase-sensitive detection is used, the signal is the first derivative of the absorption intensity

Describing the energy levels

- Based upon the spin of an electron and its associated magnetic moment
- For a molecule with one unpaired electron
  - In the presence of a magnetic field, the two electron spin energy levels are:

$$E = g\mu_B B_0 M_S$$

g = proportionality factor

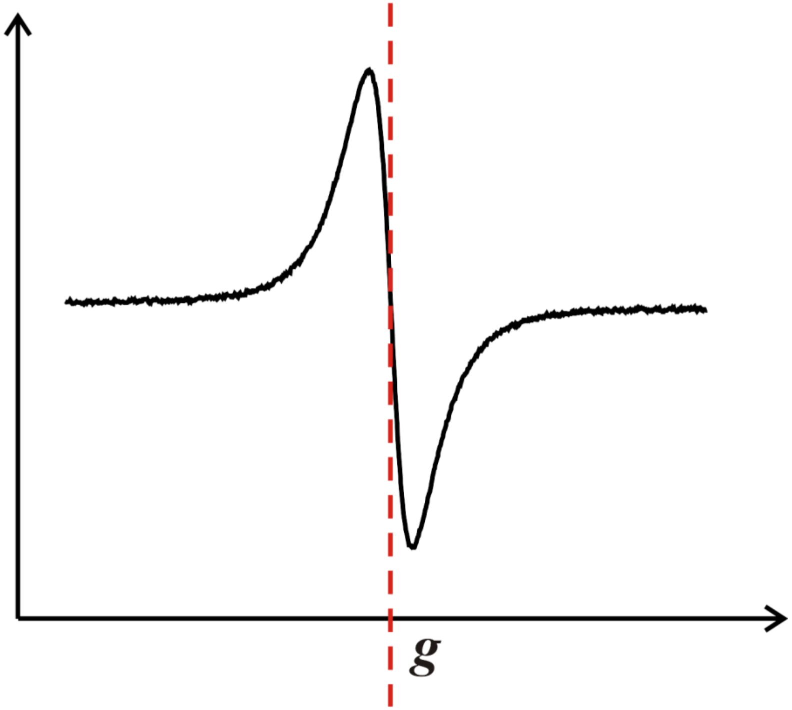
μ_B = Bohr magneton

M_S = electron spin quantum number (+½ or -½)

B_0 = Magnetic field

Proportionality Factor

- Measured from the center of the signal
- For a free electron
  - 2.00232
- For organic radicals
  - Typically close to free-electron value
  - 1.99-2.01
- For transition metal compounds
  - Large variations due to spin-orbit coupling and zero-field splitting
  - 1.4-3.0



Proportionality Factor

$MoO(SCN)_5^{2-}$	1.935
$VO(acac)_2$	1.968
e^-	2.0023
CH_3	2.0026
$C_{14}H_{10}$ (anthracene) cation	2.0028
$C_{14}H_{10}$ (anthracene) anion	2.0029
$Cu(acac)_2$	2.13

Atherton, N. M. *Principles of Electron Spin Resonance*; Ellis Horwood: Chichester, 1993.

Hyperfine Interactions

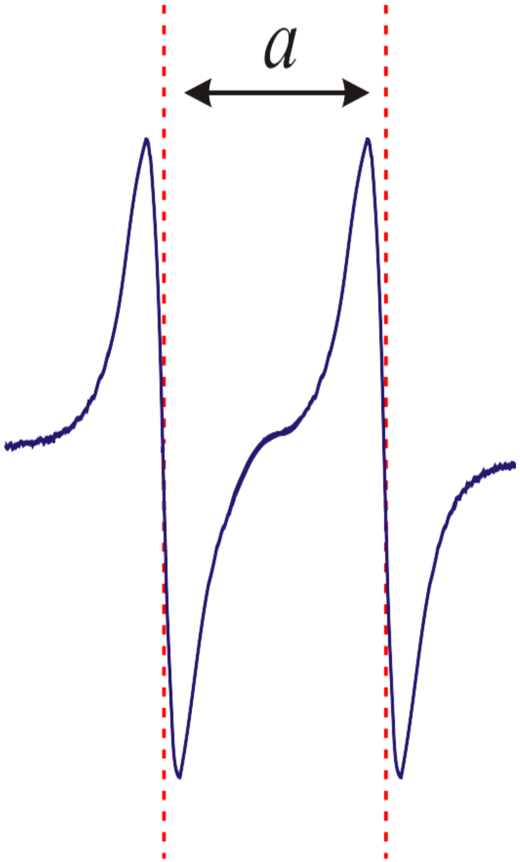
- EPR signal is ‘split’ by neighboring nuclei
  - Called hyperfine interactions
- Can be used to provide information
  - Number and identity of nuclei
  - Distance from unpaired electron
- Interactions with neighboring nuclei

$$E = g\mu_B B_0 M_S + a M_s m_I$$

a = hyperfine coupling constant

m_I = nuclear spin quantum number

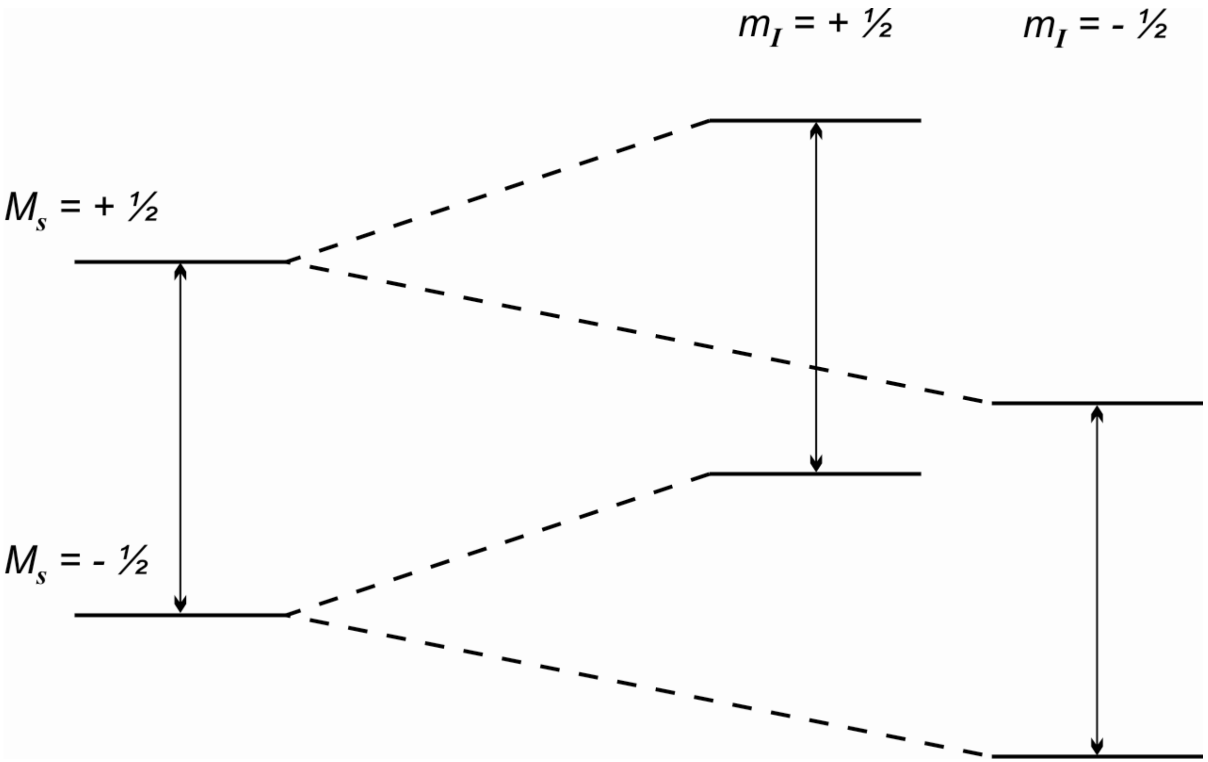
- Measured as the distance between the centers of two signals



Which nuclei will interact?

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

Hyperfine Interactions



Interaction with a single nucleus of spin ½

Ebsworth, E. A. V.; Rankin, David W. H.; Cradock, Stephen *Structural Methods in Inorganic Chemistry*; CRC Press: Boca Raton, 1987.

Hyperfine Interactions

- Coupling patterns same as in NMR
- More common to see coupling to nuclei with spins greater than ½
- The number of lines:

$$2NI + 1$$

N = number of equivalent nuclei

I = spin

- Only determines the number of lines--not the intensities

Hyperfine Interactions

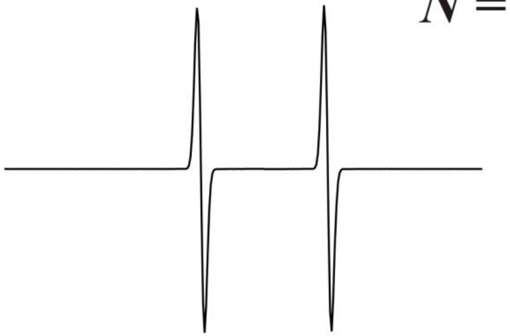
- Relative intensities determined by the number of interacting nuclei
- If only one nucleus interacting
  - All lines have equal intensity
- If multiple nuclei interacting
  - Distributions derived based upon spin
  - For spin ½ (most common), intensities follow binomial distribution

Relative Intensities for $I = \frac{1}{2}$

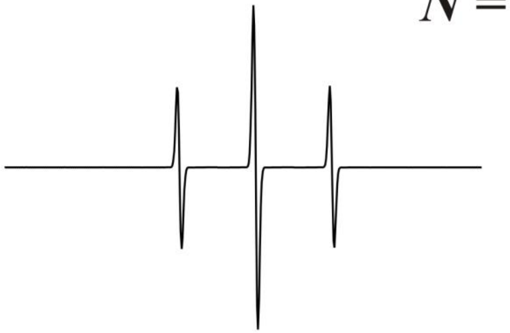
N	Relative Intensities
0	1
1	1 : 1
2	1 : 2 : 1
3	1 : 3 : 3 : 1
4	1 : 4 : 6 : 4 : 1
5	1 : 5 : 10 : 10 : 5 : 1
6	1 : 6 : 15 : 20 : 15 : 6 : 1

Relative Intensities for $I = \frac{1}{2}$

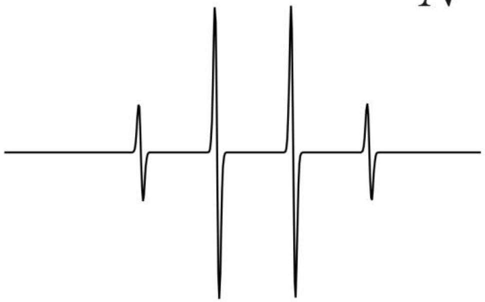
$N = 1$



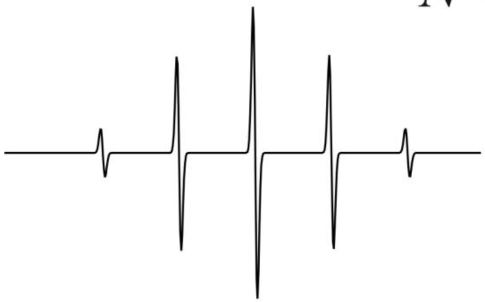
$N = 2$



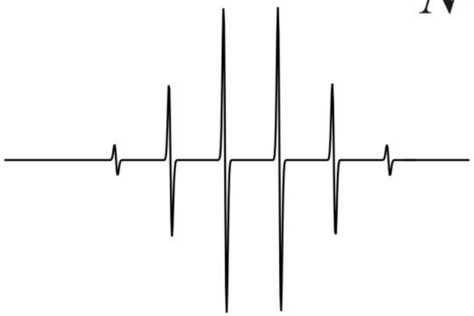
$N = 3$



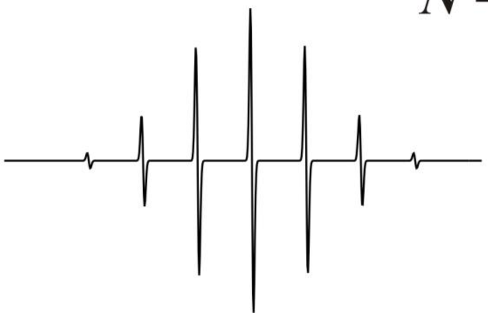
$N = 4$



$N = 5$



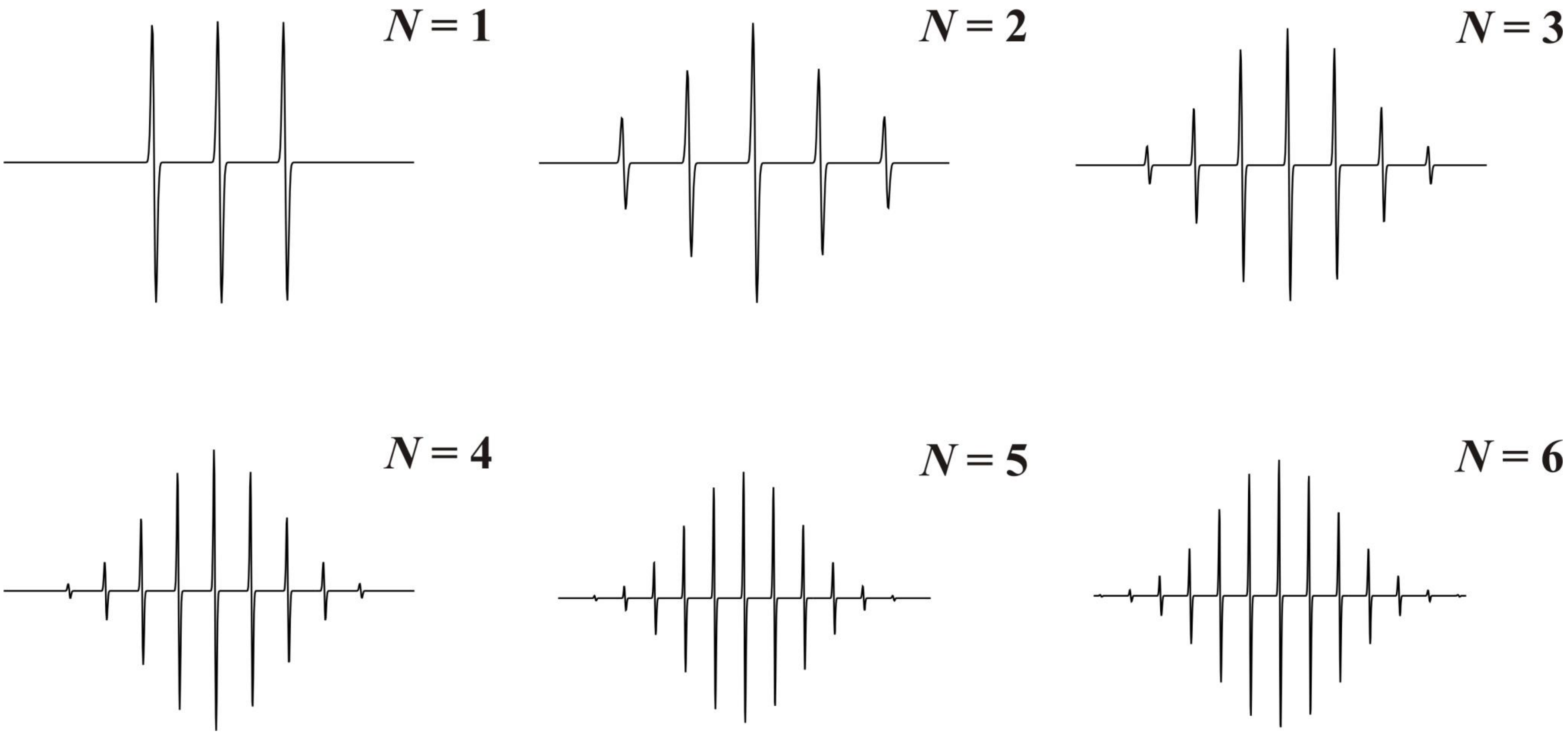
$N = 6$



Relative Intensities for $I = 1$

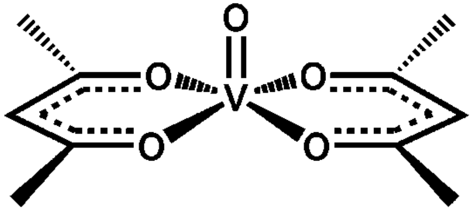
N	Relative Intensities
0	1
1	1 : 1 : 1
2	1 : 2 : 3 : 2 : 1
3	1 : 3 : 6 : 7 : 6 : 3 : 1
4	1 : 4 : 10 : 16 : 19 : 16 : 10 : 4 : 1
5	1 : 5 : 15 : 20 : 45 : 51 : 45 : 20 : 15 : 5 : 1
6	1 : 6 : 21 : 40 : 80 : 116 : 141 : 116 : 80 : 40 : 21 : 6 : 1

Relative Intensities for $I = 1$



Hyperfine Interactions

- Example:
  - $VO(acac)_2$
  - Interaction with vanadium nucleus

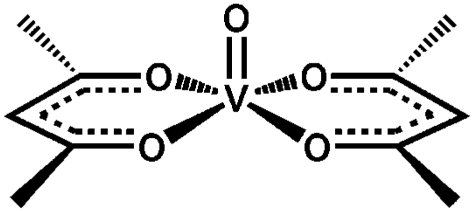


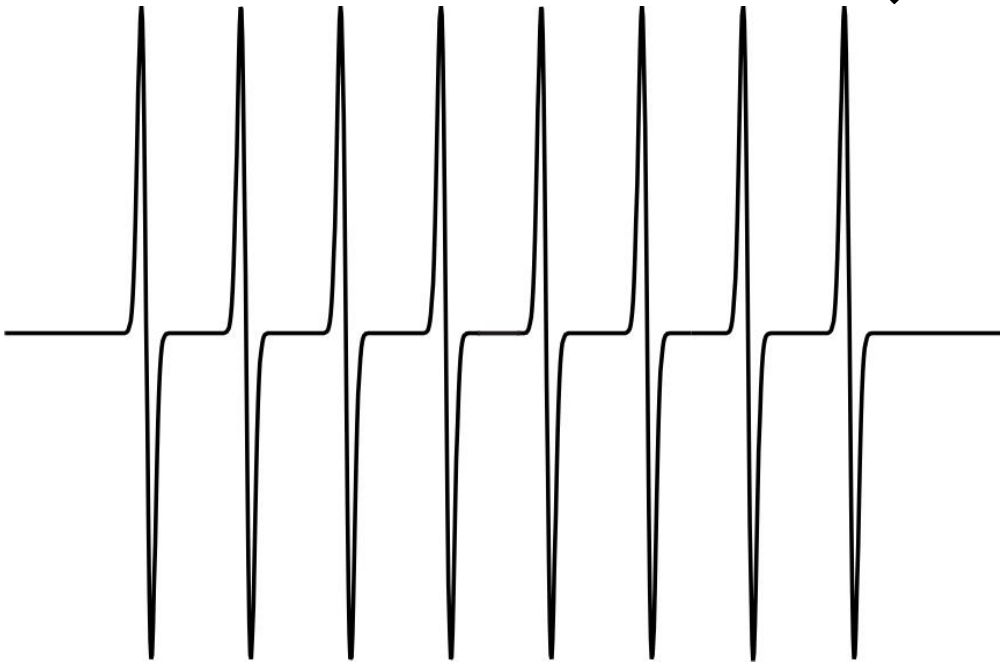
  - For vanadium, $I = 7/2$
  - So,

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

  - You would expect to see 8 lines of equal intensity

Hyperfine Interactions

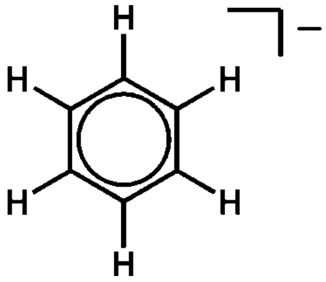




EPR spectrum of vanadyl acetylacetonate

Hyperfine Interactions

- Example:
  - Radical anion of benzene $[C_6H_6]^-$

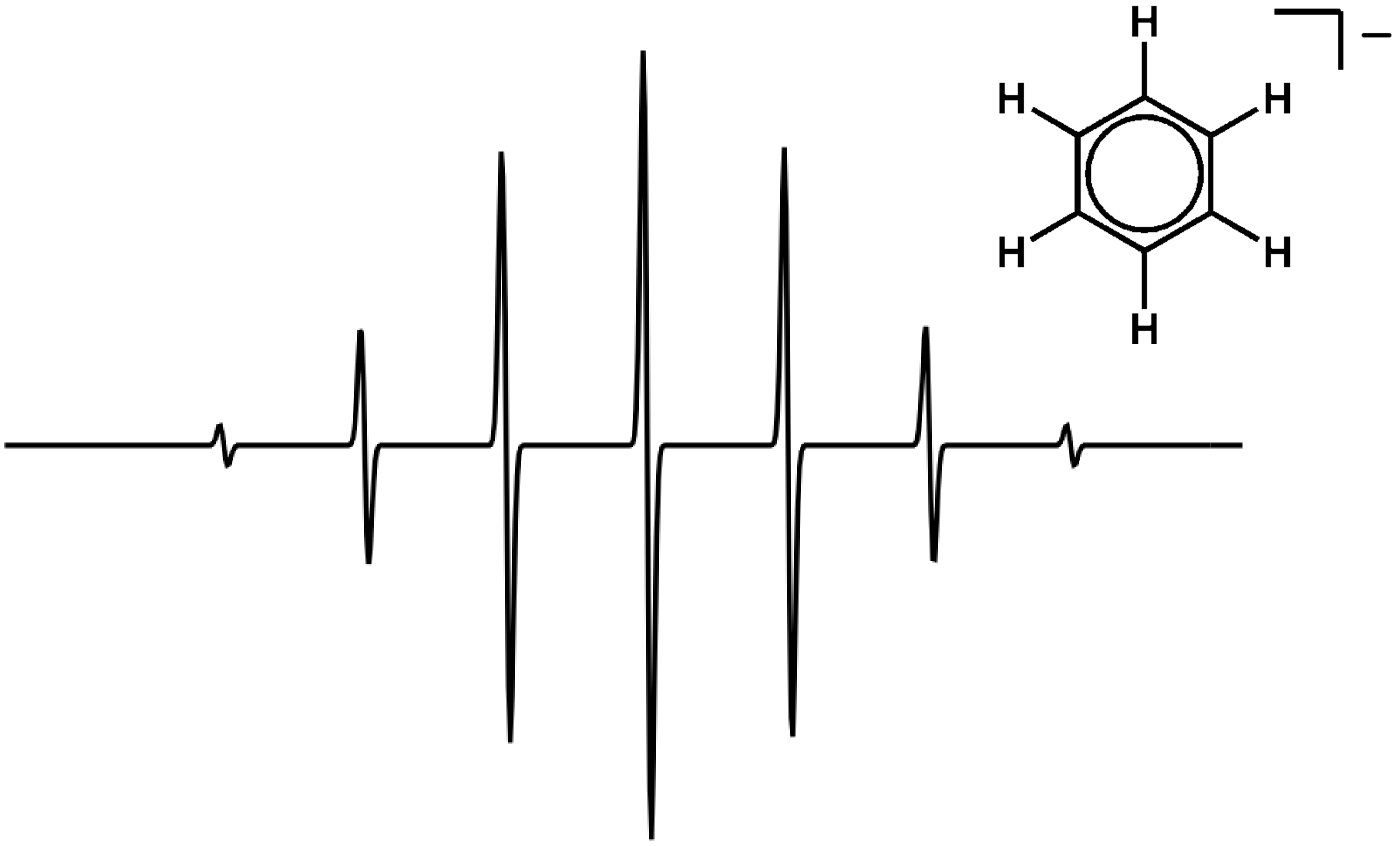


  - Electron is delocalized over all six carbon atoms
    - Exhibits coupling to six equivalent hydrogen atoms
  - So,

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

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

Hyperfine Interactions



EPR spectrum of benzene radical anion

Hyperfine Interactions

- Coupling to several sets of nuclei
  - – First couple to the nearest set of nuclei
    - Largest ***a*** value
  - – Split each of those lines by the coupling to the next closest nuclei
    - Next largest ***a*** value
  - – Continue 2-3 bonds away from location of unpaired electron

Hyperfine Interactions

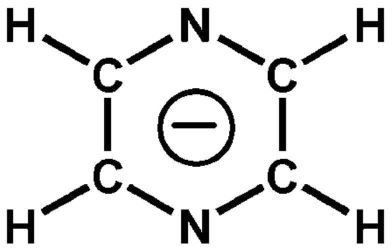
- Example:
  - Pyrazine anion
  - Electron delocalized over ring
    - Exhibits coupling to two equivalent N ($I = 1$)

$$2NI + 1 = 2(2)(1) + 1 = 5$$

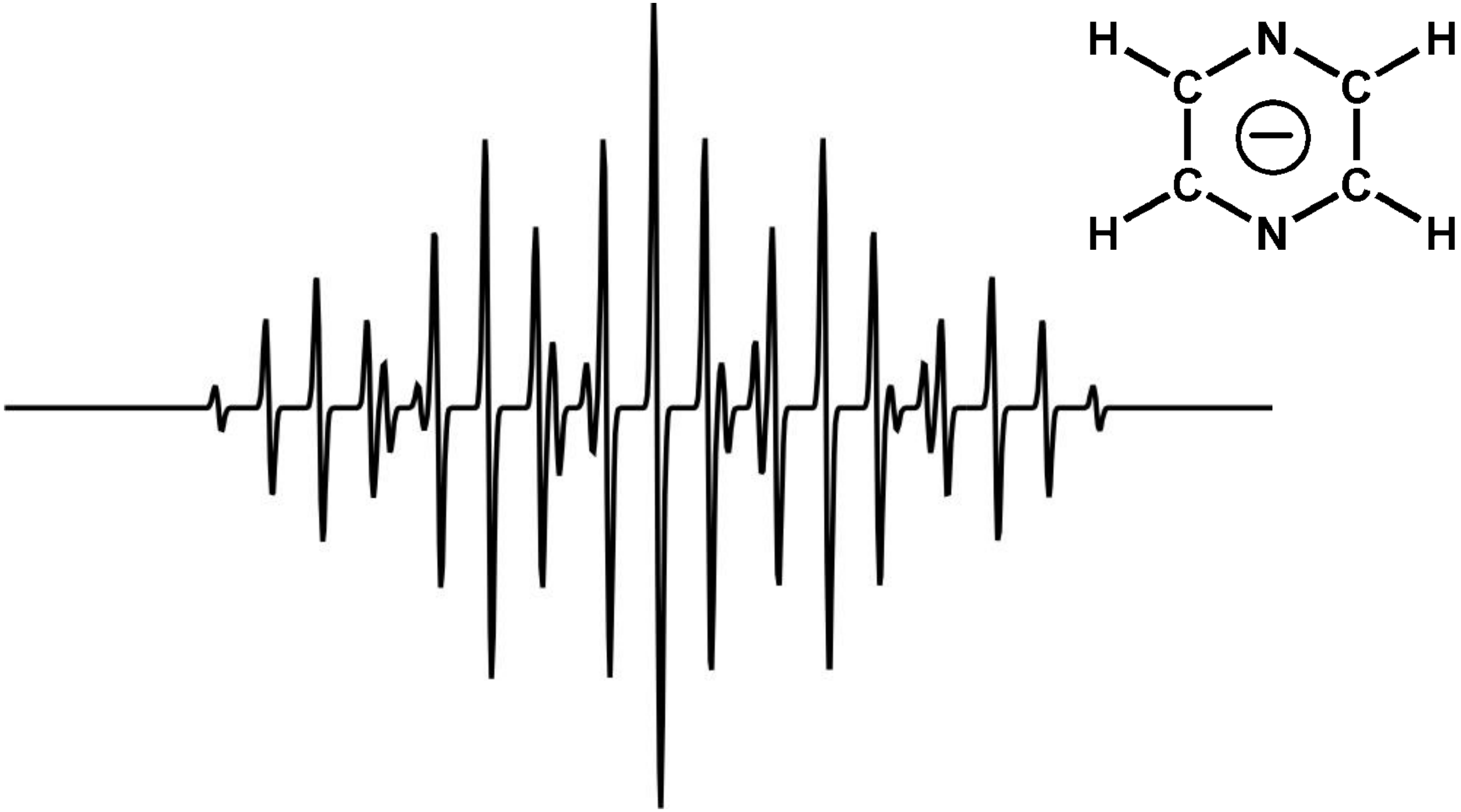
    - Then couples to four equivalent H ($I = \tfrac{1}{2}$)

$$2NI + 1 = 2(4)(1/2) + 1 = 5$$

  - So spectrum should be a quintet with intensities 1:2:3:2:1 and each of those lines should be split into quintets with intensities 1:4:6:4:1



Hyperfine Interactions



EPR spectrum of pyrazine radical anion

Conclusions

- Analysis of paramagnetic compounds
  - Compliment to NMR
- Examination of proportionality factors
  - Indicate location of unpaired electron
    - On transition metal or adjacent ligand
- Examination of hyperfine interactions
  - Provides information on number and type of nuclei coupled to the electrons
  - Indicates the extent to which the unpaired electrons are delocalized