

# Application of Spectroscopy, Part – III, M.Sc. IV Sem.

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# This presentation includes

- NMR Spectroscopy:-
- Introduction
- Magnetic moment and Gyro magnetic ratio
- Principle of NMR spectroscopy
- Orientation of Spin
- Distribution of energy levels
- Frequency of absorption
- Nuclear Shielding
- Relaxation
- Application of NMR
- Double resonance
- ENDOR
- Spin tickling
- NOE – Nuclear Overhauser Effect
- Assignment/ set of questions

# NMR Spectroscopy

- Introduction
- Nuclear Magnetic Resonance (NMR) is a nuclei (Nuclear) specific spectroscopy that has far reaching applications throughout the physical sciences and industry.
- NMR uses a large magnet (Magnetic) to probe the intrinsic spin properties of atomic nuclei. Like all spectroscopies, NMR uses a component of electromagnetic radiation (radio frequency waves) to promote transitions between nuclear energy levels (Resonance).
- Most chemists use NMR for structure determination of small molecules.

# NMR Spectroscopy

- In 1946, NMR was co-discovered by Purcell, Pound and Torrey of Harvard University and Bloch, Hansen and Packard of Stanford University.
- The discovery first came about when it was noticed that magnetic nuclei, such as  $^1\text{H}$  and  $^{31}\text{P}$  (proton and Phosphorus 31) were able to absorb radio frequency energy when placed in a magnetic field of a strength that was specific to the nucleus.

# NMR Spectroscopy

- Upon absorption, the nuclei begin to resonate and different atoms within a molecule resonated at different frequencies.
- This observation allowed a detailed analysis of the structure of a molecule.
- Since then, NMR has been applied to solids, liquids and gasses, kinetic and structural studies, resulting in 6 Nobel prizes being awarded in the field of NMR.

# Magnetic Moment & Gyro magnetic Ratio

- All molecules with a non-zero spin have a magnetic moment,  $\mu$ , given by
- $\mu = \gamma I$
- where  $\gamma$  is the gyro magnetic ratio, a proportionality constant between the magnetic dipole moment and the angular momentum, specific to each nucleus.

# Gyromagnetic Ratio

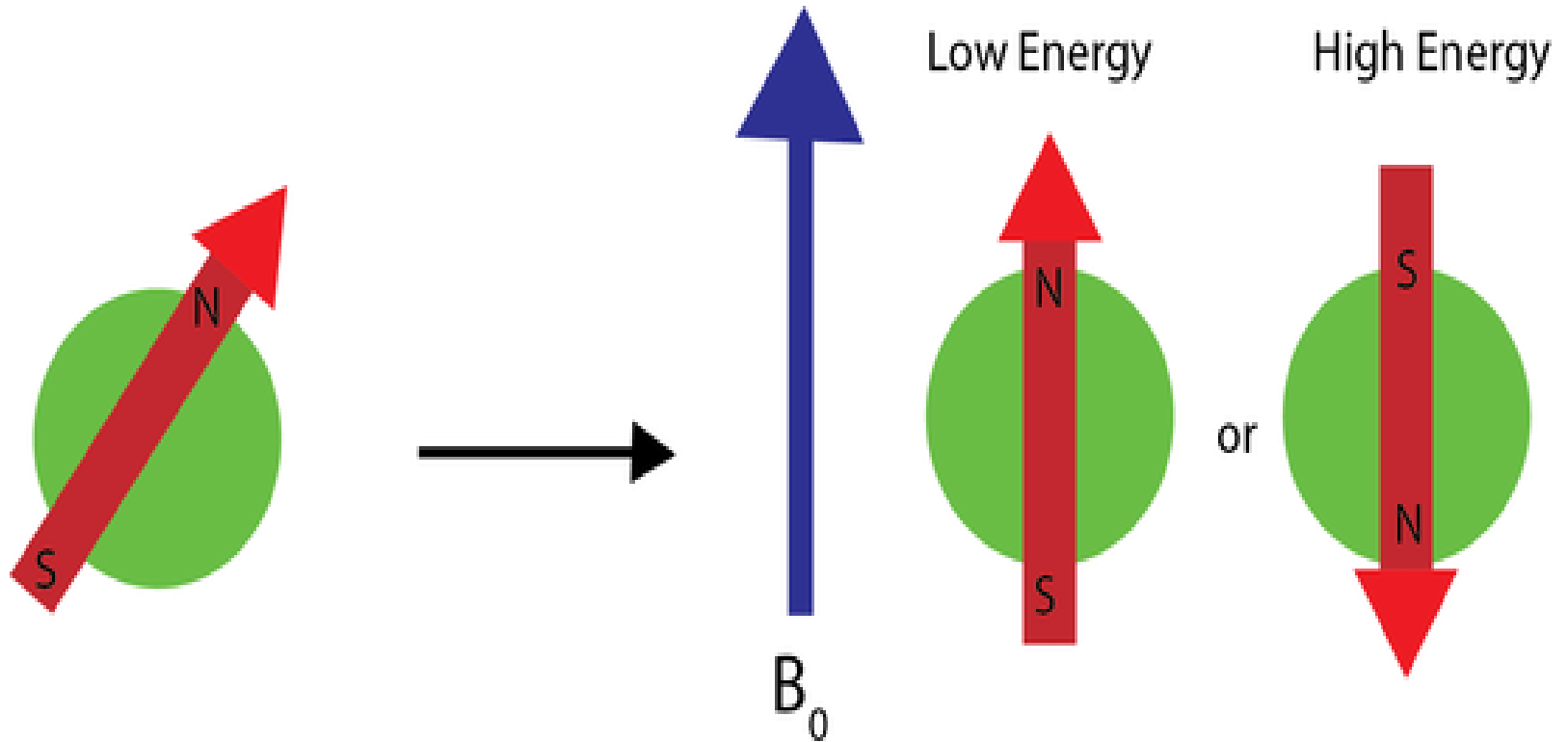
Nuclei	Spin	Gyromagnetic Ratio (MHz/T)	Natural Abundance (%)
$^1\text{H}$	1/2	42.576	99.9985
$^{13}\text{C}$	1/2	10.705	1.07
$^{31}\text{P}$	1/2	17.235	100
$^{27}\text{Al}$	5/2	11.103	100
$^{23}\text{Na}$	3/2	11.262	100
$^7\text{Li}$	3/2	16.546	92.41
$^{29}\text{Si}$	1/2	-8.465	4.68
$^{17}\text{O}$	5/2	5.772	0.038
$^{15}\text{N}$	1/2	-4.361	0.368

# Principle

- The magnetic moment of the nucleus forces the nucleus to behave as a tiny bar [magnet](#).
- In the absence of an external magnetic field, each magnet is randomly oriented.
- During the NMR experiment the sample is placed in an external magnetic field,  $B_0$ , which forces the bar magnets to align with (low energy) or against (high energy) the  $B_0$ .
- During the NMR experiment, a spin flip of the magnets occurs, requiring an exact quanta of energy.



# Orientation of Spins



# Distribution in Energy Levels

- An exact quanta of energy must be used to induce the spin flip or transition. For any  $m$ , there are  $2m+1$  energy levels. For a spin  $1/2$  nucleus, there are only two energy levels, the low energy level occupied by the spins which aligned with  $B_0$  and the high energy level occupied by spins aligned against  $B_0$ . Each energy level is given by

$$E = -m\hbar\gamma B_0$$

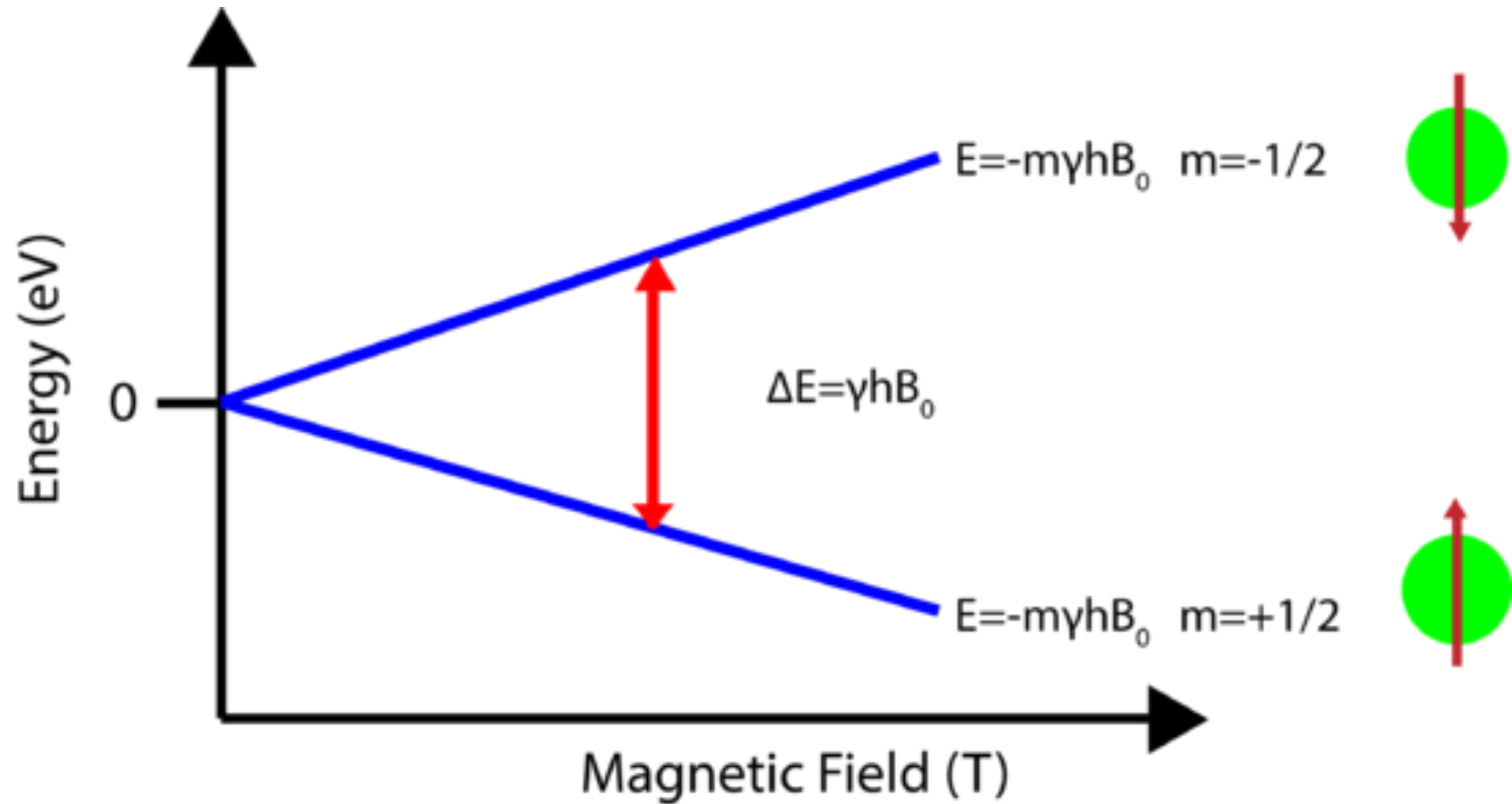
where  $m$  is the magnetic quantum number, in this case  $\pm 1/2$ .

- The energy levels for  $m > 1/2$ , known as quadrupolar nuclei, are more complex and information regarding them can be found [here](#).
- The energy difference between the energy levels is then

$$\Delta E = \hbar\gamma B_0$$

- where  $\hbar$  is Planks constant.

# Energy Levels



# Frequency for absorption

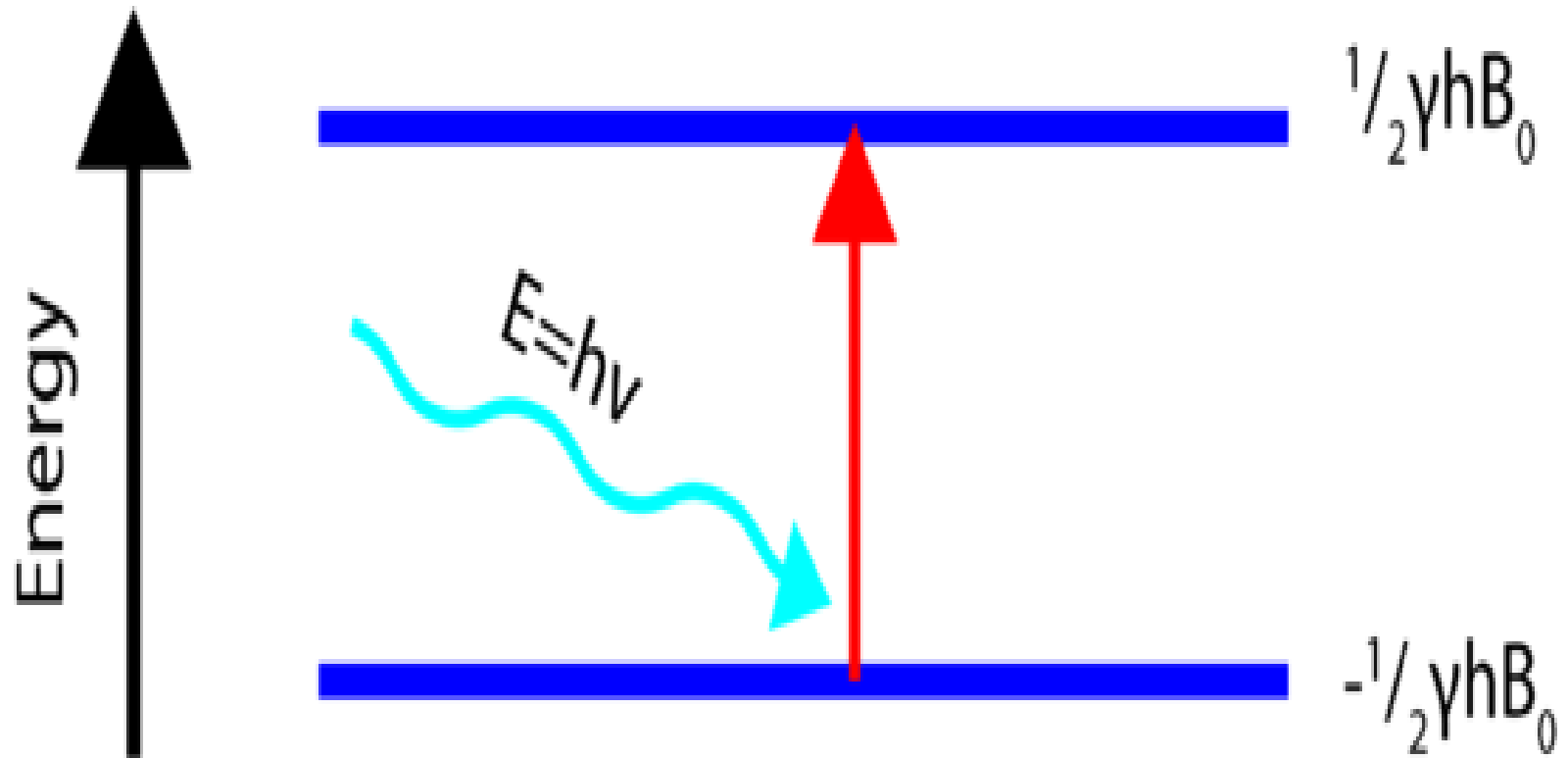
- For most NMR spectrometers,  $B_0$  is on the order of Tesla (T) while  $\gamma$  is on the order of  $10^7$ . Consequently, the electromagnetic radiation required is on the order of Hz. The energy of a photon is represented by

$$E=h\nu$$

- and thus the frequency necessary for absorption to occur is represented as:

$$\nu=\gamma B_0/2\pi$$

# Frequency of Absorption



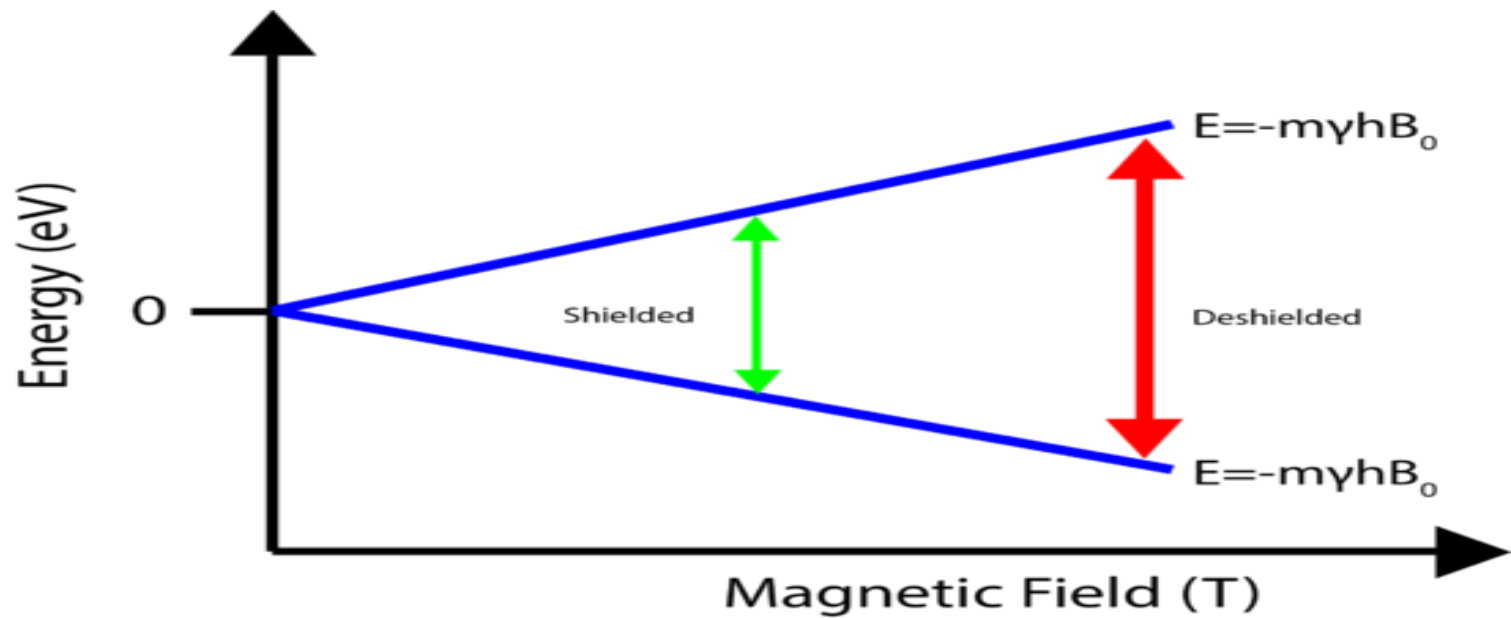
# Nuclear Shielding

- The power of NMR is based on the concept of nuclear shielding, which allows for structural assignments.
- Every atom is surrounded by electrons, which orbit the nucleus.
- Charged particles moving in a loop will create a magnetic field which is felt by the nucleus.
- Therefore the local electronic environment surrounding the nucleus will slightly change the magnetic field experienced by the nucleus, which in turn will cause slight changes in the energy levels! This is known as shielding.

# Nuclear Shielding

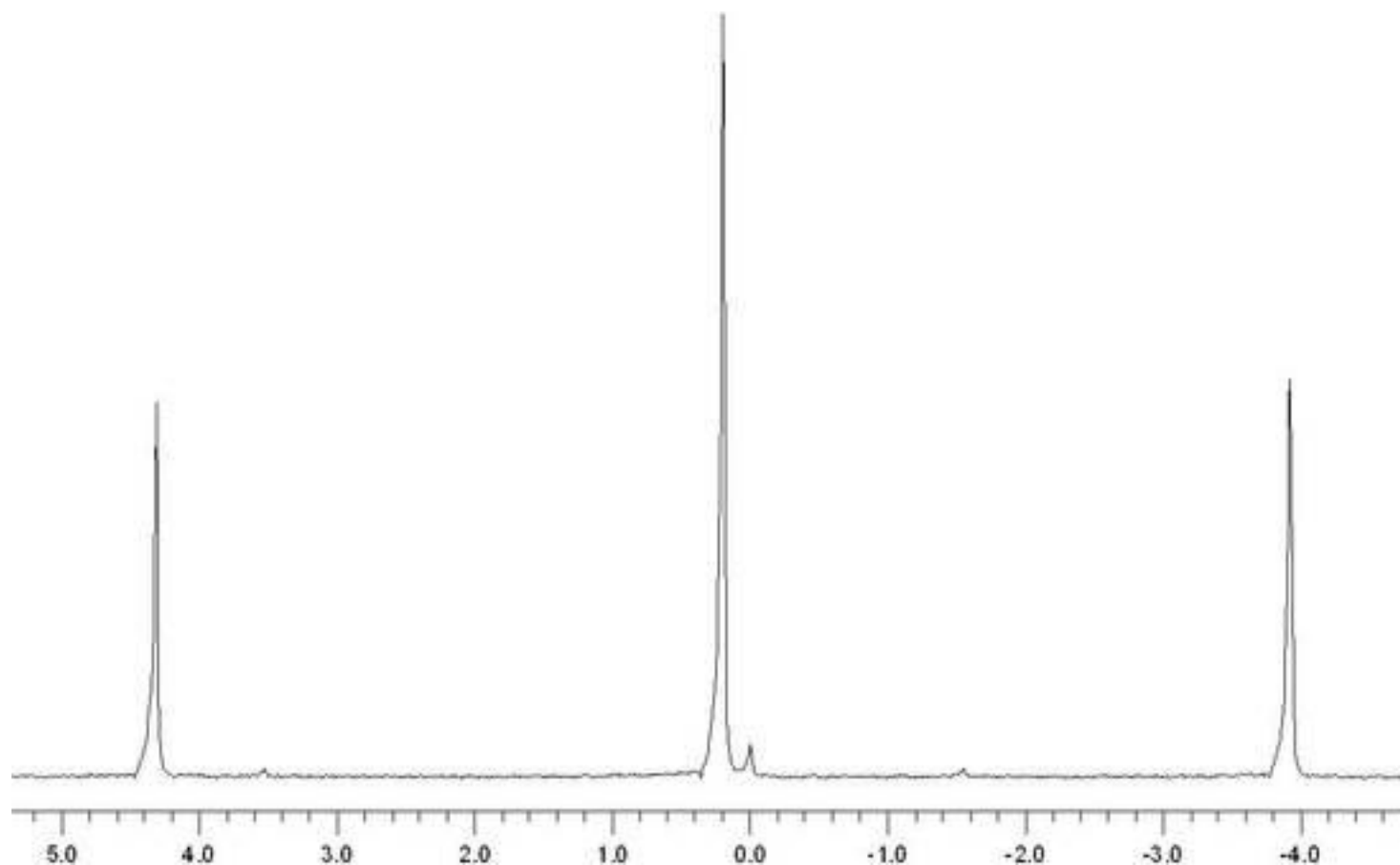
- Nuclei that experience different magnetic fields due to the local electronic interactions are known as inequivalent nuclei.
- The change in the energy levels requires a different frequency to excite the spin flip, which as will be seen below, creates a new peak in the NMR spectrum.

# Nuclear Shielding





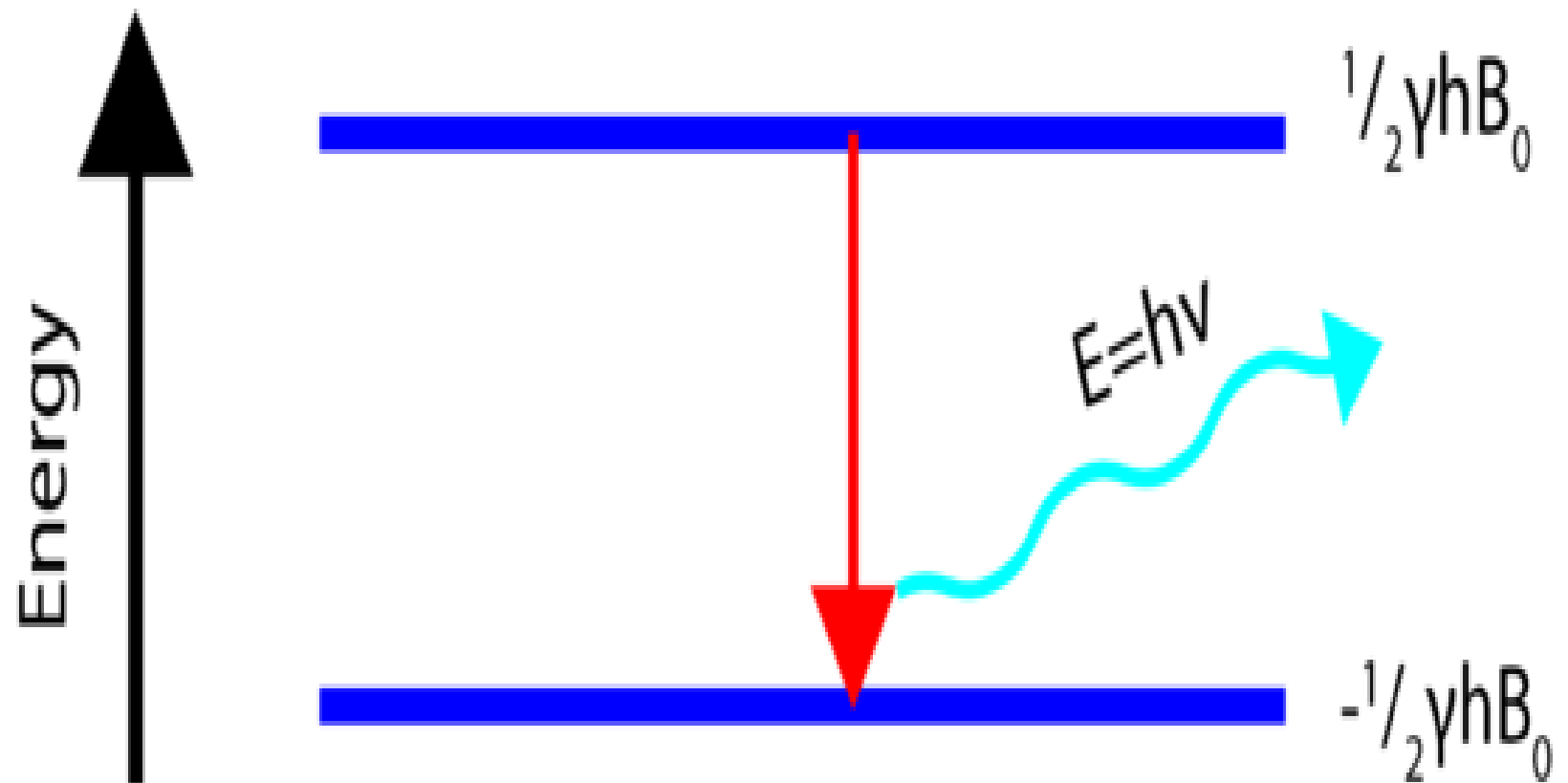
# A Typical NMR Spectrum



# Relaxation

- Relaxation refers to the phenomenon of nuclei returning to their thermodynamically stable states after being excited to higher energy levels.
- The energy absorbed when a transition from a lower energy level to a high energy level occurs is released when the opposite happens.
- This can be a fairly complex process based on different timescales of the relaxation.
- The two most common types of relaxation are spin lattice relaxation ( $T_1$ ) and spin spin relaxation ( $T_2$ ).

# Relaxation



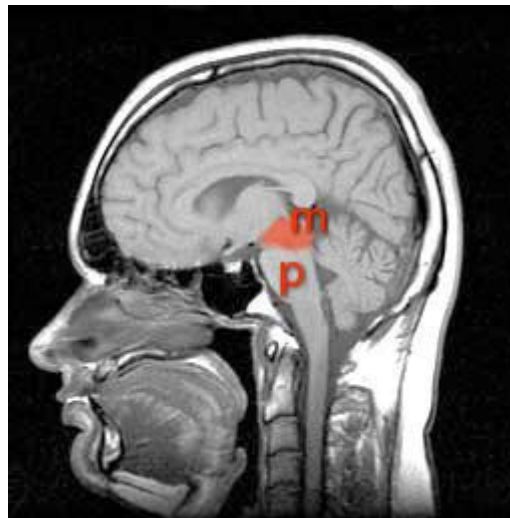
# Relaxation

- To understand relaxation, the entire sample must be considered.
- By placing the nuclei in an external magnetic field, the nuclei create a bulk magnetization along the z-axis.
- The spins of the nuclei are also coherent. The NMR signal may be detected as long as the spins are coherent with one another

# Applications

- **Medicine**

Nuclear magnetic resonance imaging, better known as magnetic resonance imaging (MRI) is an important medical diagnostic tool used to study the function and structure of the human body. It provides detailed images of any part of the body, especially soft tissue, in all possible planes and has been used in the areas of cardiovascular, neurological, musculoskeletal and oncological imaging.



# Application

- **Chemistry**

In many laboratories today, chemists use nuclear magnetic resonance to determine structures of important chemical and biological compounds.

In NMR spectra, different peaks give information about different atoms in a molecule according specific chemical environments and bonding between atoms.

The most common isotopes used to detect NMR signals are  $^1\text{H}$  and  $^{13}\text{C}$  but there are many others, such as  $^2\text{H}$ ,  $^3\text{He}$ ,  $^{15}\text{N}$ ,  $^{19}\text{F}$ , etc., that are also in use

# Application

- **Other Fields**
- NMR has also proven to be very useful in other areas such as environmental testing, petroleum industry, process control, earth's field NMR and magnetometers.

Non-destructive testing saves a lot of money for expensive biological samples and can be used again if more trials need to be run.

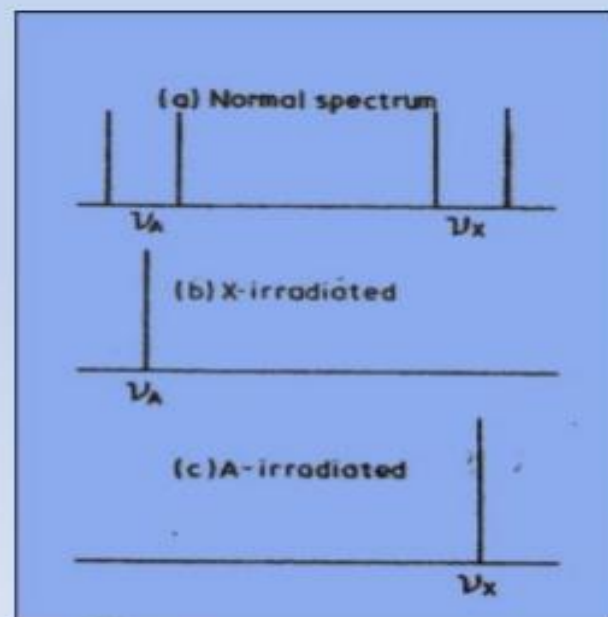
The petroleum industry uses NMR equipment to measure porosity of different rocks and permeability of different underground fluids.

# Double resonance technique in NMR

## Nuclear Magnetic Double Resonance

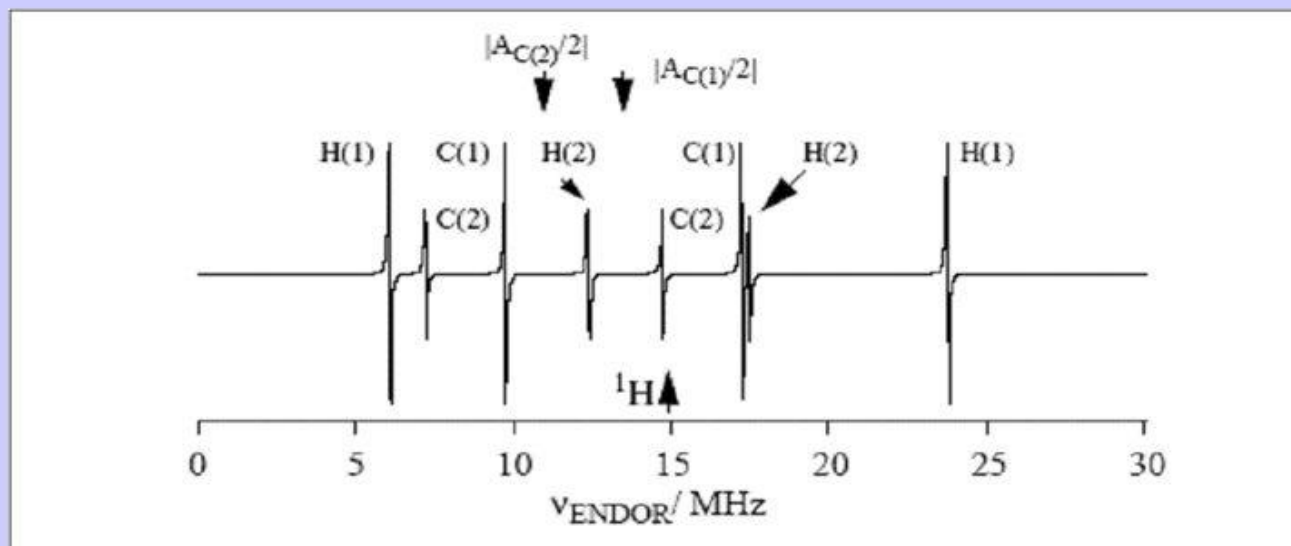
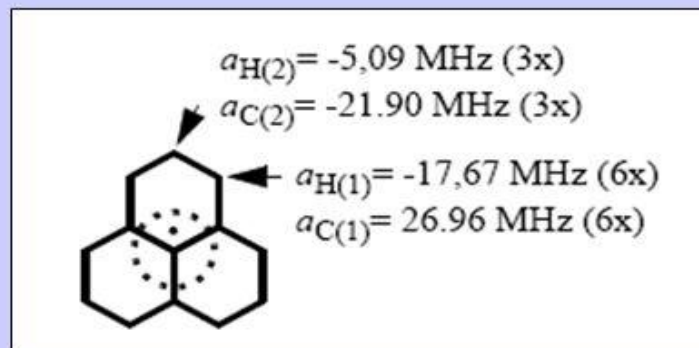
### SPIN DECOUPLING

- Coupling between neighbouring nuclei gives splitting patterns-in some cases complex patterns-spin decoupling
- Irradiation of protons with intense radiofrequency energy-eliminates complete coupling

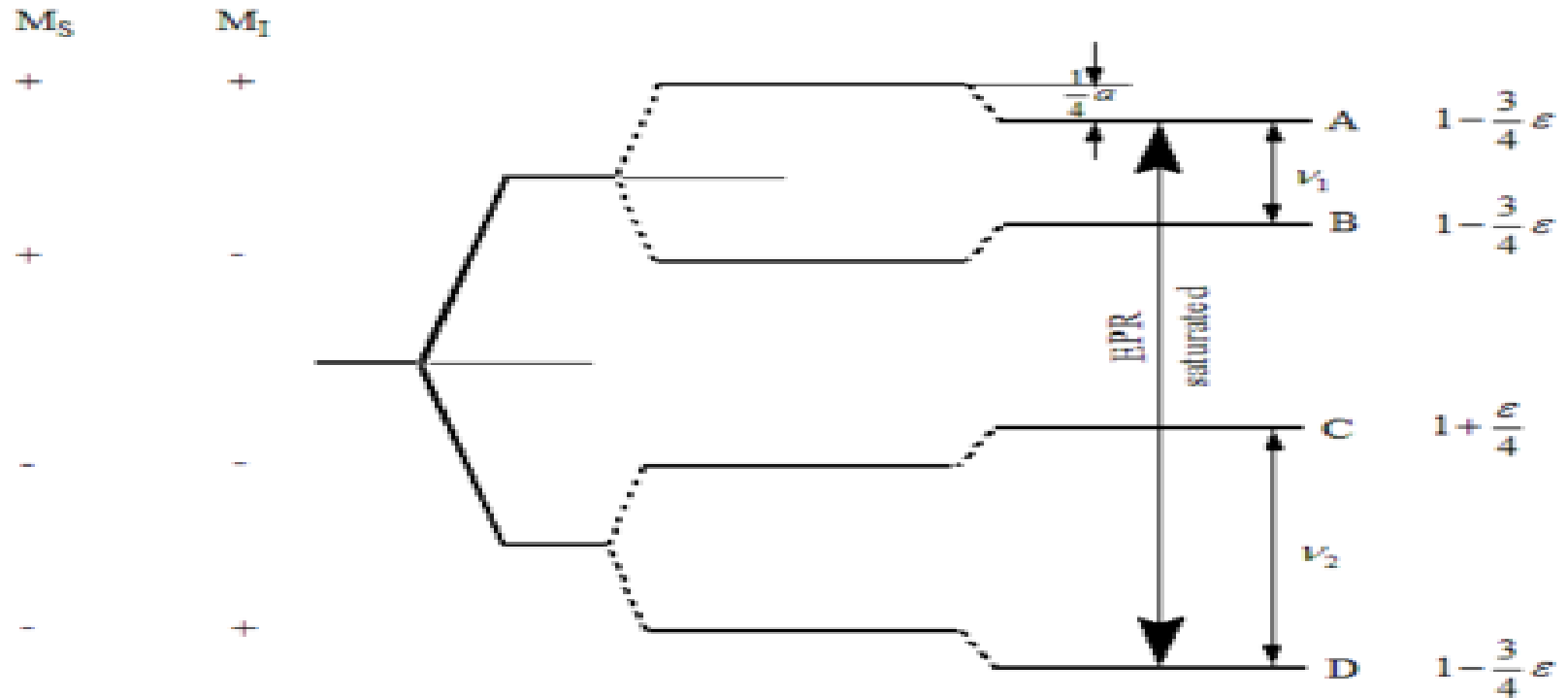




# Electron Nuclear Double Resonance



# Spin arrangements in Double Resonance



# Spin Tickling Technique in NMR

- **Spin tickling** experiments involve irradiation of single lines in the spectrum with a weak field,  $H_2$ , ( $H_2/2 < |J|$ ) while simultaneously with a second field,  $H_1$ , observing which of the unperturbed lines are split into doublets; transitions having an energy level in common with the **tickled** transition are split.

# Nuclear Overhauser effect (NOE)

- The **nuclear Overhauser effect (NOE)** is the transfer of [nuclear spin polarization](#) from one population of [spin-active](#) nuclei (e.g.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$  etc.) to another via [cross-relaxation](#). A phenomenological definition of the NOE in [nuclear magnetic resonance spectroscopy](#) (NMR) is the change in the integrated intensity (positive or negative) of one NMR resonance that occurs when another is saturated by irradiation with an RF field. The change in resonance intensity of a nucleus is a consequence of the nucleus being close in space to those directly affected by the RF perturbation.
- The NOE is particularly important in the assignment of NMR resonances, and the elucidation and confirmation of the structures or configurations of organic and biological molecules. The two-dimensional NOE experiment (NOESY) is an important tool to identify stereochemistry of proteins and other biomolecules in solution, whereas in solid form crystal x-ray diffraction must be used to identify the stereochemistry.

# Assignment / Set of Questions

- Q1. Define magnetic moment
- Q2. What do you understand by gyro magnetic ratio?
- Q3. Explain the principle of NMR spectroscopy.
- Q4. What is spin orientation?
- Q5. What is the phenomenon of relaxation?
- Q6. Explain the process of nuclear shielding
- Q7. Explain applications of NMR Spectroscopy.
- Q8. Write a note on Double RESONANCE.
- Q9. What do you understand by ENDOR?
- Q10. Write a note of spin tickling.
- Q11. Write an explicit note on NOE.

- Best of Luck

# Applications of Spectroscopy, Part – IV, M.Sc. IV Semester, Chemistry

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# This presentation Contains

- C-13 NMR –
- Introduction
- Features
- Chemical Shift
- Sensitivity
- Coupling modes
- DEPT
- Pt – NMR-
- Introduction
- Features
- Chemical shift
- Sn- NMR-
- Introduction
- Features
- Chemical shift
- Assignment/ Set of Questions



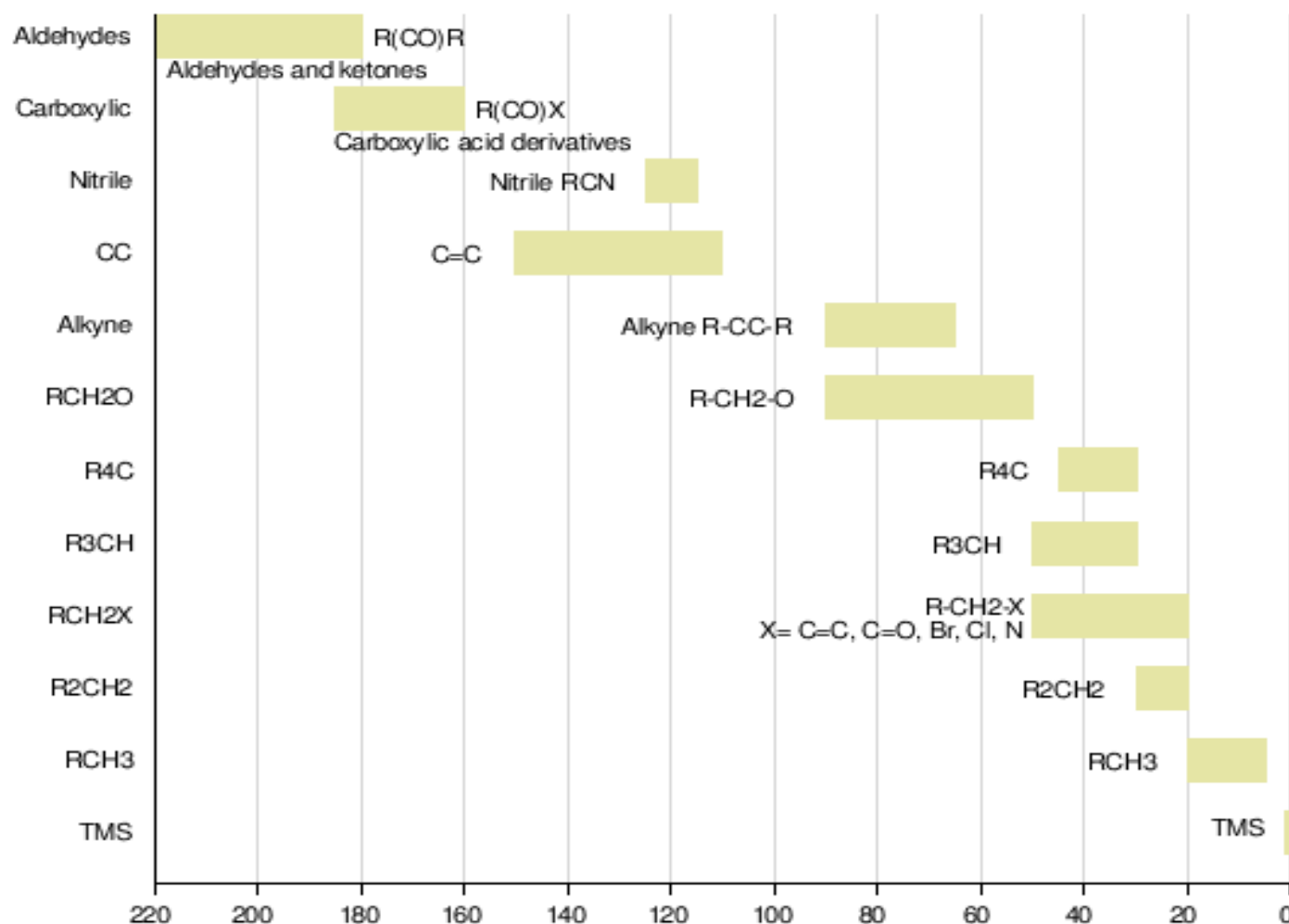
# C-13 NMR (Introduction)

- **Carbon-13 (C13) nuclear magnetic resonance** (most commonly known as **carbon-13 NMR** or  $^{13}\text{C}$  NMR or sometimes simply referred to as **carbon NMR**) is the application of nuclear magnetic resonance (NMR) spectroscopy to carbon. It is analogous to proton NMR ( $^1\text{H}$  NMR) and allows the identification of carbon atoms in an organic molecule just as proton NMR identifies hydrogen atoms. As such  $^{13}\text{C}$  NMR is an important tool in chemical structure elucidation in organic chemistry.  $^{13}\text{C}$  NMR detects only the  $^{13}\text{C}$  isotope of carbon, whose natural abundance is only 1.1%, because the main carbon isotope,  $^{12}\text{C}$ , is not detectable by NMR since its nucleus has zero spin.

# C-13 NMR , (Chemical Shift)

- $^{13}\text{C}$  [chemical shifts](#) follow the same principles as those of  $^1\text{H}$ , although the typical range of chemical shifts is much larger than for  $^1\text{H}$  (by a factor of about 20). The chemical shift reference standard for  $^{13}\text{C}$  is the carbons in [tetramethylsilane](#) (TMS), whose chemical shift is considered to be 0.0 ppm.

# Typical chemical shifts in $^{13}\text{C}$ -NMR



# Sensitivity- C-13 NMR

- $^{13}\text{C}$  NMR has a number of complications that are not encountered in proton NMR.  $^{13}\text{C}$  NMR is much less sensitive to carbon than  $^1\text{H}$  NMR is to hydrogen since the major isotope of carbon, the  $^{12}\text{C}$  isotope, has a [spin quantum number](#) of zero and so is not magnetically active and therefore not detectable by NMR. Only the much less common  $^{13}\text{C}$  isotope, present naturally at 1.1% natural abundance, is magnetically active with a spin quantum number of  $1/2$  (like  $^1\text{H}$ ) and therefore detectable by NMR. Therefore, only the few  $^{13}\text{C}$  nuclei present resonate in the magnetic field, although this can be overcome by isotopic enrichment of e.g. [protein](#) samples. In addition, the [gyromagnetic ratio](#) ( $6.728284 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ ) is only  $1/4$  that of  $^1\text{H}$ , further reducing the sensitivity. The overall *receptivity* of  $^{13}\text{C}$  is about 4 orders of magnitude lower than  $^1\text{H}$ .
- High field magnets with internal bores capable of accepting larger sample tubes (typically 10 mm in diameter for  $^{13}\text{C}$  NMR versus 5 mm for  $^1\text{H}$  NMR), the use of relaxation reagents, for example  $\text{Cr}(\text{acac})_3$  ([Chromium\(III\) acetylacetonate](#)), and appropriate pulse sequences have reduced the time needed to acquire quantitative spectra and have made quantitative carbon-13 NMR a commonly used technique in many industrial labs. Applications range from quantification of [drug](#) purity to determination of the composition of high molecular weight synthetic [polymers](#).
- In a typical run on an organic compound, a  $^{13}\text{C}$  NMR may require several hours to record the spectrum of a one-milligram sample, compared to 15–30 minutes for  $^1\text{H}$  NMR, and that spectrum would be of lower quality. The [nuclear dipole](#) is weaker, the difference in energy between alpha and beta states is one-quarter that of proton NMR, and the [Boltzmann population](#) difference is correspondingly less.

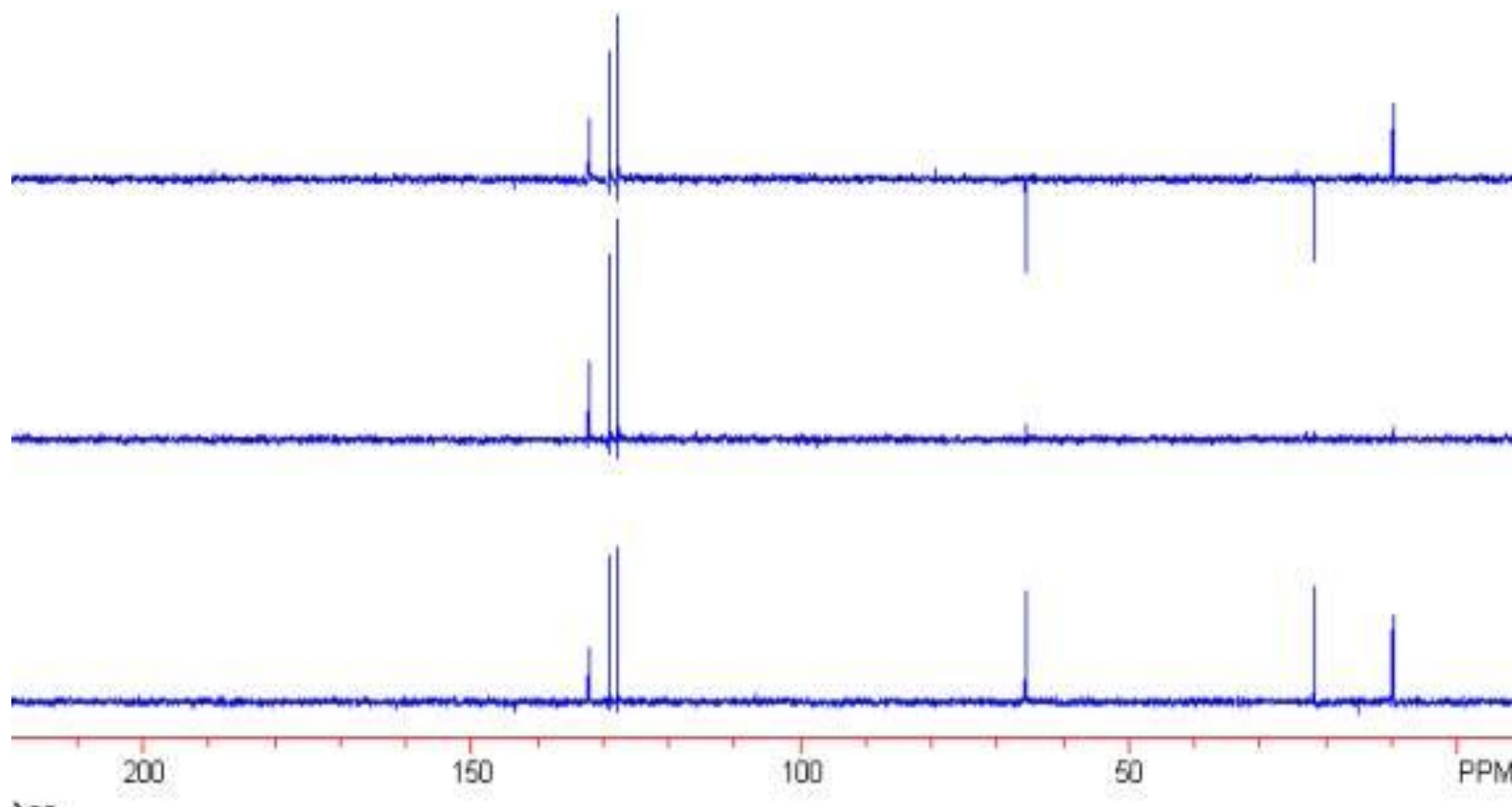
# C-13 NMR (Coupling Modes)

- Another potential complication results from the presence of large one bond [J-coupling](#) constants between carbon and hydrogen (typically from 100 to 250 Hz). In order to suppress these couplings, which would otherwise complicate the spectra and further reduce sensitivity, carbon NMR spectra are usually proton [decoupled](#) to remove the signal splitting. Couplings between carbons can be ignored due to the low natural abundance of  $^{13}\text{C}$ . Hence in contrast to typical proton NMR spectra which show multiplets for each proton position, carbon NMR spectra show a single peak for each chemically non-equivalent carbon atom.
- In further contrast to  $^1\text{H}$  NMR, the intensities of the signals are not normally proportional to the number of equivalent  $^{13}\text{C}$  atoms and are instead strongly dependent on the number of surrounding [spins](#) (typically  $^1\text{H}$ ). Spectra can be made more quantitative if necessary by allowing sufficient time for the nuclei to [relax](#) between repeat scans.
- The most common modes of recording  $^{13}\text{C}$  spectra are proton-noise decoupling (also known as noise, proton, or broadband decoupling), off-resonance decoupling, and gated decoupling. These modes are meant to address the large J values for  $^{13}\text{C}$  - H (110–320 Hz),  $^{13}\text{C}$  - C - H (5–60 Hz), and  $^{13}\text{C}$  - C - C - H (5–25 Hz) which otherwise make completely proton coupled  $^{13}\text{C}$  spectra difficult to interpret

# Distortionless enhancement by polarization transfer (DEPT)

- **Distortionless enhancement by polarization transfer (DEPT)** is an NMR method used for determining the presence of primary, secondary and [tertiary carbon](#) atoms. The DEPT experiment differentiates between CH, CH<sub>2</sub> and CH<sub>3</sub> groups by variation of the selection angle parameter (the tip angle of the final <sup>1</sup>H pulse): 135° angle gives all CH and CH<sub>3</sub> in a phase opposite to CH<sub>2</sub>; 90° angle gives only CH groups, the others being suppressed; 45° angle gives all carbons with attached protons (regardless of number) in phase.
- Signals from quaternary carbons and other carbons with no attached protons are always absent (due to the lack of attached protons).
- The polarization transfer from <sup>1</sup>H to <sup>13</sup>C has the secondary advantage of increasing the sensitivity over the normal <sup>13</sup>C spectrum (which has a modest enhancement from the [nuclear overhauser effect](#) (NOE) due to the <sup>1</sup>H decoupling).

# Various DEPT Spectra of Propyl Benzoate

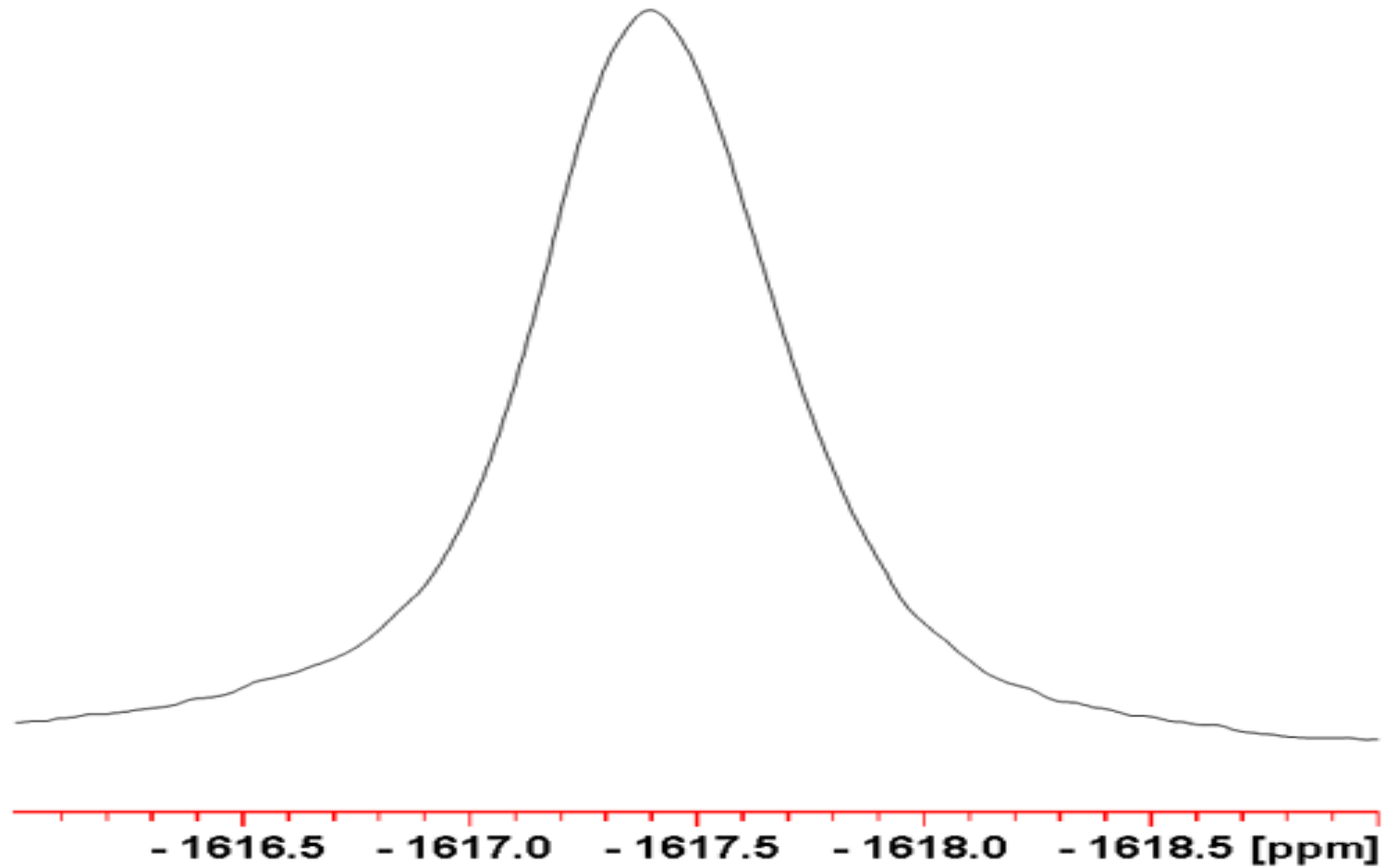


# $^{195}\text{Pt}$ Platinum NMR

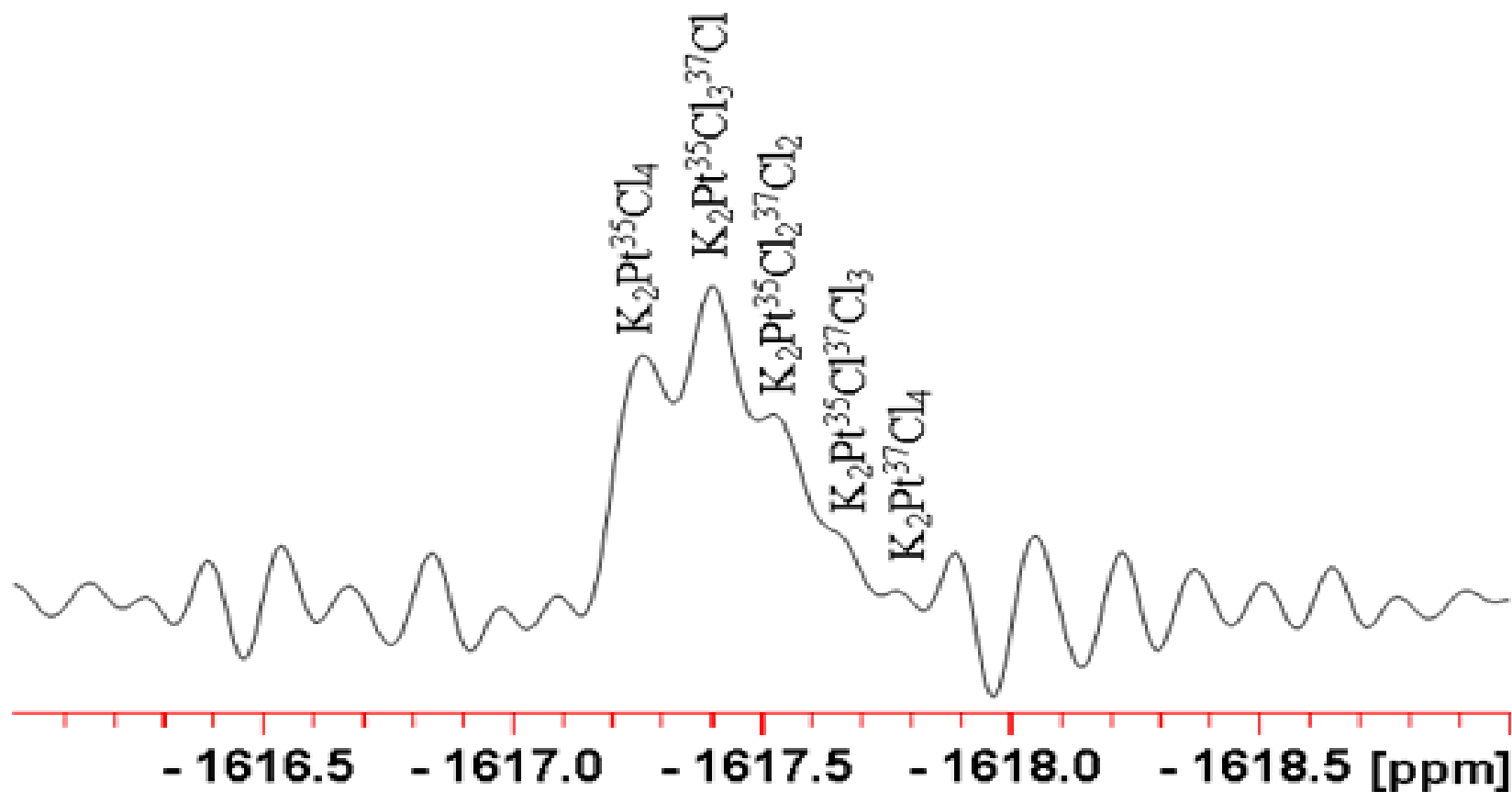
- Platinum (Pt) has one medium sensitivity NMR spin- $\frac{1}{2}$  nucleus,  $^{195}\text{Pt}$  that yields narrow signals over a very wide chemical shift range.
- $^{195}\text{Pt}$  Platinum NMR is mostly used for studying platinum complexes, their structure, conformation and dynamics, and platinum binding in biological systems.
- Because platinum is widely used as an industrial catalyst and in medicine, its chemistry and NMR has been widely studied.



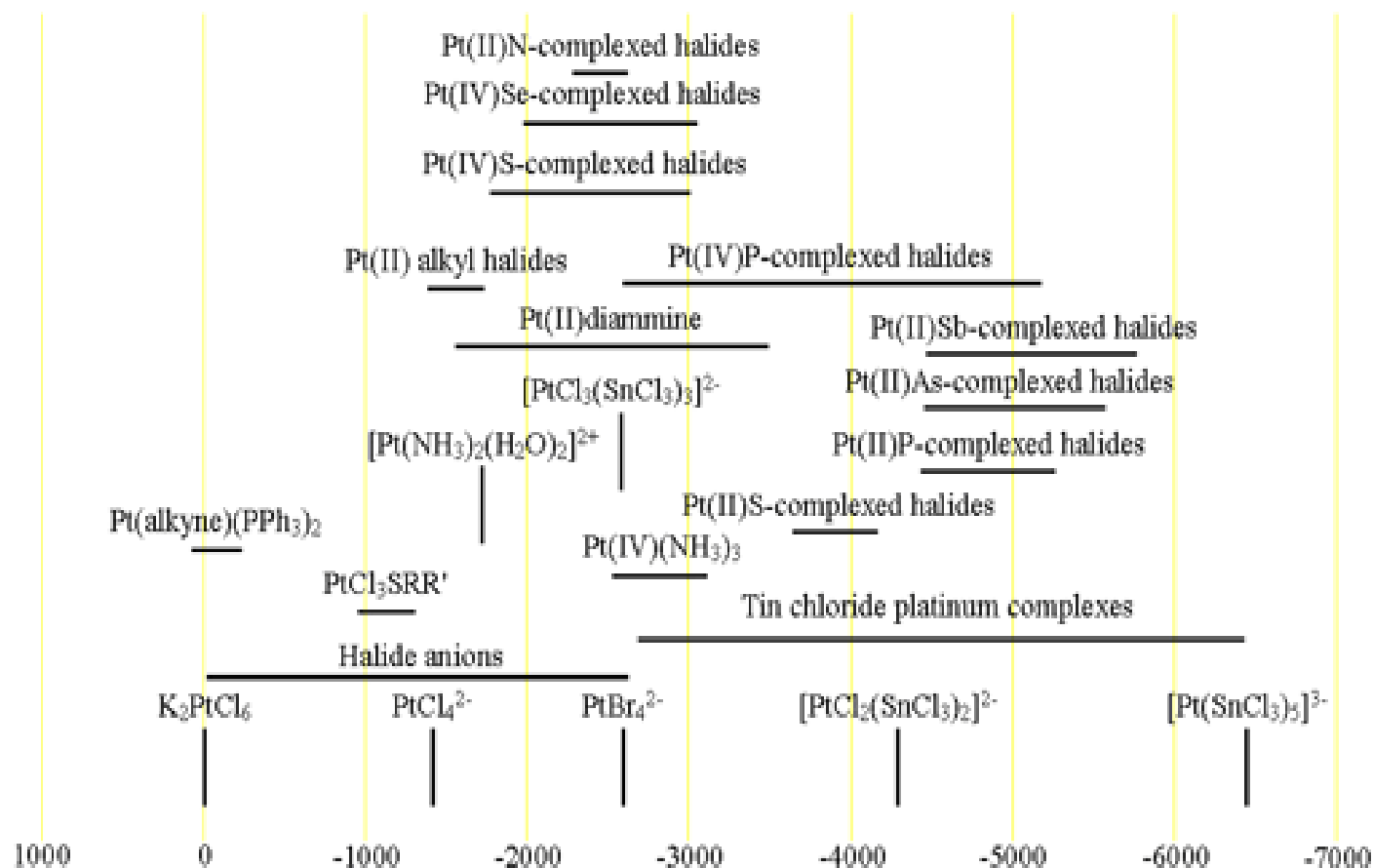
# $^{195}\text{Pt}$ -NMR spectrum of $\text{K}_2\text{PtCl}_4$ in $\text{D}_2\text{O}$



Resolution enhanced  $^{195}\text{Pt}$ -NMR spectrum of  $\text{K}_2\text{PtCl}_4$  in  $\text{D}_2\text{O}$   
showing isotopomers



# Chemical shift ranges for platinum NMR



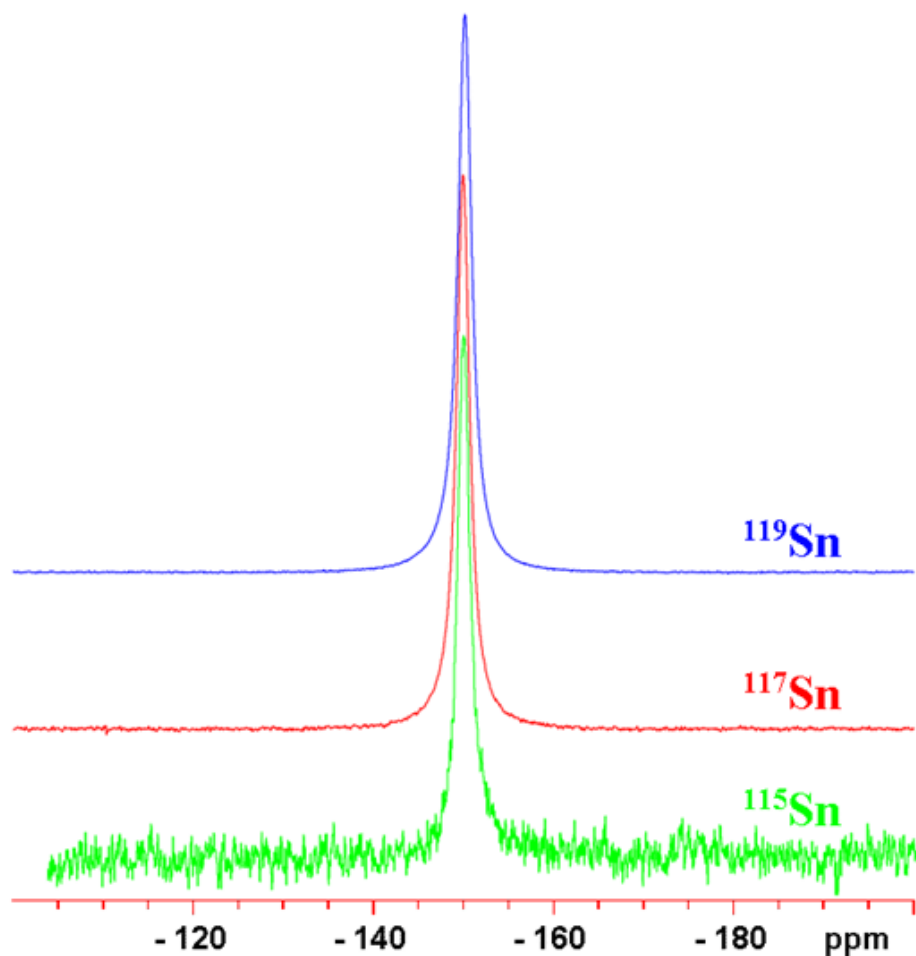
# $^{195}\text{Pt}$ Platinum NMR

- Platinum shows a wide variety of couplings with other nuclei,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{31}\text{P}$ , *etc.*
- Two-bond couplings to protons are between 25 and 90 Hz.
- One-bond  $^{195}\text{Pt}$ - $^{15}\text{N}$  couplings are in the region of 160 to 390 Hz.
- Couplings to  $^{31}\text{P}$  are around 1300 to 4000 Hz for one-bond and 30 Hz for two-bond.
- The one-bond coupling to  $^{77}\text{Se}$  is between 80 and 250 Hz.
- The platinum coupling to  $^{119}\text{Sn}$  is especially large and can be over 33000 Hz.
- Homonuclear platinum couplings can also be observed.

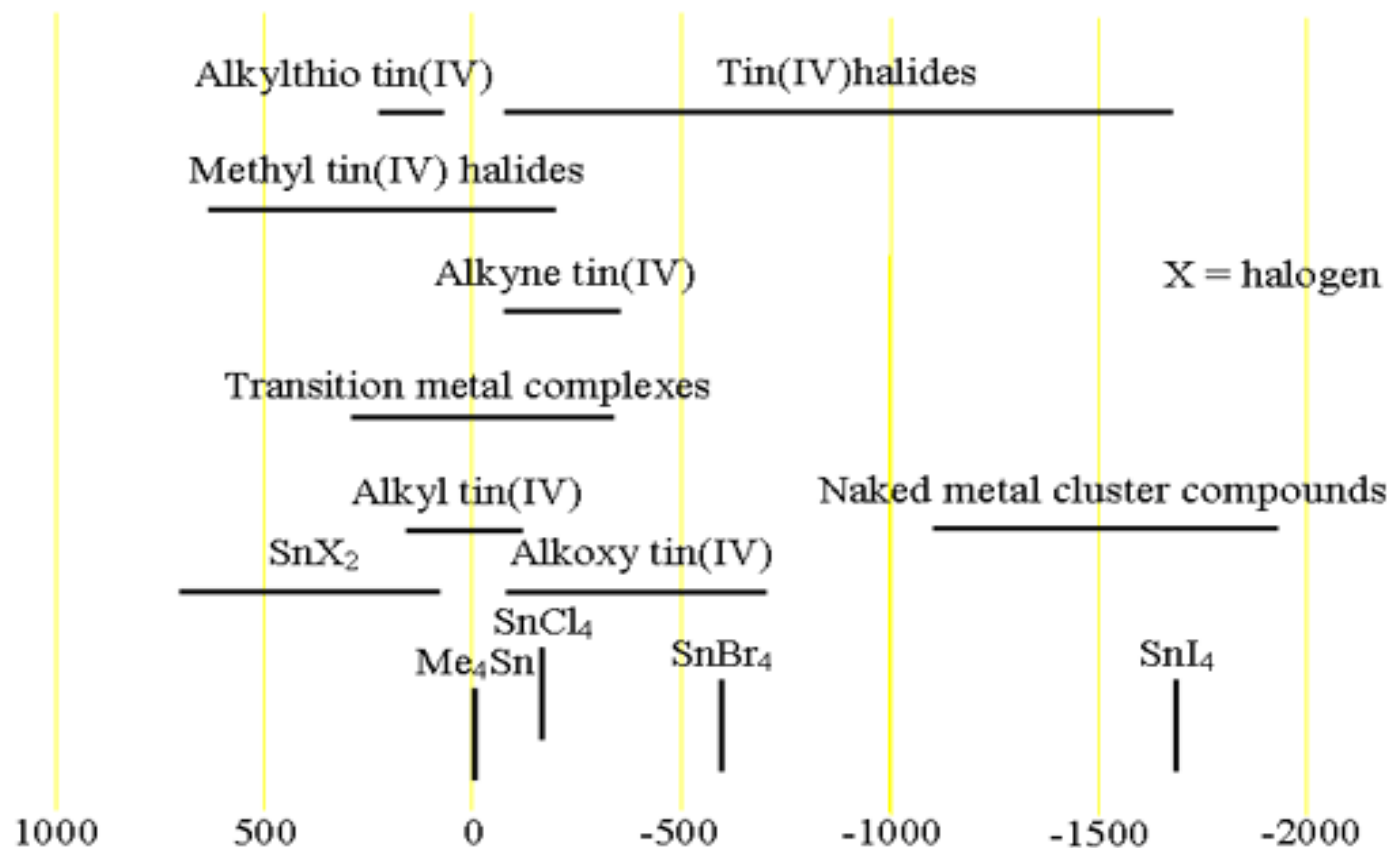
# (Sn) Tin NMR

- Tin is unique in that it has no less than three NMR active spin  $\frac{1}{2}$  nuclei,  $^{115}\text{Sn}$ ,  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$ , that yield narrow signals
- $^{119}\text{Sn}$  is very slightly the more sensitive than  $^{117}\text{Sn}$  so  $^{119}\text{Sn}$  is therefore usually the preferred nucleus.
- $^{115}\text{Sn}$  is much less sensitive than either  $^{117}\text{Sn}$  or  $^{119}\text{Sn}$ .
- Tin NMR is mostly used for the study of organotin compounds, but is also applicable to inorganic tin compounds.

# Comparison of the NMR spectra of the tin isotopes $^{115}\text{Sn}$ , $^{117}\text{Sn}$ and $^{119}\text{Sn}$ for $\text{SnCl}_4$ (neat)



# Chemical shift ranges for tin NMR



# Sn – NMR (Features)

- All the tin nuclei couple to other nuclei,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ , *etc.*, couplings have been reported.
- One bond couplings to  $^{13}\text{C}$  are between 1200 and 1500 Hz. To  $^1\text{H}$  one bond couplings are from 1750 to 3000 Hz, to  $^{19}\text{F}$  from 130 to 2000 Hz and to  $^{31}\text{P}$  they are from 50 to 2400 Hz.
- Two-bond Sn-H coupling constants are approximately 50 Hz. homonuclear  $^{119}\text{Sn}$ - $^{119}\text{Sn}$  and heteronuclear  $^{119}\text{Sn}$ - $^{117}\text{Sn}$  have been reported from 200 to 4500 Hz.
- Three and four bond couplings have been reported.



# Assignment/ Set of Questions

- Q1. Write a note on C-13 NMR.
- Q2.Explain Chemical Shift in C-13 NMR.
- Q3. Explain sensitivity of C-13 NMR
- Q4. Write a note on Coupling modes of C-13 NMR.
- Q5. Write a note on DEPT.
- Q6.Write a note on Platinum NMR.
- Q7. Explain chemical shift ranges for Platinum NMR.
- Q8. Write a note on Sn NMR.
- Q9. Explain chemical shift ranges for Sn NMR.
- Q10 Discuss comparison between various types of Sn NMR

- Best of Luck

# Applications Of Spectroscopy

## Part –II, M.Sc. IV Sem.

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# This presentation includes

- **IR spectroscopy**
- Introduction
- Theory
- Features
- Types of vibrations
- Normal Modes/ Selection Rules
- Instrumentation
- Application of IR spectroscopy
- Spectral Interpretation of normal compounds
- ✓ Hydrocarbons
- ✓ Alcohol
- ✓ Phenol
- ✓ Carbonyl Compounds
- ✓ Carboxylic acid
- ✓ Esters
- ✓ Organic Nitro compounds
- ✓ Organic Halogen Compounds
- Types of IR bands:
  - Fundamental band
  - Overtones
  - Hot bands
  - Fermi resonance
- Assignment/ Set of Questions

# IR Spectroscopy

- **Introduction**
- **Infrared spectroscopy** (IR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light.
- It covers a range of techniques, mostly based on absorption spectroscopy.
- it can be used to identify and study chemicals.
- For a given sample which may be solid, liquid, or gaseous, the method or technique of infrared spectroscopy uses an instrument called an **infrared spectrometer**

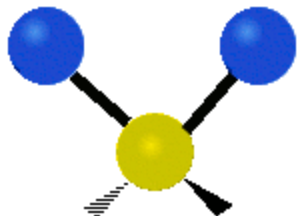
# IR Spectroscopy

- Features
- The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far-infrared, named for their relation to the visible spectrum.
- The higher-energy near-IR, approximately  $14000\text{--}4000\text{ cm}^{-1}$  ( $0.8\text{--}2.5\text{ }\mu\text{m}$  wavelength) can excite [overtone](#) or [harmonic](#) vibrations.
- The mid-infrared, approximately  $4000\text{--}400\text{ cm}^{-1}$  ( $2.5\text{--}25\text{ }\mu\text{m}$ ) may be used to study the fundamental vibrations and associated [rotational-vibrational](#) structure.
- The far-infrared, approximately  $400\text{--}10\text{ cm}^{-1}$  ( $25\text{--}1000\text{ }\mu\text{m}$ ), lying adjacent to the [microwave](#) region, has low energy and may be used for [rotational spectroscopy](#).

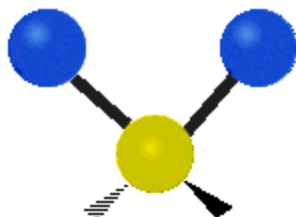
# IR Spectroscopy

- Selection Rules/ Normal Modes
- In the Born–Oppenheimer and harmonic approximations, i.e. when the molecular Hamiltonian corresponding to the electronic ground state can be approximated by a harmonic oscillator in the neighborhood of the equilibrium molecular geometry, the resonant frequencies are associated with the normal modes corresponding to the molecular electronic ground state potential energy surface.
- The resonant frequencies are also related to the strength of the bond and the mass of the atoms at either end of it. Thus, the frequency of the vibrations are associated with a particular normal mode of motion and a particular bond type.

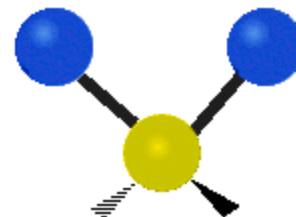
# Types of Vibrations



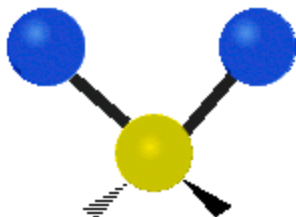
**Symmetrical  
stretching**



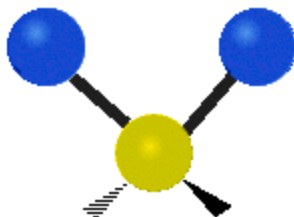
**Antisymmetrical  
stretching**



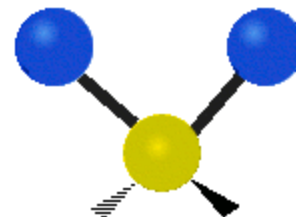
**Scissoring**



**Rocking**



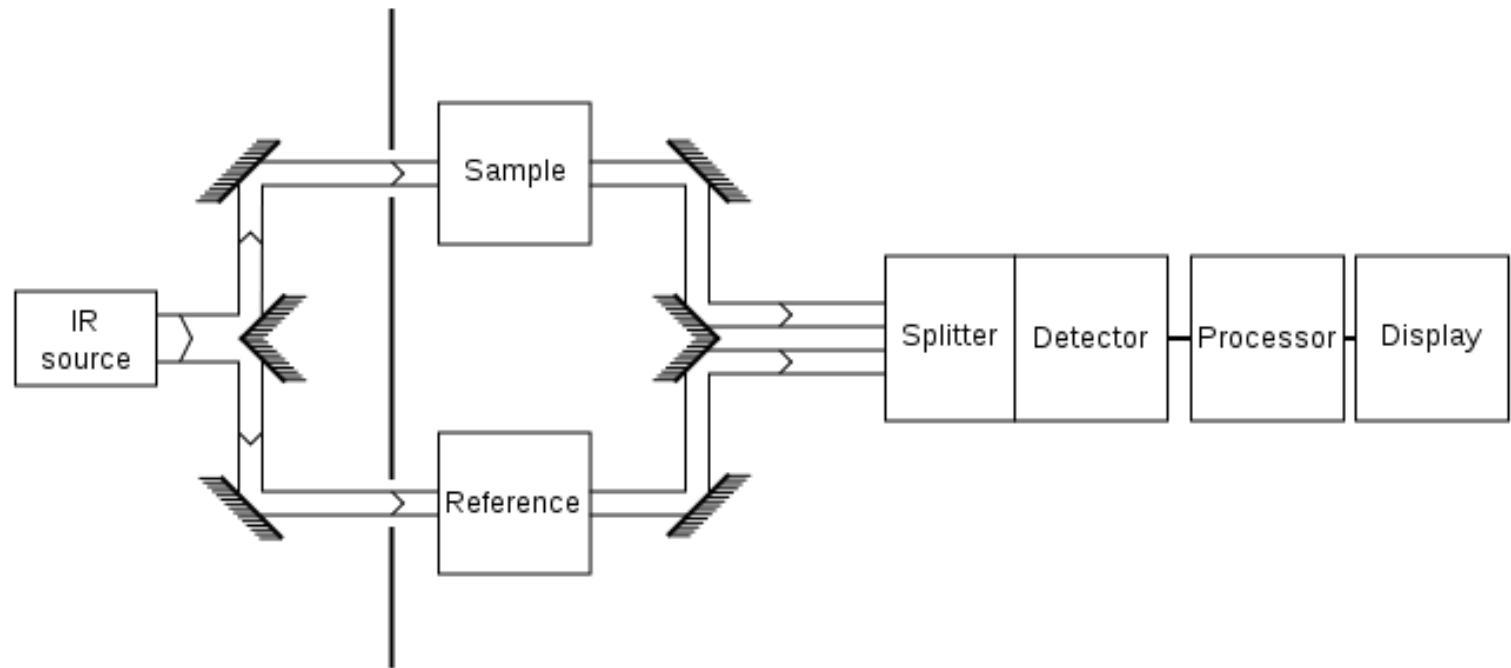
**Wagging**



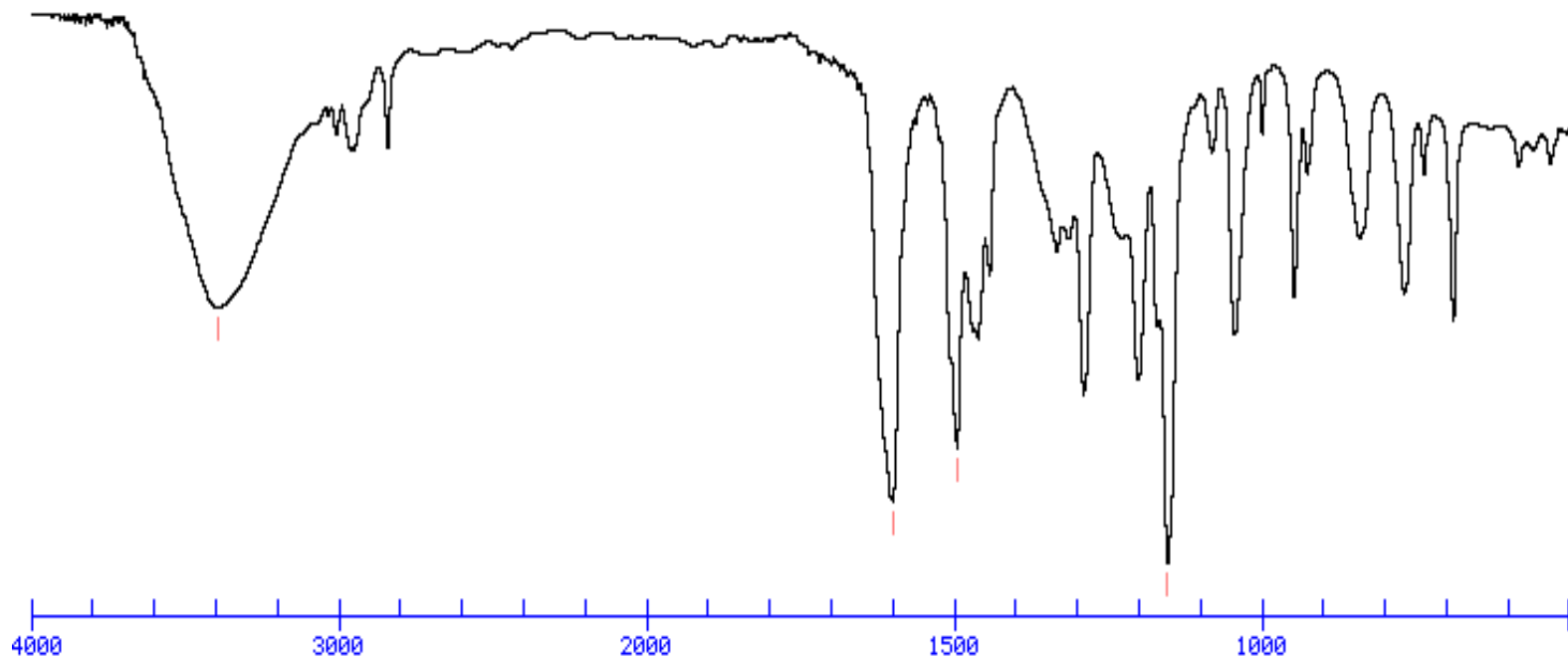
**Twisting**



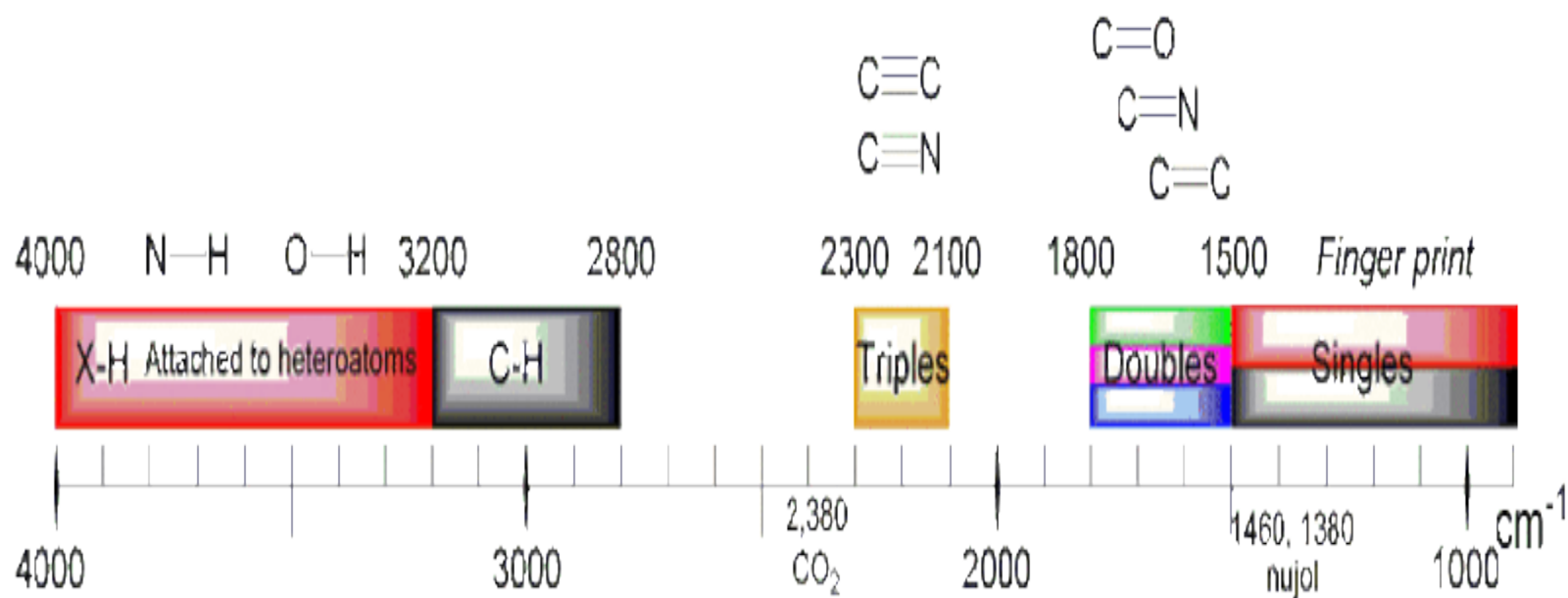
# IR Spectrophotometer



# A typical IR Spectrum



# Applications of IR Spectrophotometer



# Applications of IR Spectroscopy

- Infrared spectroscopy is a simple and reliable technique widely used in both organic and inorganic chemistry, in research and industry. It is used in quality control, dynamic measurement, and monitoring applications such as the long-term unattended measurement of CO<sub>2</sub> concentrations in greenhouses and growth chambers by infrared gas analyzers.
- It is also used in [forensic analysis](#) in both criminal and civil cases, for example in identifying [polymer degradation](#). It can be used in determining the [blood alcohol content](#) of a suspected drunk driver.

# Applications of IR Spectroscopy

- A useful way of analyzing solid samples without the need for cutting samples uses ATR or attenuated total reflectance spectroscopy. Using this approach, samples are pressed against the face of a single crystal. The infrared radiation passes through the crystal and only interacts with the sample at the interface between the two materials.
- With increasing technology in computer filtering and manipulation of the results, samples in solution can now be measured accurately (water produces a broad absorbance across the range of interest, and thus renders the spectra unreadable without this computer treatment).

# Applications of IR Spectroscopy

- Infrared spectroscopy is also useful in measuring the degree of polymerization in [polymer](#) manufacture. Changes in the character or quantity of a particular bond are assessed by measuring at a specific frequency over time. Modern research instruments can take infrared measurements across the range of interest as frequently as 32 times a second. This can be done whilst simultaneous measurements are made using other techniques. This makes the observations of chemical reactions and processes quicker and more accurate.
- Infrared spectroscopy has also been successfully utilized in the field of semiconductor microelectronics: for example, infrared spectroscopy can be applied to semiconductors like [silicon](#), [gallium arsenide](#), [gallium nitride](#), [zinc selenide](#), amorphous silicon, [silicon nitride](#), etc.
- The instruments are now small, and can be transported, even for use in field trials.

## **Spectral Interpretation by Application of Group Frequencies**

- One of the most common application of infrared spectroscopy is to the identification of organic compounds. The major classes of organic molecules are shown in this category and also linked on the bottom page for the number of collections of spectral information regarding organic molecules.

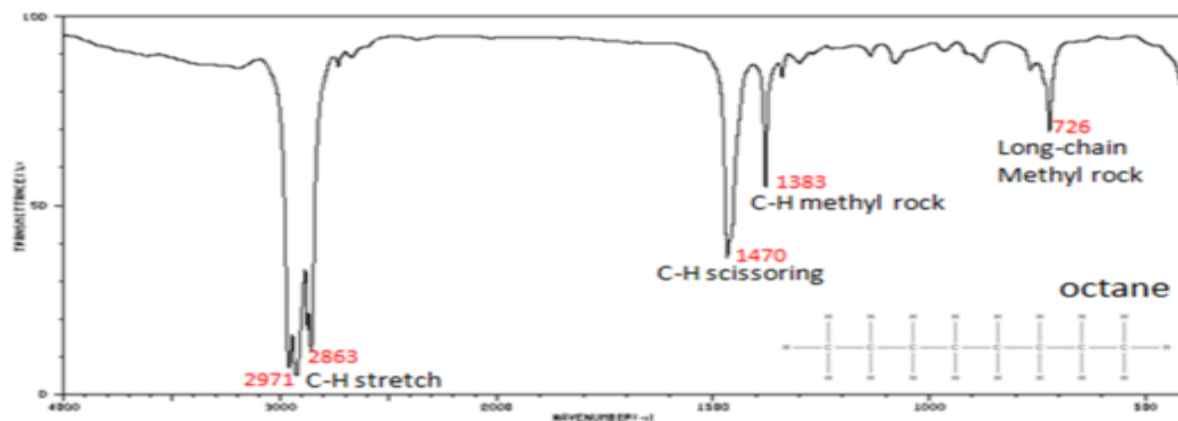
# *Hydrocarbons*

- Hydrocarbons compounds contain only C-H and C-C bonds, but there is plenty of information to be obtained from the infrared spectra arising from C-H stretching and C-H bending.
- In alkanes, which have very few bands, each band in the spectrum can be assigned:
- C-H stretch from 3000–2850  $\text{cm}^{-1}$
- C-H bend or scissoring from 1470-1450  $\text{cm}^{-1}$
- C-H rock, methyl from 1370-1350  $\text{cm}^{-1}$
- C-H rock, methyl, seen only in long chain alkanes, from 725-720  $\text{cm}^{-1}$



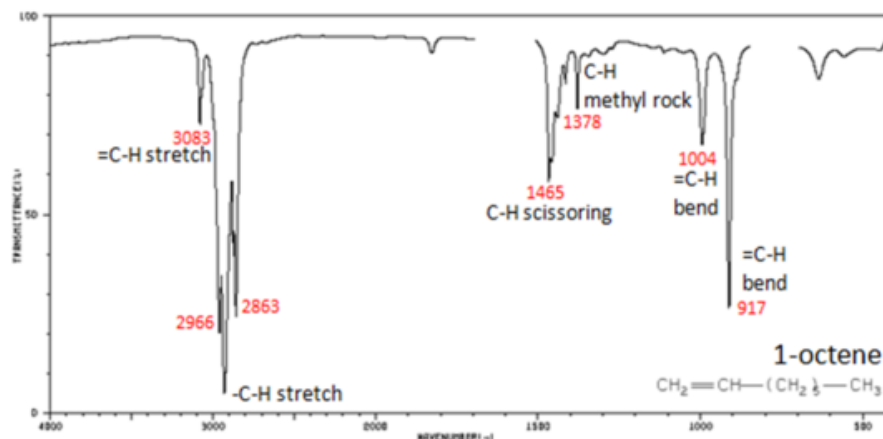
# Hydrocarbons

- Figure shows the IR spectrum of octane. Since most organic compounds have these features, these C-H vibrations are usually not noted when interpreting a routine IR spectrum. Note that the change in dipole moment with respect to distance for the C-H stretching is greater than that for others shown, which is why the C-H stretch band is the more intense.



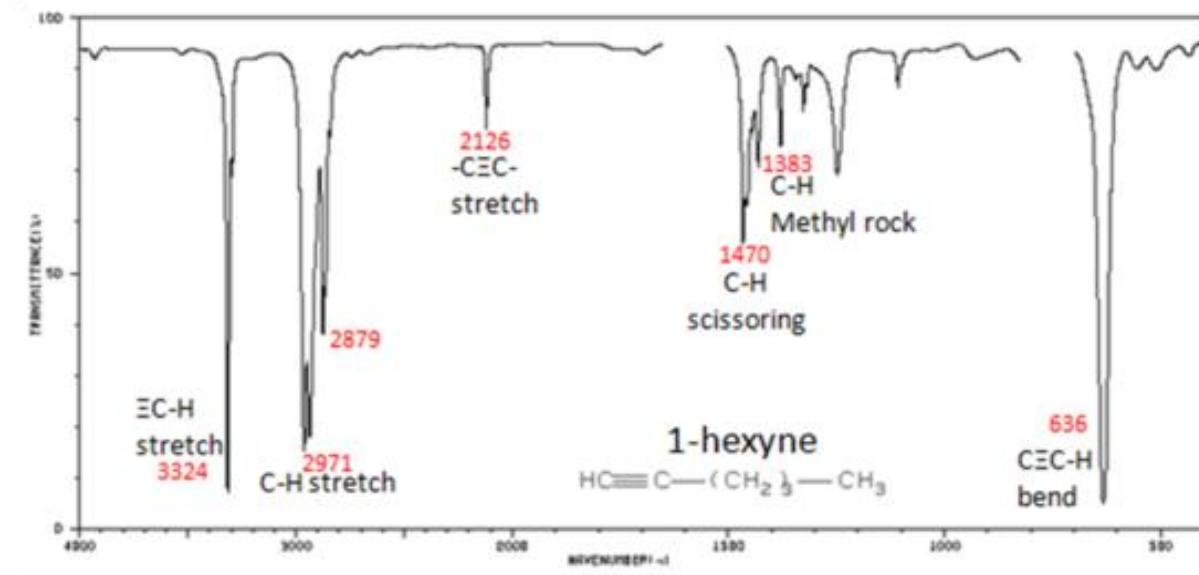
# Hydrocarbons

- In alkenes compounds, each band in the spectrum can be assigned:
- C=C stretch from 1680-1640  $\text{cm}^{-1}$
- =C-H stretch from 3100-3000  $\text{cm}^{-1}$
- =C-H bend from 1000-650  $\text{cm}^{-1}$
- Figure shows the IR spectrum of 1-octene. As alkanes compounds, these bands are not specific and are generally not noted because they are present in almost all organic molecules.



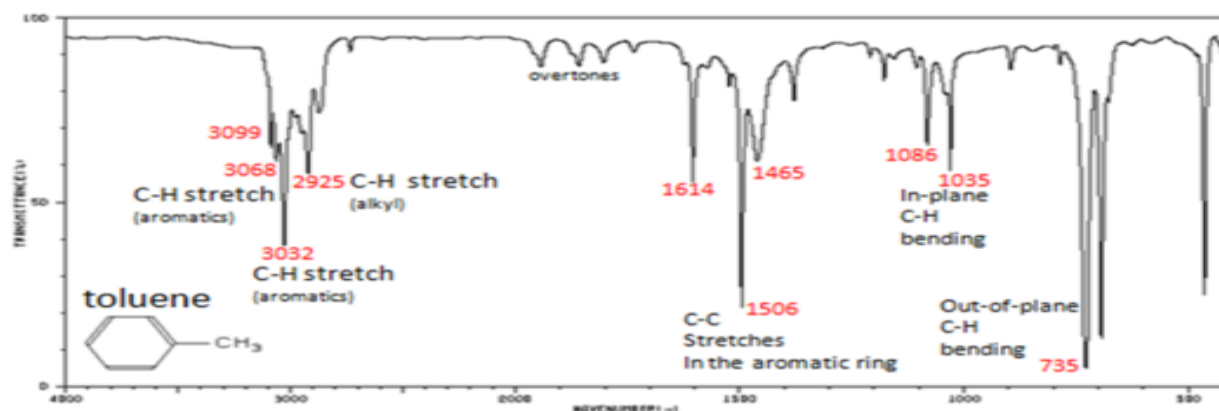
# Hydrocarbons

- In alkynes, each band in the spectrum can be assigned:
- $\text{—C}\equiv\text{C—}$  stretch from  $2260\text{--}2100\text{ cm}^{-1}$
- $\text{—C}\equiv\text{C—H}$ : C—H stretch from  $3330\text{--}3270\text{ cm}^{-1}$
- $\text{—C}\equiv\text{C—H}$ : C—H bend from  $700\text{--}610\text{ cm}^{-1}$
- The spectrum of 1-hexyne, a terminal alkyne, is shown below.



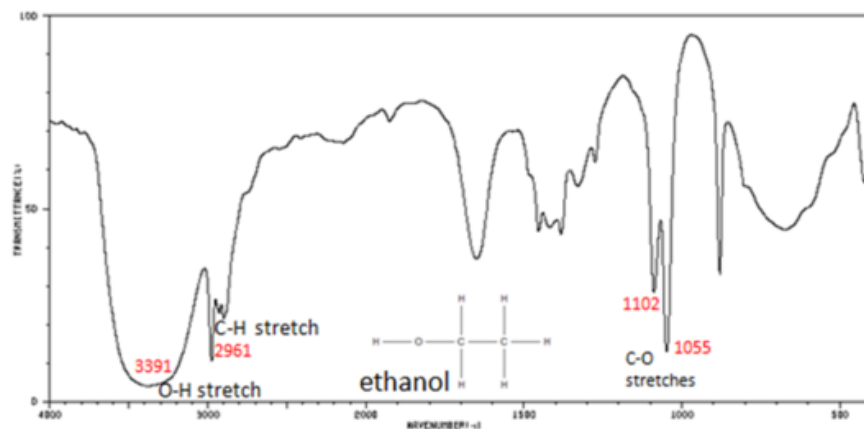
# Hydrocarbons

- In aromatic compounds, each band in the spectrum can be assigned:
- C–H stretch from 3100-3000  $\text{cm}^{-1}$
- overtones, weak, from 2000-1665  $\text{cm}^{-1}$
- C–C stretch (in-ring) from 1600-1585  $\text{cm}^{-1}$
- C–C stretch (in-ring) from 1500-1400  $\text{cm}^{-1}$
- C–H "oop" from 900-675  $\text{cm}^{-1}$
- Note that this is at slightly higher frequency than is the –C–H stretch in alkanes. This is a very useful tool for interpreting IR spectra. Only alkenes and aromatics show a C–H stretch slightly higher than 3000  $\text{cm}^{-1}$ .
- Following Figure shows the spectrum of toluene.



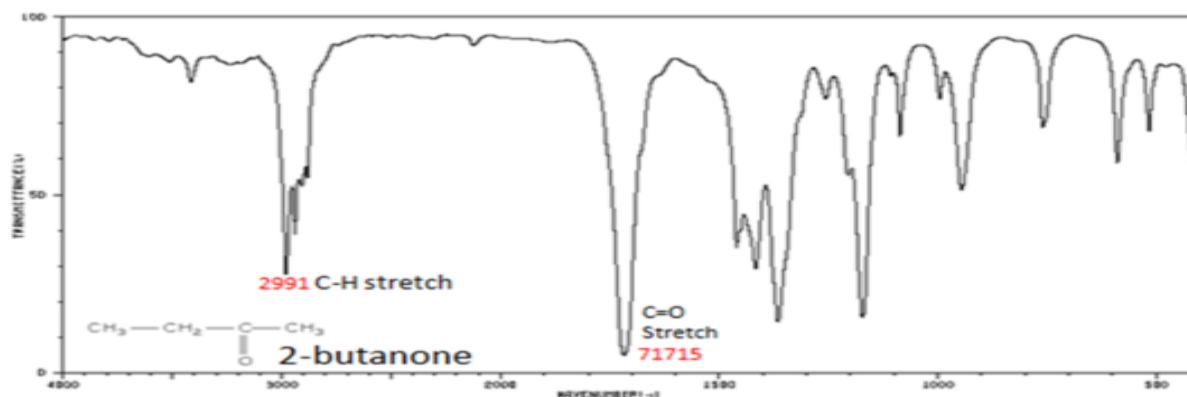
# Functional Groups Containing the C-O Bond

- Alcohols have IR absorptions associated with both the O-H and the C-O stretching vibrations.
- O-H stretch, hydrogen bonded 3500-3200  $\text{cm}^{-1}$
- C-O stretch 1260-1050  $\text{cm}^{-1}$  (s)
- Figure shows the spectrum of ethanol. Note the very broad, strong band of the O-H stretch.



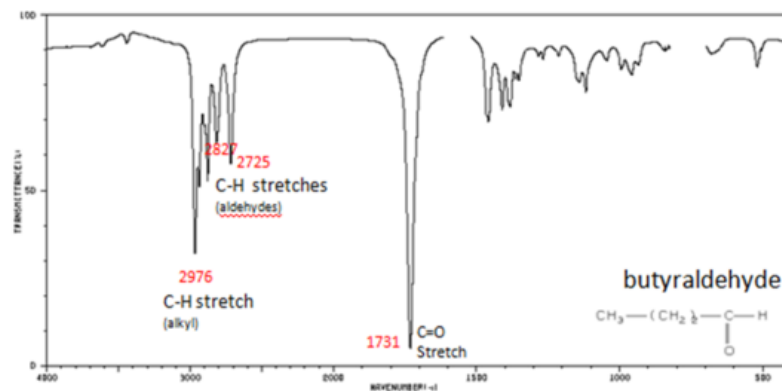
# Carbonyl Compounds

- The carbonyl stretching vibration band C=O of saturated aliphatic ketones appears:
- C=O stretch - aliphatic ketones  $1715\text{ cm}^{-1}$
- -  $\alpha, \beta$ -unsaturated ketones  $1685\text{--}1666\text{ cm}^{-1}$
- Figure shows the spectrum of 2-butanone. This is a saturated ketone, and the C=O band appears at  $1715$ .



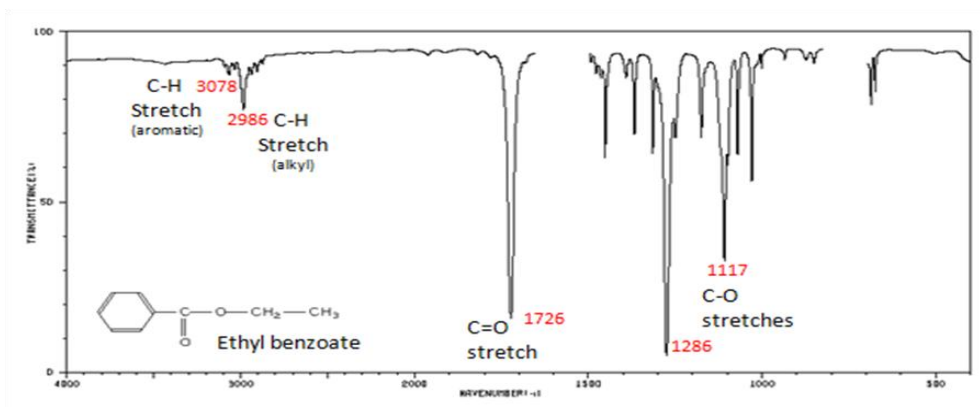
# Carbonyl compounds (Aldehydes)

- If a compound is suspected to be an aldehyde, a peak always appears around  $2720\text{ cm}^{-1}$  which often appears as a shoulder-type peak just to the right of the alkyl C–H stretches.
- H–C=O stretch  $2830\text{--}2695\text{ cm}^{-1}$
- C=O stretch:
  - aliphatic aldehydes  $1740\text{--}1720\text{ cm}^{-1}$
  - alpha, beta-unsaturated aldehydes  $1710\text{--}1685\text{ cm}^{-1}$
- Figure shows the spectrum of butyraldehyde.



# Carbonyl Compounds (Esters)

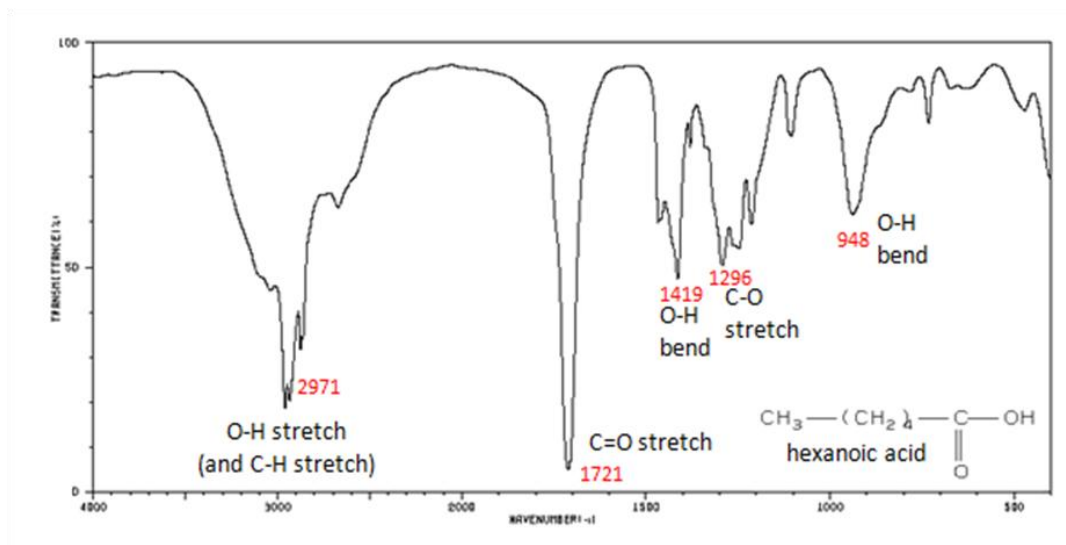
- The carbonyl stretch C=O of esters appears:
- C=O stretch
  - aliphatic from 1750-1735  $\text{cm}^{-1}$
  - $\alpha, \beta$ -unsaturated from 1730-1715  $\text{cm}^{-1}$
- C–O stretch from 1300-1000  $\text{cm}^{-1}$
- Figure shows the spectrum of ethyl benzoate.





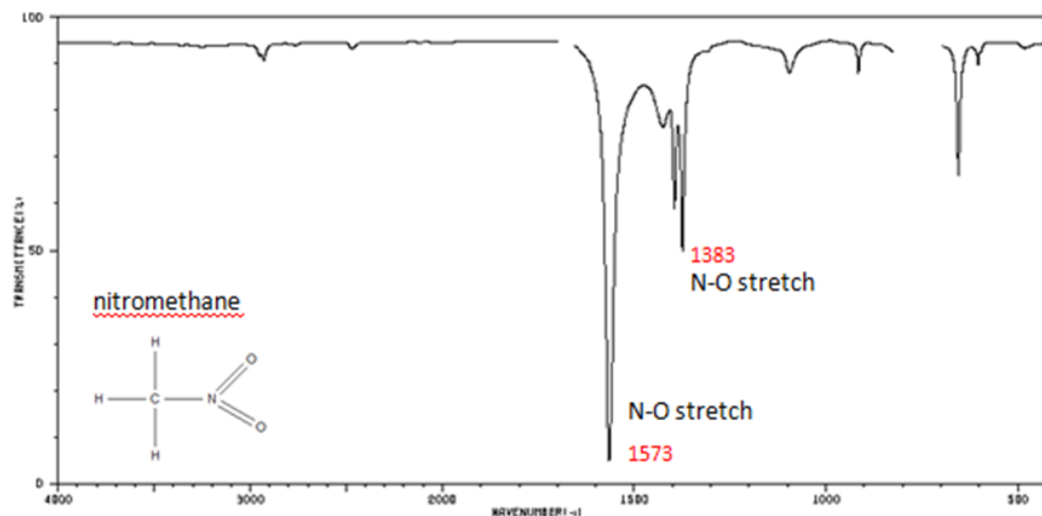
# Carbonyl Compounds (Carboxylic Acids)

- The carbonyl stretch C=O of a carboxylic acid appears as an intense band from 1760-1690  $\text{cm}^{-1}$ . The exact position of this broad band depends on whether the carboxylic acid is saturated or unsaturated, dimerized, or has internal hydrogen bonding.
- O-H stretch from 3300-2500  $\text{cm}^{-1}$
- C=O stretch from 1760-1690  $\text{cm}^{-1}$
- C-O stretch from 1320-1210  $\text{cm}^{-1}$
- O-H bend from 1440-1395 and 950-910  $\text{cm}^{-1}$



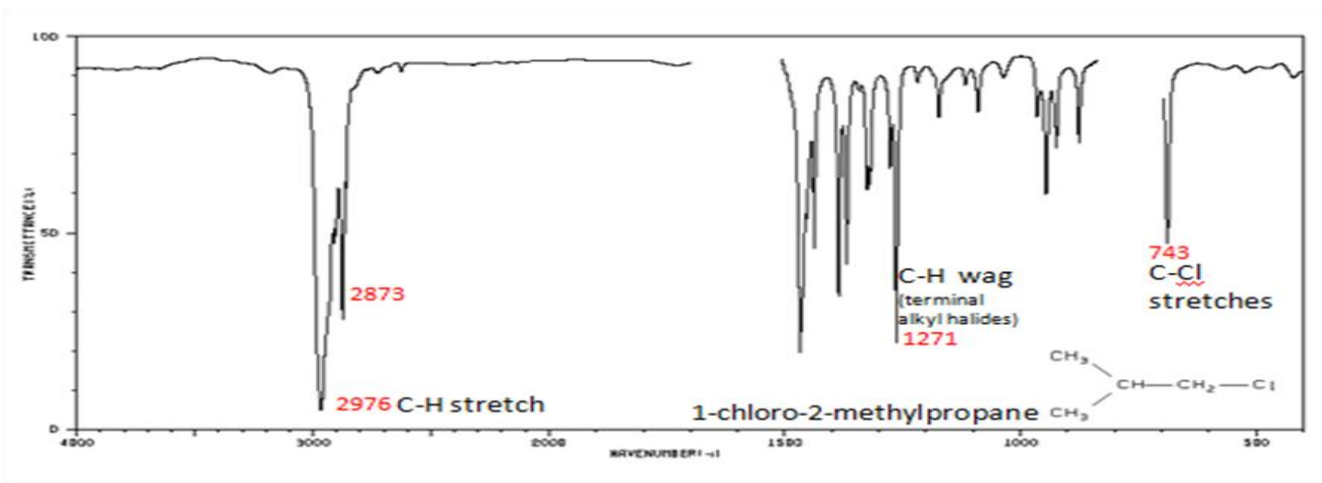
# Organic Nitrogen Compounds

- Notable Peaks are :-
- N–O asymmetric stretch from 1550-1475  $\text{cm}^{-1}$
- N–O symmetric stretch from 1360-1290  $\text{cm}^{-1}$
- Figure shows the IR spectrum of Nitro methane



# Organic Compounds Containing Halogens

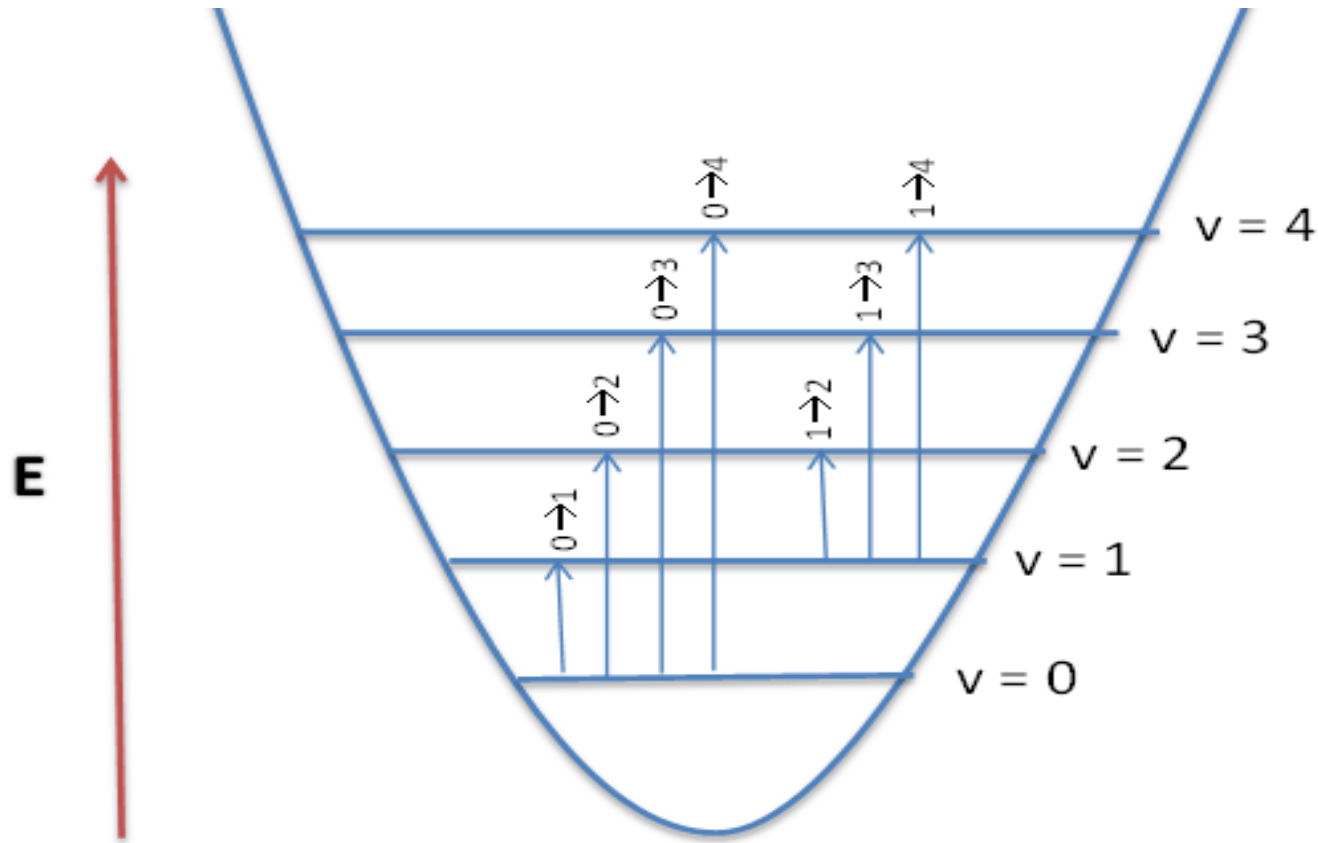
- Alkyl halides are compounds that have a C–X bond, where X is a halogen: bromine, chlorine, fluorene, or iodine.
- C–H wag ( $-\text{CH}_2\text{X}$ ) from  $1300\text{--}1150\text{ cm}^{-1}$
- C–X stretches (general) from  $850\text{--}515\text{ cm}^{-1}$ 
  - C–Cl stretch  $850\text{--}550\text{ cm}^{-1}$
  - C–Br stretch  $690\text{--}515\text{ cm}^{-1}$
- The spectrum of 1-chloro-2-methylpropane are shown below.



# Types of bands

- Introduction
- Fundamental vibrational frequencies of a molecule corresponds to transition from  $v=0$  to  $v=1$ . For a non-linear molecule there will be  $3N-6$  (where  $N$  is the number of atoms) number vibrations. The same holds true for linear molecules, however the equation  $3N-5$  is used, because a linear molecule has one less rotational degrees of freedom. Figure shows a diagram for a vibrating diatomic molecule. The levels denoted by vibrational quantum numbers  $v$  represent the potential energy for the harmonic (quadratic) oscillator. The transition  $0 \rightarrow 1$  is fundamental, transitions  $0 \rightarrow n$  ( $n > 1$ ) are called overtones, and transitions  $1 \rightarrow n$  ( $n > 1$ ) are called hot transitions (hot bands).
- Combination bands, overtones, and Fermi resonances are used to help explain and assign peaks in vibrational spectra that do not correspond with known fundamental vibrations.
- Combination bands and overtones generally have lower intensities than the fundamentals, and Fermi resonance causes a split and shift in intensity of peaks with similar energies and identical symmetries

# Potential energy diagram for a vibrating diatomic molecule



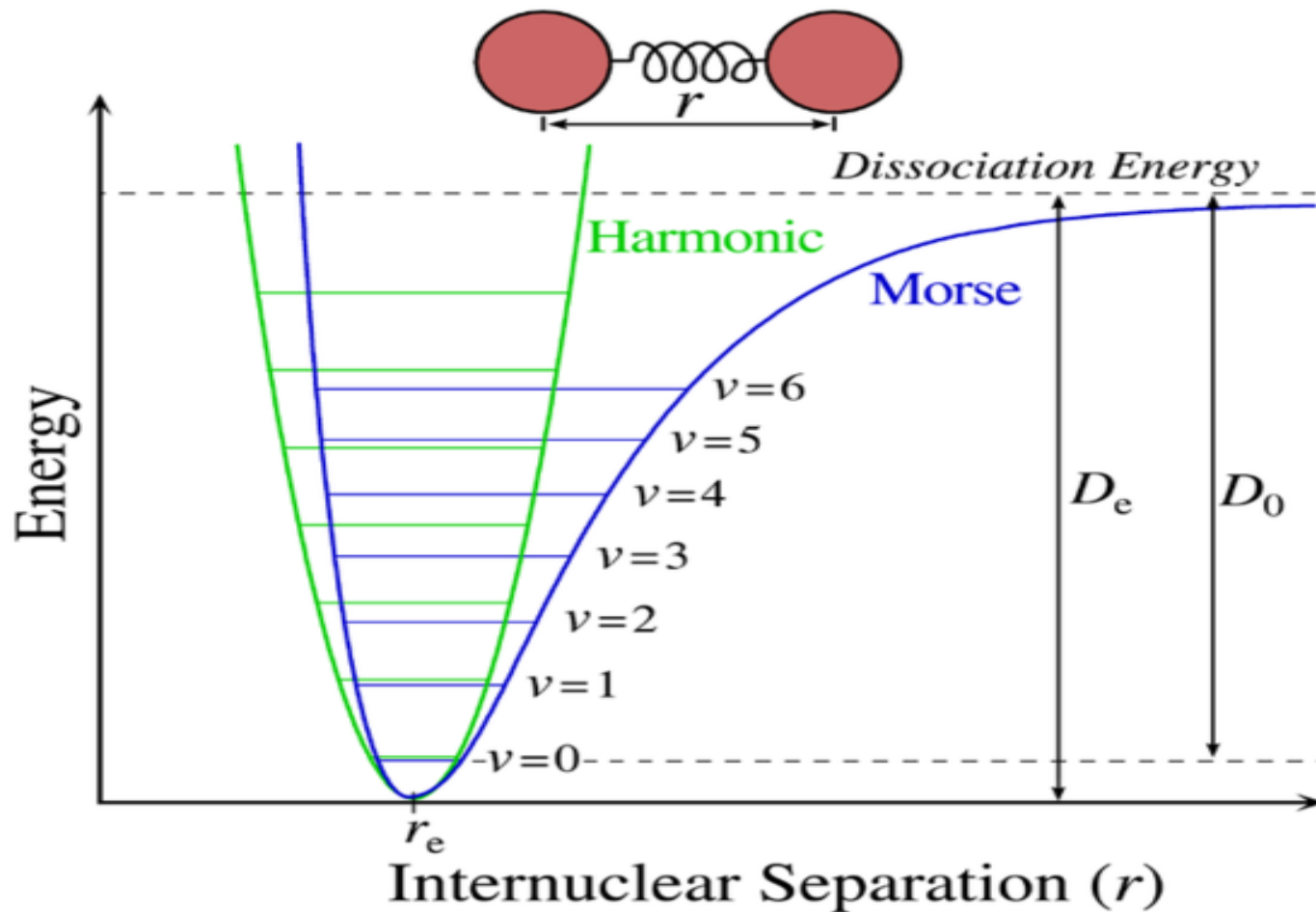
# *Symmetry Requirements*

- The symmetry requirement of vibrational transition is given by the transition moment integral,
- $\mu = \int \psi^* \mu \psi d\tau \neq 0$  (1)
- where,
- $\mu = i\mu_x + j\mu_y + k\mu_z$  (2)
- These integrals can be separated into each component: x, y, and z. Because the ground state contains the totally symmetric representation, the coordinate x, y, or z and  $\psi^*$  must belong to the same representation so that the direct product will contain the totally symmetric representation

# *Harmonic Oscillator Breakdown*

- The harmonic oscillator approximation is convenient to use for diatomic molecules with quantized vibrational energy levels given by the following equation:
- $E_v(\text{cm}^{-1}) = (v+1/2)\omega_e$
- A more accurate description of the vibrational energies is given by the anharmonic oscillator (also called Morse potential) with energy of
- $E_v(\text{cm}^{-1}) = \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 + \omega_e y_e(v+1/2)^3 + \dots$
- where  $\omega_e$  is the vibrational frequency for the  $r_e$  internuclear separation and  $\omega_e \gg \omega_e x_e \gg \omega_e y_e$ . This accounts for the fact that as the higher vibrational states deviate from the perfectly parabolic shape, the level converge with increasing quantum numbers. It is because of this anharmonicity that overtones can occur.
- While it may seem that the harmonic oscillator and the anharmonic oscillator are closely related, this is in fact not the case. The differences in the wavefunctions lead to a breakdown of selection rules, specifically,  $\Delta v = \pm 1$  selection rule can not be applied, and higher order terms must be accounted in the energy calculations.

# Harmonic and Anharmonic Oscillator





# Overtone

- Overtone occurs when a vibrational mode is excited from  $v=0$  to  $v=2$ , which is called the first overtone, or  $v=0$  to  $v=3$ , the second overtone. The fundamental transitions,  $v=\pm 1$ , are the most commonly occurring, and the probability of overtones rapidly decreases as the number of quanta ( $\Delta v=\pm n$ ) increases. Based on the harmonic oscillator approximation, the energy of the overtone transition would be  $n$  times larger than the energy of the fundamental transition frequency, but the anharmonic oscillator calculations show that the overtones are less than a multiple of the fundamental frequency. This is demonstrated with the vibrations of the diatomic HCl in the gas phase:

# *HCl vibrational spectrum.*

Transition	Frequency Observed (cm-1)	Frequency of vibration (Harmonic Oscillator) (cm-1)	Frequency of vibration (Anharmonic Oscillator) (cm-1)
0-1 (Fundamental)	2885.9	2885.9	2885.3
0-2 (Ist overtone)	5668.0	5771.8	5665.0
0-3 (IIInd Overtone)	8347.0	8657.7	8339.0
0-4 (IIIrd overtone)	10923.1	11543.6	10907.4
0-5 (IV overtone)	13396.5	14429.5	13370.0

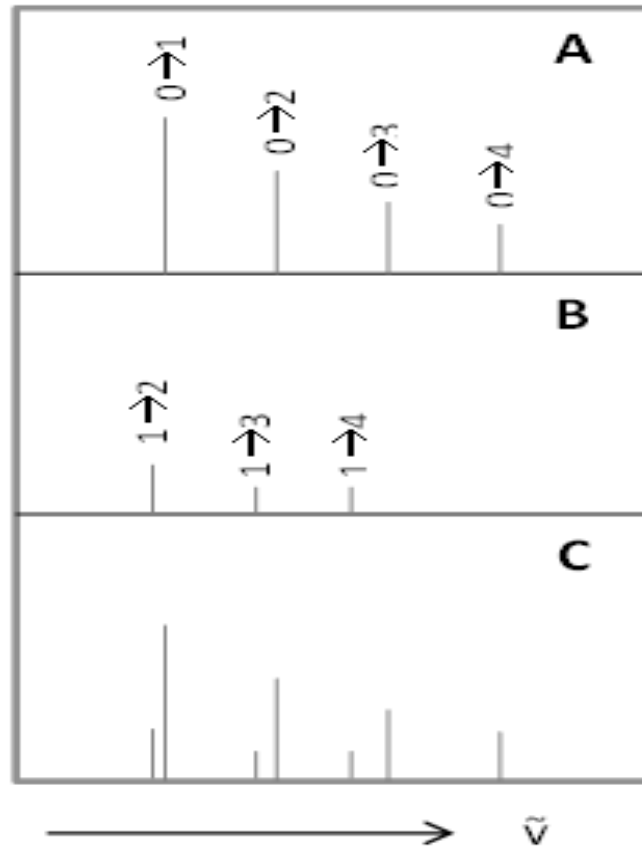
# Combination Bands

- Combination bands are observed when more than two or more fundamental vibrations are excited simultaneously. One reason a combination band might occur is if a fundamental vibration does not occur because of symmetry. This is comparable to **vibronic coupling** in electronic transitions in which a fundamental mode can be excited and allowed as a “doubly excited state.” Combination implies addition of two frequencies, but it also possible to have a difference band where the frequencies are subtracted.
- A practical use for understanding overtones and combination bands is applied to organic solvents used in spectroscopy. Most organic liquids have strong overtone and combination bands in the mid-infrared region, therefore, acetone, DMSO, or acetonitrile should only be used in very narrow spectral regions. Solvents such as  $\text{CCl}_4$ ,  $\text{CS}_2$  and  $\text{CDCl}_3$  can be used above  $1200\text{ cm}^{-1}$ .

# Hot Bands

- Hot bands are observed when an already excited vibration is further excited. For example an  $\nu_1$  to  $\nu_1'$  transition corresponds to a hot band in its IR spectrum. These transitions are temperature dependent, with lower signal intensity at lower temperature, and higher signal intensity at higher temperature. This is because at room temperature only the ground state is highly populated ( $kT \sim 200 \text{ cm}^{-1}$ ), based on the Boltzmann distribution. The Maxwell-Boltzmann distribution law states that if molecules in thermal equilibrium occupy two states of energy  $\epsilon_j$  and  $\epsilon_i$ , the relative populations of molecules occupying these states will be,
- $$\frac{n_j}{n_i} = \frac{e^{-\epsilon_j/RT}}{e^{-\epsilon_i/RT}} = e^{-\Delta\epsilon/RT}$$
- where,  $k$  is the Boltzmann constant and  $T$  is the temperature in Kelvin.
- In the harmonic oscillator model, hot bands are not easily distinguished from fundamental transitions because the energy levels are equally spaced. Because the spacing between energy levels in the anharmonic oscillator decrease with increasing vibrational levels, the hot bands occur at lower frequencies than the fundamentals. Also, the transition moment integrals are slightly different since the ground state will not necessarily be totally symmetric since it is not in  $\nu=0$ .
- $\psi_1(0)\psi_2(0)\psi_3(1) \rightarrow \psi_1(0)\psi_2(0)\psi_3(2)$

Example of hot bands in a vibrational line spectrum of a diatomic molecule: (A) harmonic frequencies; (B) hot band transitions; (C) combination of both spectra.

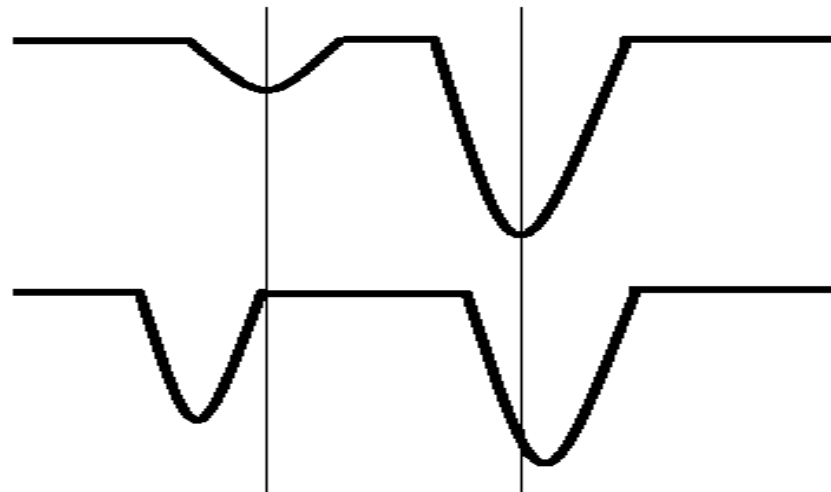


# Fermi resonance

- Fermi resonance results in the splitting of two vibrational bands that have nearly the same energy and symmetry in both IR and Raman spectroscopies. The two bands are usually a fundamental vibration and either an overtone or combination band. The wavefunctions for the two resonant vibrations mix according to the harmonic oscillator approximation, and the result is a shift in frequency and a change in intensity in the spectrum. As a result, two strong bands are observed in the spectrum, instead of the expected strong and weak bands. It is not possible to determine the contribution from each vibration because of the resulting mixed wave function.

# Fermi resonance

- Example of intensity and frequency shifts due to Fermi resonance. The top bands represent two fundamental vibrations without Fermi resonance, and the bottom bands show the change in bands as a result. The two energy levels are split such that one increases and the other decreases in energy, known as a “Fermi doublet,” and they move away from each other.



# Fermi Resonance

- A typical example of Fermi resonance is found in the vibrational spectra of aldehydes, where the C-H bond in the CHO group interacts with the second harmonic level,  $2\delta(\text{CHO})$ , derived from the fundamental frequency of the deformation vibration of the CHO group ( $2 \times 1400 \text{ cm}^{-1}$ ). The result is a Fermi doublet with branches around  $2830$  and  $2730 \text{ cm}^{-1}$ . It is important for Fermi resonance that the vibrations connected with the two interacting levels be localized in the same part of the molecule.



# Assignment/ Set of Questions

- Q1.Explain theory of IR spectroscopy.
- Q2. Explain in detail the instrumentation used for IR spectroscopy.
- Q3. Write a note on types of vibrations.
- Q4. What do you understand by a harmonic oscillator?
- Q5. How harmonic and anharmonic oscillator differs?
- Q6. Explain the applications of IR spectroscopy
- Q7. Explain the use of IR spectroscopy in the structure identification of hydrocarbons.
- Q8. Explain the IR spectra of alcohols.
- Q9. Explain the important peaks as observed in the IR spectroscopy of esters.
- Q10. Write a note on IR spectrum of carbonyl compounds

# Assignment/ Set of Questions

- Q11. Write a note on fundamental vibrations.
- Q12. write a note on hot bands.
- Q13. What are overtones? Explain.
- Q14. What do you understand by Fermi Resonance?
- Q15. What are combination bands?

- Best of Luck