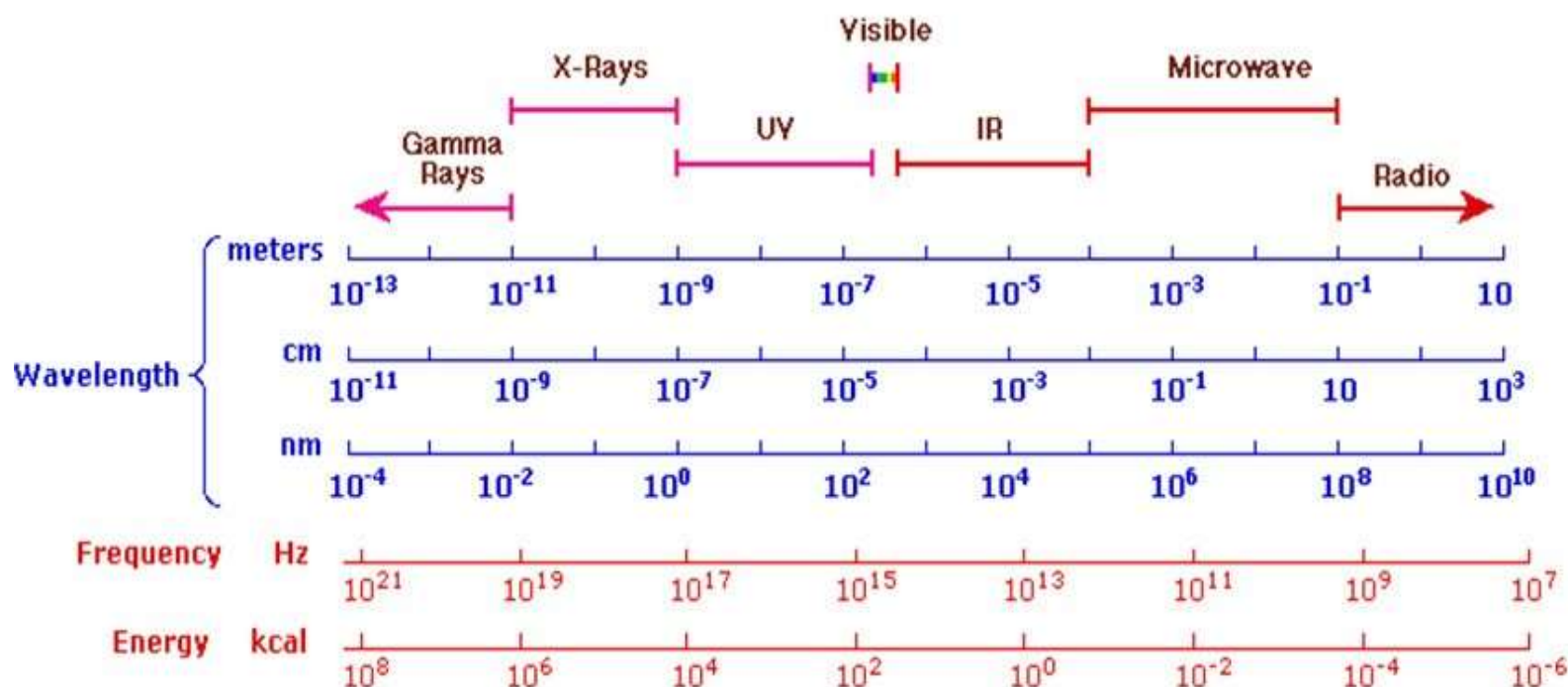


Spectroscopy

Spectroscopy is the study of the interaction between matter and electromagnetic radiation. It is a scientific measurement technique which measures light that is emitted, absorbed, or scattered by materials and can be used to study, identify and quantify those materials.

Electromagnetic energy travels in waves and spans a broad spectrum from very short gamma rays, beyond which lie cosmic rays, to very long radio waves.

The Electromagnetic Spectrum



Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha
Dept. of Science & Mathematics
IIITG, Guwahati

All these waves have same velocity, i.e. 3×10^{10} cm/sec. Their frequency is related to wavelength as $c = \nu\lambda$

c = the speed of light (cm/sec)

ν = frequency in Hertz (sec^{-1})

λ = wavelength in cm

$$W = 1/\lambda$$

W = wavenumber in cm^{-1}

λ = wavelength in cm

When a molecule absorbs radiation, it gains energy. This gain in energy,

$$\Delta E = \frac{hc}{\lambda}$$

h = Planck's constant

c = velocity of light

λ = wavelength

The particular frequency of radiation that a given molecule can absorb depends upon the changes in vibrations or rotations or electronic states that are permitted for a molecule having a particular structure. The spectrum of a compound is a plot that shows how much electromagnetic radiation is absorbed (or transmitted) at each frequency and is characteristic of a compound.

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IIITG, Guwahati

| <i>Rays or waves incident on molecules</i> | <i>Spectroscopy</i> | <i>Inference/ Information</i> |
|-------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <i>X-rays are scattered by atoms</i> | <i>Measures the scattering pattern</i> | <i>Bond lengths and angles</i> |
| <i>Radio waves make nuclei resonate</i> | <i>Plots charts of resonant frequencies</i> | <i>Symmetry and connectivity of the hydrocarbon skeleton</i> |
| <i>Absorption of lower energy IR radiation make bonds vibrational & rotational excitation of gps of atoms within mols</i> | <i>Plots charts of absorption</i> | <i>The functional groups in the molecule</i> |
| <i>Mass spectrum- molecules are ionized by high energy electrons</i> | <i>Ion fragmentation patterns is related to structure of the mol^r ion</i> | <i>The mass to charge ratio of these ions is measured very accurately by electrostatic acceleration and magnetic field perturbation</i> |
| <i>Absorption high-energy ultraviolet light causes electronic excitation</i> | <i>Plots charts of absorption</i> | <i>Molecule shows absorption only if conjugated pi-electron systems are present</i> |
| <i>Absorption in the low-energy radio-frequency part of the spectrum (NMR) causes excitation of nuclear spin states</i> | <i>Plots charts of excited spin states revealing different H nuclei</i> | <i>High-resolution NMR distinguishes & counts atoms (e.g. ¹H, ¹³C, ¹⁹F & ³¹P) in diff locations in the mol, infers C-H framework of org compound. H atoms</i> |

Course Code: SC202

Presented by

Course Instructor: **Dr Bhar Saha**
 Dept. of Science & Mathematics
 IIITG, Guwahati

Mass spectrometry: is used to determine mass of the molecule and atomic composition. It can be used in two ways: (a) prove identity of two isomers (b) establish structure of a new compound.

Ultraviolet-Visible Spectroscopy: Absorption of this relatively high-energy light causes electronic excitation. The easily accessible part of this region (wavelengths of 200 to 800 nm) shows absorption only if conjugated pi-electron systems (double bonds) are present.

IR spectroscopy: (to determine the functional groups in the molecule). These wavelengths lie in the infrared, just to the long wavelength side of visible light (wavelengths 700 nm - 1 mm). The emission or absorption spectrum of a substance is as unique to that substance as a fingerprint is to a human being.

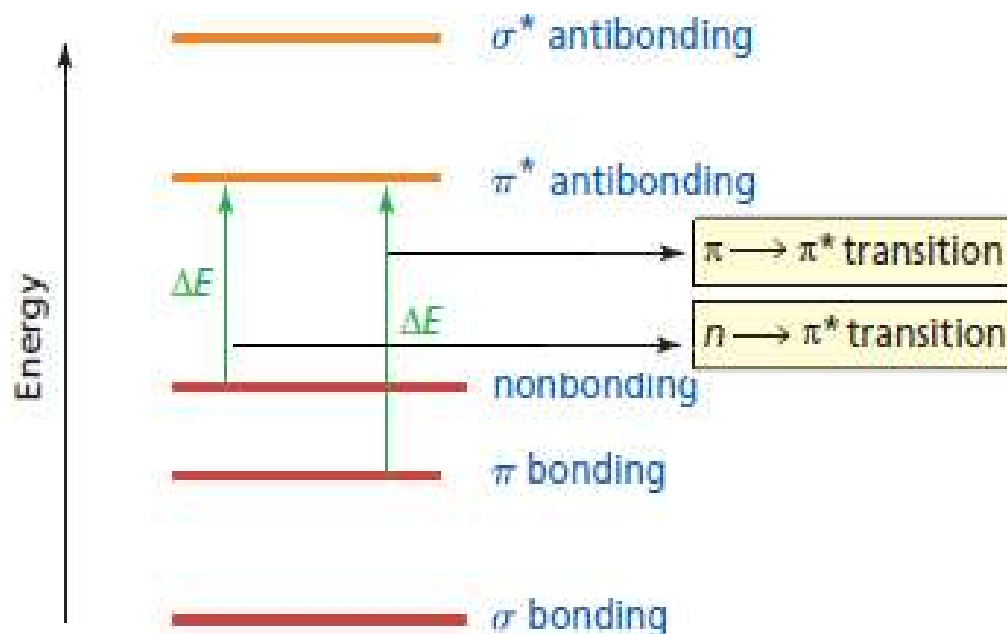
^1H NMR: (to determine symmetry, branching, and connectivity in the molecule). Nuclear magnetic resonance (NMR) allows us to detect atomic nuclei and say what sort of environment they are in within the molecule. Some atomic nuclei act like tiny compass needles when placed in a magnetic field and have different energy levels according to the direction in which they are 'pointing'. A ^1H or ^{13}C nucleus in a magnetic field can have two energy levels, and energy is needed to flip the nucleus from the more stable state to the less stable state. But since the amount of energy needed is so small, it can be provided by low-energy electromagnetic radiation of radio-wave frequency.

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha
Dept. of Science & Mathematics
IIITG, Guwahati

Ultraviolet-Visible Spectroscopy: Ultraviolet light is electromagnetic radiation with wavelengths ranging from 180-400 nm and visible light has wavelengths ranging from 400-780 nm. The normal electronic configuration of a molecule is known as its **ground state** — all the electrons are in the lowest-energy molecular orbitals. When a molecule absorbs light of an appropriate wavelength and an electron is promoted to a higher energy molecular orbital, the molecule is then in an **excited state**. Thus, an **electronic transition** is the promotion of an electron from its ground state to a higher energy molecular orbital. The energies of the bonding, nonbonding, and antibonding molecular orbitals are in ascending order.



Course Code: SC202

Presented by

Course Instructor: **Dr Bhar Saha**
Dept. of Science & Mathematics
IIITG, Guwahati

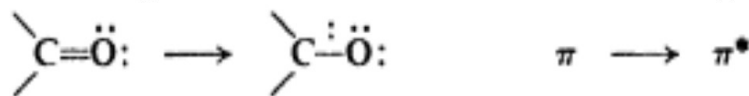
Resonance stabilizes the excited state more than it stabilizes the ground state, and thus reduces the difference between them. As opposed to IR spectrum, the UV spectrum is not used primarily to show presence of individual functional groups, but rather to show relationships between them, mainly conjugation:

- between two or more carbon-carbon double (or triple) bonds;
- between carbon-carbon and carbon-oxygen double bonds;
- between double bonds and an aromatic ring; and
- the presence of an aromatic ring itself
- number and location of substituents attached to the carbons of the conjugated system

Conjugation requires double bonds separated by one single bond.

A typical ultraviolet spectrum can be described in terms of the position of the top of the hump (λ_{max}) and the intensity of that absorption (ϵ_{max} , the extinction coefficient). An electron has been changed from one orbital to another orbital of higher energy can be of any of the kinds we have encountered: a σ electron, a π electron, or an n electron (a non-bonding electron i.e., one of an unshared pair). UV and visible light have enough energy to cause only the two electronic transitions (σ e s require more energy to be activated)

- nonbonding (lone-pair) e^- into antibonding molecular orbital (n to π^*), $\text{>C=}\ddot{\text{O}}\text{:} \longrightarrow \text{>}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}\text{=}\ddot{\text{O}}\text{:} \quad n \longrightarrow \pi^*$
- transition of an e^- from a bonding molecular orbital into an antibonding molecular orbital (π to π^*).



Only organic compounds with n , π e^- s can produce UV Vis spectra.

Course Code: SC202

Presented by

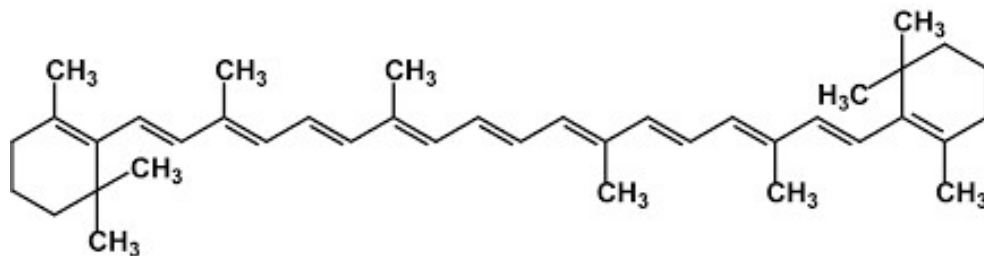
Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

Energy of the right wavelength can promote an electron from a filled orbital (HOMO: Highest energy Occupied Molecular Orbital) to an unfilled one (for example the LUMO: Lowest energy Unoccupied Molecular Orbital), and plotting the absorption of energy against wavelength gives rise to a UV-visible spectrum. The more conjugated a compound is, the smaller the energy transition between its HOMO and LUMO, and hence the longer the wavelength of light it can absorb. Both ethene and butadiene absorb in the UV region of the electromagnetic spectrum. Butadiene absorbs at 215 nm compared to 185 nm for ethene. The conjugation in butadiene means it absorbs light of a longer wavelength than ethene (energy difference between HOMO & LUMO is less for butadiene than for ethene, $\psi_2 - \psi_3 < \pi - \pi^*$). As conjugated pi systems become larger, the energy gap for a $\pi - \pi^*$ transition becomes increasingly narrow, and the wavelength of light absorbed correspondingly becomes longer. The absorbance due to the $\pi - \pi^*$ transition in 1,3,5-hexatriene, for example, occurs at 258 nm. If the conjugation increases, the gap between HOMO and LUMO will eventually be small enough to allow the compound to absorb visible light and hence have a colour. If a compound has enough conjugated double bonds, it will absorb visible light ($\lambda_{max} > 400 \text{ nm}$) and the compound will be coloured. β - Carotene, a precursor of vitamin A, is an orange substance found in carrots, apricots. All dyes and pigments based on organic compounds are highly conjugated. The λ_{max} and the molar absorptivity increase as the number of conjugated double bonds increases.

β - Carotene



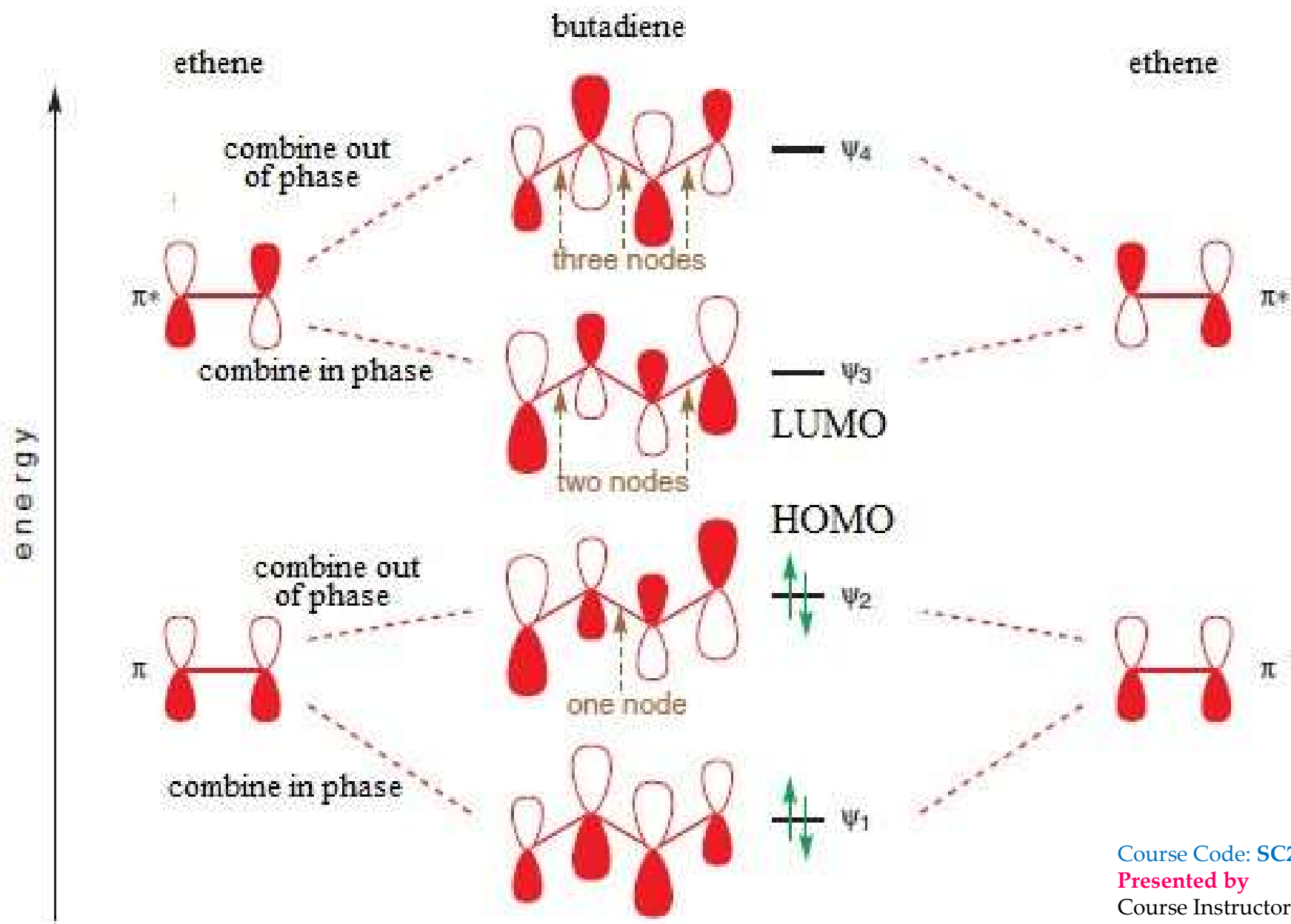
Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IIITG, Guwahati



Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IIITG, Guwahati

The λ_{max} and the molar absorptivity increase as the number of conjugated double bonds increases.

| Absorbed frequency, nm | Colour absorbed | Colour transmitted | $R(\text{CH}=\text{CH})_nR$, $n =$ |
|------------------------|-----------------|--------------------|-------------------------------------|
| 200–400 | ultraviolet | — | < 8 |
| 400 | violet | yellow–green | 8 |
| 425 | indigo–blue | yellow | 9 |
| 450 | blue | orange | 10 |
| 490 | blue–green | red | 11 |
| 510 | green | purple | |
| 530 | yellow–green | violet | |
| 550 | yellow | indigo–blue | |
| 590 | orange | blue | |
| 640 | red | blue–green | |
| 730 | purple | green | |

Course Code: SC202

Presented by

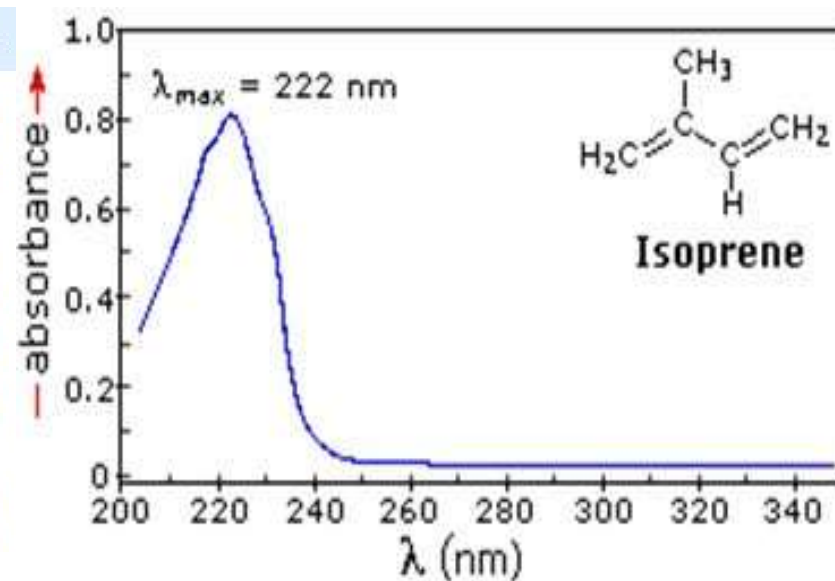
Course Instructor: **Dr Bhar Saha**

Dept. of Science & Mathematics

IIITG, Guwahati

A chromophore is that part of a molecule that absorbs UV or visible light. The carbonyl group is the chromophore of acetone. Acetone has both π electrons and lone-pair (n) electrons. Thus, there are two absorption bands: one for the π to π^* and one for the n to π^* transition. For the π to π^* transition, $\lambda_{max}=195\text{ nm}$; for the n to π^* transition $\lambda_{max}=274\text{ nm}$.

| Chromophore | Example | Excitation | λ_{max}, nm | ϵ | Solvent |
|-------------|----------------|--------------------------|----------------------------|------------|---------|
| C=C | Ethene | $\pi \rightarrow \pi^*$ | 171 | 15,000 | hexane |
| C≡C | 1-Hexyne | $\pi \rightarrow \pi^*$ | 180 | 10,000 | hexane |
| C=O | Ethanal | $n \rightarrow \pi^*$ | 290 | 15 | hexane |
| | | $\pi \rightarrow \pi^*$ | 180 | 10,000 | hexane |
| N=O | Nitromethane | $n \rightarrow \pi^*$ | 275 | 17 | ethanol |
| | | $\pi \rightarrow \pi^*$ | 200 | 5,000 | ethanol |
| C-X X=Br | Methyl bromide | $n \rightarrow \sigma^*$ | 205 | 200 | hexane |
| X=I | Methyl iodide | $n \rightarrow \sigma^*$ | 255 | 360 | hexane |



The oxygen non-bonding electrons in alcohols and ethers do not give rise to absorption above 160 nm.

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

Auxochromes: The substituents that themselves do not absorb ultraviolet radiations but their presence shifts the absorption maximum to longer wavelength are called auxochromes. The substituents like methyl, hydroxyl, alkoxy, halogen, amino, azo group etc. are some examples of auxochromes. Therefore, an auxochrome is a substituent that when attached to a chromophore, alters the λ_{max} and the intensity of the absorption, usually increasing both; OH and NH₂ groups are auxochromes. The lone-pair electrons on oxygen and nitrogen are available for interaction with the π electron cloud of the benzene ring, and such an interaction increases the λ_{max} . As anilinium ion does not have an auxochrome, its λ_{max} is similar to that of benzene. Protonating aniline (and thereby forming the anilinium ion) decreases the λ_{max} because the lone pair is no longer available to interact with the cloud of the benzene ring. Because wavelengths of red light are longer than those of blue light, a shift to a longer wavelength is called a red shift, and a shift to a shorter wavelength is called a blue shift. Deprotonation of phenol results in a red shift, whereas protonation of aniline produces a blue shift.

Wavelengths absorbed (nm)

380–460

380–500

440–560

480–610

540–650

380–420 and 610–700

Observed color

yellow

orange

red

purple

blue

green

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IIITG, Guwahati

Bathochromic/Red shift: A shift of an absorption maximum towards longer wavelength or lower energy.

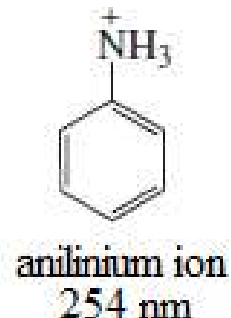
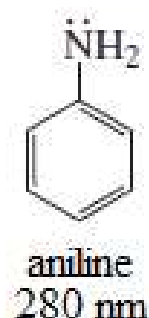
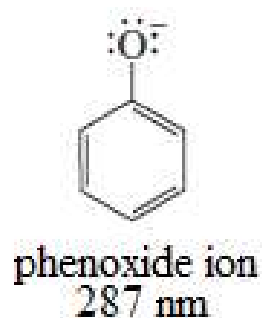
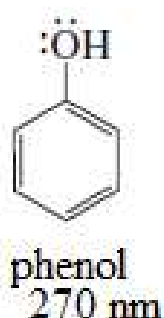
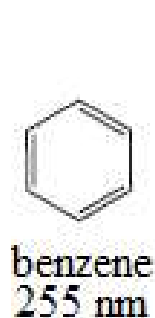
Hypsochromic/Blue Shift: A shift of an absorption maximum towards shorter wavelength or higher energy.

Hypochromic Effect: An effect that results in decreased absorption intensity.

Hyperchromic Effect: An effect that results in increased absorption intensity.

Anilinium ion does not have an auxochrome, its λ_{max} is almost that of benzene.

Protonating aniline decreases the λ_{max} because the lone pair is no longer available to interact with the cloud of the benzene ring. Deprotonation of phenol results in a red shift, whereas protonation of aniline produces a blue shift.



Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha
Dept. of Science & Mathematics
IIITG, Guwahati

Infrared (IR) spectroscopy is used to detect the stretching of unsymmetrical bonds as in functional groups such as OH, CO, NH₂, and NO₂. The amount of energy needed for stretching and bending individual bonds, is very small, and therefore corresponds to much longer wavelengths. These wavelengths lie in the infrared, just to the long wavelength side of visible light (wavelengths between 700 nm - 1 mm; wavenumber 4000-400 cm⁻¹). When the carbon skeleton of a molecule vibrates, all the bonds stretch and relax in combination. Some bonds stretch essentially independently of the rest of the molecule, and we can use these to identify functional groups. This occurs if the bond is either:

- much stronger or weaker than others nearby, or*
- between atoms that are much heavier or lighter than their neighbours*

IR spectra don't usually indicate the wavelength but instead a value known as the 'wavenumber', in cm⁻¹, which is simply the number of wavelengths in one centimetre. For a typical bond this will fall between 4000 (short wavelengths, i.e. high frequency) and 500 (long wavelengths, i.e. low frequency).

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha
Dept. of Science & Mathematics
IIITG, Guwahati

A stretch is a vibration occurring along the line of the bond; it changes the bond length.

A bend is a vibration that does not occur along the line of the bond; a bending vibration changes the bond angle. Bending vibrations are often referred to as rock, scissor, wag and twist.

A diatomic molecule such as HCl undergoes only stretching vibration as it has no bond angles. When a molecule absorbs infrared radiation, its chemical bonds vibrate. The bonds can stretch & contract, and bend. This is why infrared spectroscopy is a type of vibrational spectroscopy. Different molecules vibrate at different frequencies because their structures are different. The necessary condition for a molecule to absorb infrared light is that the molecule must have a vibration during which the change in dipole moment with respect to distance is non-zero. This condition can be summarized in equation form as follows:

$$\frac{\partial \mu}{\partial x} \neq 0 \quad \begin{array}{l} \partial \mu = \text{change in dipole moment} \\ \partial x = \text{change in bond distance} \end{array}$$

For bonds between unlike atoms, the larger the difference in electronegativity, the greater the dipole moment and the more it changes when stretched.

Bending of bonds, particularly C–H and N–H bonds, also leads to quite strong peaks.

These are called deformations.

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha
Dept. of Science & Mathematics
IIITG, Guwahati

In IR spectrum, absorption maxima are shown upside down (IR spectra plot 'transmission') i.e. IR spectra are upside down and back to front.

There are four important regions of the infrared spectrum

1. The first region, from 4000 to 2500 cm^{-1} is the region for C–H, N–H, and O–H bond stretching.

Most of the atoms in an organic molecule (C, N, O, for example) are about the same weight (12, 14, 16. . .). Hydrogen is an order of magnitude lighter than any of these and so it dominates the stretching frequency by the large effect it has on the reduced mass, so any bond to H comes right at the left-hand end of the spectrum.

2. The strongest bonds between non-H atoms—triple bonds such as $\text{C}\equiv\text{C}$ or $\text{C}\equiv\text{N}$ —absorb at slightly lower frequencies than bonds to hydrogen: these are in the next region, the triple bond region from about 2500 to 2000 cm^{-1} .

3. C=C and C=O double bonds appear about 2000–1500 cm^{-1} and,

4. At the right-hand end of the spectrum come single bonds, below 1500 cm^{-1} .

The single bond region is used as a molecular fingerprint.

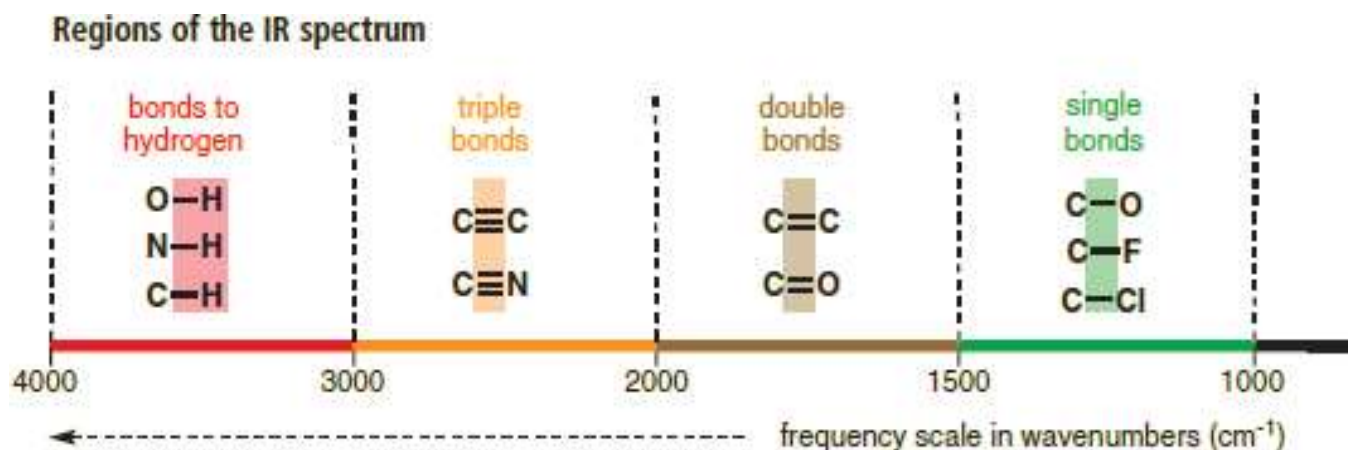
Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IIITG, Guwahati



The strength of an IR absorption depends on dipole moment. Dipole moment depends on the variation in distribution of electrons along the bond and also its length, which is why stretching a bond can change its dipole moment. For bonds between unlike atoms, the larger the difference in electronegativity, the greater the dipole moment and the more it changes when stretched. For identical atoms (C=C, for example) the dipole moment, and its capacity to change with stretching, is much smaller. Stretching frequencies for symmetrical molecules can be measured using an alternative method known as Raman spectroscopy. This is an IR-based technique using scattered light that relies on the polarizability of bonds.

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha
Dept. of Science & Mathematics
IIITG, Guwahati

Absorption Frequencies of some common bonds

| <i>bond</i> | | <i>type of compound</i> | <i>frequency</i> |
|----------------------------------------------------------------------------|-----------|----------------------------------------|--------------------------------------------------|
| $\begin{array}{c} \\ -\text{C}-\text{H} \\ \end{array}$ | (stretch) | alkanes | 2800–3000 |
| $\begin{array}{c} \\ =\text{C}-\text{H} \end{array}$ | (stretch) | alkenes, aromatics | 3000–3100 |
| $=\text{C}-\text{H}$ | (stretch) | alkynes | 3300 |
| $-\text{O}-\text{H}$ | (stretch) | alcohols, phenols | 3600–3650 (free) 3200–3500 (H-bonded) (broad) |
| $-\text{O}-\text{H}$ | (stretch) | carboxylic acids | 2500–3300 |
| $\begin{array}{c} \\ -\text{N}-\text{H} \end{array}$ | (stretch) | amines | 3300–3500 (doublet for NH_2) |
| $\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{H} \end{array}$ | (stretch) | aldehydes | 2720 and 2820 |
| $\begin{array}{c} & \\ -\text{C} & = & \text{C}- \\ & \end{array}$ | (stretch) | alkenes | 1600–1680 |
| $\begin{array}{c} & \\ -\text{C} & = & \text{C}- \end{array}$ | (stretch) | aromatics | 1500–1600 |
| $-\text{C}\equiv\text{C}-\text{H}$ | (stretch) | alkynes | 2100–2270 |
| $\begin{array}{c} \text{O} \\ \\ -\text{C}- \end{array}$ | (stretch) | aldehyde, ketones, carboxylic acids | 1680–1740 |
| $-\text{C}\equiv\text{N}$ | (stretch) | nitriles | 2220–2260 |
| $\text{C}-\text{N}$ | (stretch) | amines | 1180–1360 |
| $-\text{C}-\text{H}$ | (bending) | alkanes | 1375 (methyl) |
| $-\text{C}-\text{H}$ | (bending) | alkanes | 1460 (methyl and methylene) |
| $-\text{C}-\text{H}$ | (bending) | alkanes | 1370 and 1385 (isopropyl split) |

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha
Dept. of Science & Mathematics
IIITG, Guwahati

Characteristic IR Absorptions [Stretching & Bending]

| <i>frequency, cm⁻¹</i> | <i>bond</i> | <i>functional group</i> | <i>frequency, cm⁻¹</i> | <i>bond</i> | <i>functional group</i> |
|-----------------------------------|----------------------------|-------------------------------------|-----------------------------------|------------------------------|--------------------------------------------|
| 3640–3610 (s, sh) | O–H stretch, free hydroxyl | alcohols, phenols | 1650–1580 (m) | N–H bend | 1° amines |
| 3500–3200 (s,b) | O–H stretch, H-bonded | alcohols, phenols | 1600–1585 (m) | C–C stretch (in-ring) | aromatics |
| 3400–3250 (m) | N–H stretch | 1°, 2° amines, amides | 1550–1475 (s) | N–O asymmetric stretch | nitro compounds |
| 3300–2500 (m) | O–H stretch | carboxylic acids | 1500–1400 (m) | C–C stretch (in-ring) | aromatics |
| 3330–3270 (n, s) | –C≡C–H: C–H stretch | alkynes (terminal) | 1470–1450 (m) | C–H bend | alkanes |
| 3100–3000 (s) | C–H stretch | aromatics | 1370–1350 (m) | C–H rock | alkanes |
| 3100–3000 (m) | =C–H stretch | alkenes | 1360–1290 (m) | N–O symmetric stretch | nitro compounds |
| 3000–2850 (m) | C–H stretch | alkanes | 1335–1250 (s) | C–N stretch | aromatic amines |
| 2830–2695 (m) | H–C=O: C–H stretch | aldehydes | 1320–1000 (s) | C–O stretch | alcohols, carboxylic acids, esters, ethers |
| 2260–2210 (v) | C≡N stretch | nitriles | 1300–1150 (m) | C–H wag (–CH ₂ X) | alkyl halides |
| 2260–2100 (w) | –C≡C– stretch | alkynes | 1250–1020 (m) | C–N stretch | aliphatic amines |
| 1760–1665 (s) | C=O stretch | carbonyls (general) | 1000–650 (s) | =C–H bend | alkenes |
| 1760–1690 (s) | C=O stretch | carboxylic acids | 950–910 (m) | O–H bend | carboxylic acids |
| 1750–1735 (s) | C=O stretch | esters, saturated aliphatic | 910–665 (s, b) | N–H wag | 1°, 2° amines |
| 1740–1720 (s) | C=O stretch | aldehydes, saturated aliphatic | 900–675 (s) | C–H “oop” | aromatics |
| 1730–1715 (s) | C=O stretch | α, β-unsaturated esters | 850–550 (m) | C–Cl stretch | alkyl halides |
| 1715 (s) | C=O stretch | ketones, saturated aliphatic | 725–720 (m) | C–H rock | alkanes |
| 1710–1665 (s) | C=O stretch | α, β-unsaturated aldehydes, ketones | 700–610 (b, s) | –C≡C–H: C–H bend | alkynes |
| 1680–1640 (m) | –C=C– stretch | alkenes | 690–515 (m) | C–Br stretch | alkyl halides |

m=medium, w=weak, s=strong,
n=narrow, b=broad, sh=sharp

Course Code: SC202

Presented by

Course Instructor: **Dr Bhar Saha**
Dept. of Science & Mathematics
IITG, Guwahati

NMR requires electromagnetic waves in the radio-wave region of the spectrum to make nuclei flip from one state to another.

(Proton) ^1H NMR spectra are generally recorded in solution in deuteriochloroform (CDCl_3)—that is, chloroform (CHCl_3) with the ^1H replaced by ^2H (deuterium). The proportionality of the size of the peak to the number of protons tells you why: if you ran a spectrum in CHCl_3 , you would see a vast peak for all the solvent Hs because there would be much more solvent than the compound you wanted to look at. Using CDCl_3 cuts out all extraneous protons. ^2H atoms have different nuclear properties and so don't show up in the ^1H spectrum. Nonetheless, CDCl_3 is always unavoidably contaminated with a small amount of CHCl_3 , giving rise to the small peak at 7.25 ppm. Spectra may equally well be recorded in other deuterated solvents such as water (D_2O), methanol (CD_3OD), or benzene (C_6D_6). The reference point from which chemical shifts are measured is not the signal from a single proton, but from an actual compound: generally tetramethylsilane, $(\text{CH}_3)_4\text{Si}$. The scale of NMR spectrum is the δ (delta) scale, with $(\text{CH}_3)_4\text{Si}$ signal taken as 0.0 ppm.

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha
Dept. of Science & Mathematics
IIITG, Guwahati

To determine NMR spectra of a compound

- 1. The sample of the unknown compound is dissolved in a suitable solvent, placed in a narrow tube, and put inside a very strong electromagnet. To even out imperfections in the sample, the tube is spun very fast by a stream of air. Inside the magnetic field, any atomic nuclei with a nuclear spin now possess different energy levels, the exact number of different energy levels depending on the value of the nuclear spin. For ^1H and ^{13}C NMR there are two energy levels.*
- 2. The sample is irradiated with a short pulse of radiofrequency energy. This disturbs the equilibrium balance between the two energy levels: some nuclei absorb the energy and are promoted to a higher energy level.*
- 3. When the pulse finishes, the radiation given out as the nuclei fall back down to the lower energy level is detected using what is basically a sophisticated radio receiver.*
- 4. After lots of computation, the results are displayed in the form of intensity (i.e. number of absorptions) against frequency.*

Course Code: SC202

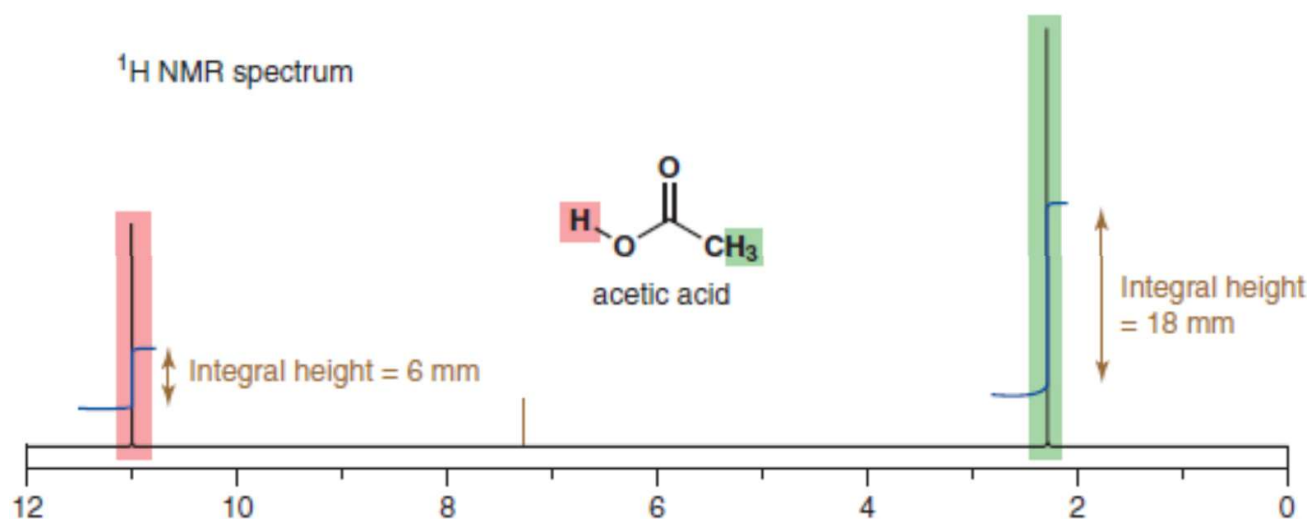
Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

Integration tells us the number of hydrogen atoms in each peak. In acetic acid the methyl group is next to the electron-withdrawing carbonyl group and so is slightly deshielded at about δ 2.0 ppm and the acidic proton itself, attached to O, is very deshielded at δ 11.2 ppm. The same factor that makes this proton acidic—the O–H bond is polarized towards oxygen—also makes it resonate at low field. In ^1H NMR the size of the peaks is also important: the area under the peaks is exactly proportional to the number of protons. Proton spectra are normally integrated, that is, the area under the peaks is computed and recorded as a line. Measuring the height of the steps gives the ratio of the numbers of protons represented by each peak. The heights are 6 mm and 18 mm, a ratio of about 1:3.

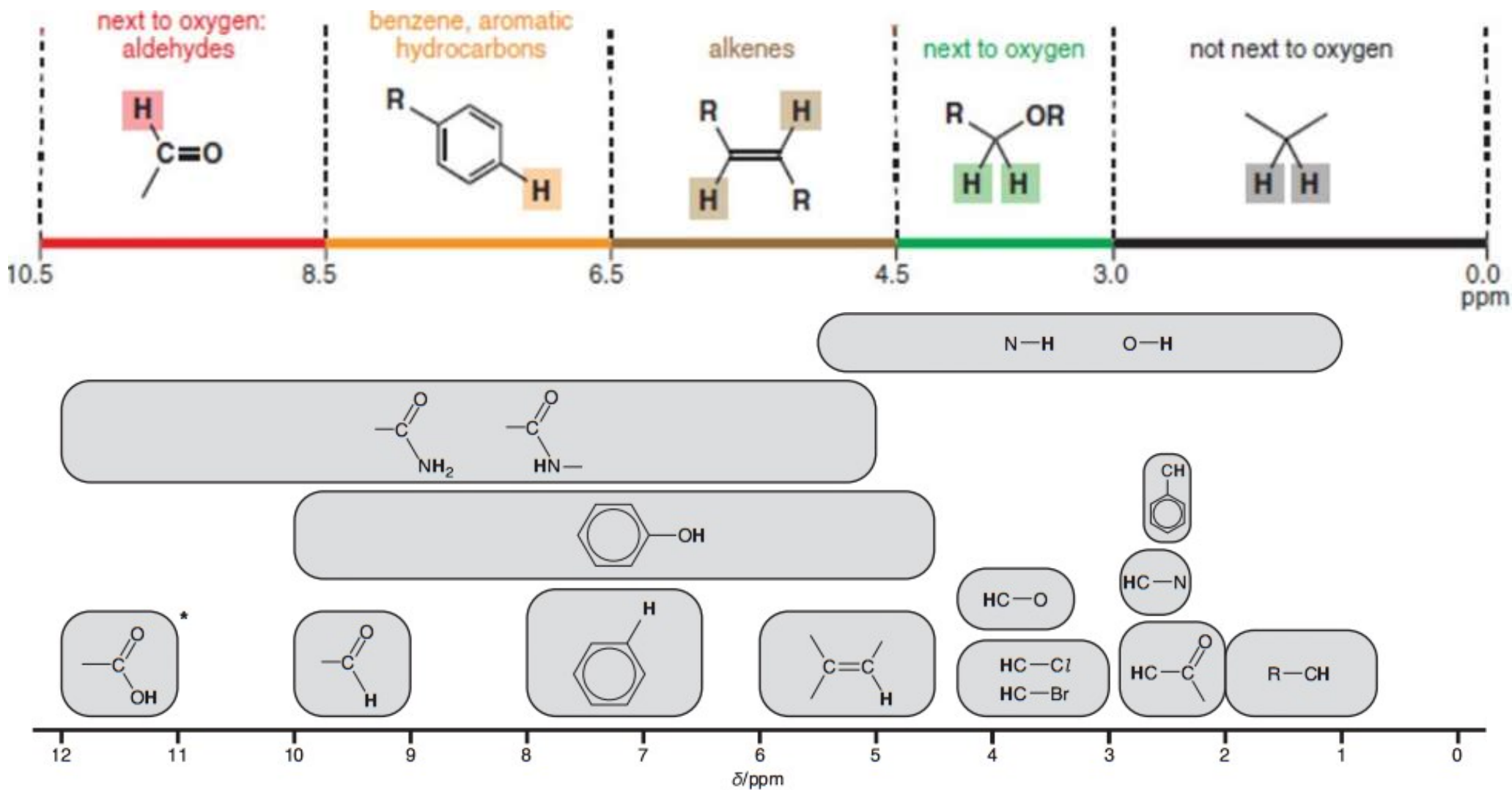


Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha
Dept. of Science & Mathematics
IIITG, Guwahati

Regions of the proton NMR spectrum



Course Code: SC202

Presented by

Course Instructor: **Dr Bhar Saha**

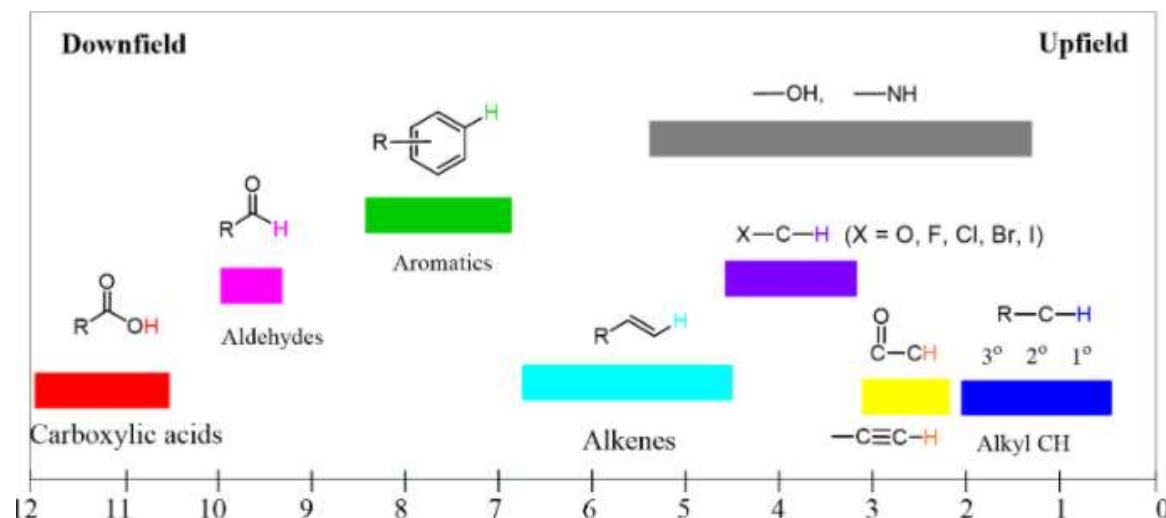
Dept. of Science & Mathematics

IIITG, Guwahati

| | | | |
|----------------------------------------------------------------------------|-----------|-------------------------------------------------------------------------------------------|-----------|
| $\text{R}-\text{CH}_3$ | 0.7 - 1.3 | $\text{I}-\text{C}-\text{H}$ | 2.0 - 4.0 |
| $\text{R}-\text{CH}_2-\text{R}$ | 1.2 - 1.4 | $\text{Br}-\text{C}-\text{H}$ | 2.7 - 4.1 |
| R_3CH | 1.4 - 1.7 | $\text{Cl}-\text{C}-\text{H}$ | 3.1 - 4.1 |
| $\text{R}-\text{C}(\text{CH}_3)=\text{C}-\text{CH}_3$ | 1.6 - 2.6 | $\text{RO}-\text{C}-\text{H}$ | 3.2 - 3.8 |
| $\text{R}=\text{H or alkyl}$ $\text{R}-\text{C}(=\text{O})-\text{CH}_3$ | 2.1 - 2.5 | $\text{R}=\text{H or alkyl}$ $\text{R}-\text{C}(=\text{O})-\text{O}-\text{C}-\text{H}$ | 3.5 - 4.8 |
| $\text{RO}-\text{C}(=\text{O})-\text{CH}_3$ | 2.1 - 2.6 | $\text{O}_2\text{N}-\text{C}-\text{H}$ | 4.1 - 4.3 |
| $\text{N}\equiv\text{C}-\text{CH}_3$ | 2.1 - 3.0 | $\text{F}-\text{C}-\text{H}$ | 4.2 - 4.8 |
| $\text{C}_6\text{H}_5-\text{C}-\text{H}$ | 2.3 - 2.7 | $\text{R}-\text{C}(\text{CH}_3)=\text{C}-\text{H}$ | 4.5 - 6.5 |
| $\text{R}-\text{C}\equiv\text{C}-\text{H}$ | 1.7 - 2.7 | $\text{C}_6\text{H}_5-\text{H}$ | 6.5 - 8.0 |
| $\text{R}-\text{N}(\text{CH}_3)-\text{C}-\text{H}$ | 2.2 - 2.9 | $\text{R}-\text{C}(=\text{O})-\text{H}$ | 9.0 - 10 |
| $\text{R}-\text{S}-\text{C}-\text{H}$ | 2.0 - 3.0 | | |

Downfield shifts more common
 NH and OH peaks are most often broad or may as well be missing completely unless the sample is very dry.
 This is also true for any proton capable of making hydrogen bonding:

| | |
|-------------------------------------------------------------|-----------|
| $\text{R}-\text{SH}$ | 1.0 - 5.0 |
| $\text{R} = \text{alkyl or aryl}$ $\text{R}-\text{NH}_2$ | 1.0 - 5.0 |
| $1^\circ, 2^\circ$ | |
| $\text{R}-\text{OH}$ | 1.0 - 5.0 |
| $1^\circ, 2^\circ, 3^\circ$ | |
| $\text{C}_6\text{H}_5-\text{OH}$ | 4.0 - 7.0 |
| $\text{R}-\text{C}(=\text{O})-\text{N}(\text{R})-\text{H}$ | 5.0 - 9.0 |
| $1^\circ, 2^\circ$ | |
| $\text{R}-\text{C}(=\text{O})-\text{OH}$ | 11 - 12 |



Course Code: SC202

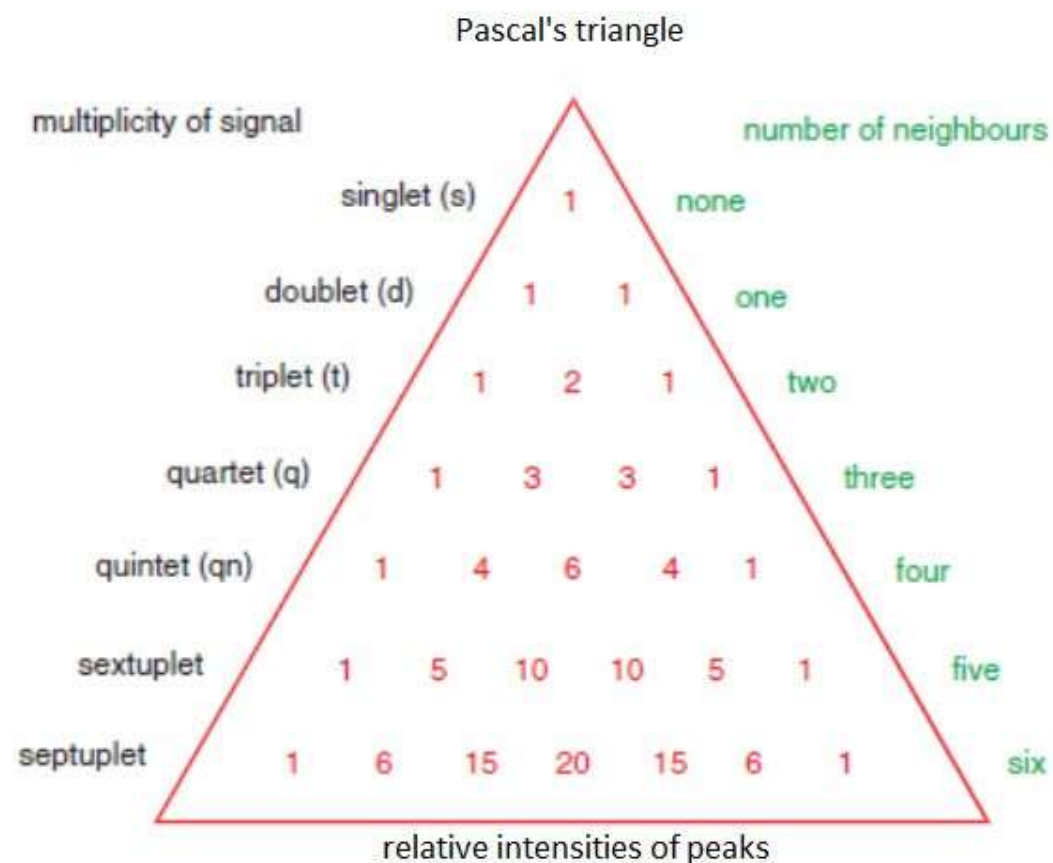
Presented by

Course Instructor: Dr Bhar Saha
 Dept. of Science & Mathematics
 IIITG, Guwahati

Coupling/neighbourhood of protons: The distance between peaks in a multiplet is a measure of the effectiveness of spin-spin coupling, and is called the coupling constant, J , measured in Hz. The size of J varies with electronegativity of substituents.

Coupling constants depend on three factors:

- 1. Through-bond distance between the protons.*
- 2. Angle between the two C–H bonds.*
- 3. Substituents.*



| Number of Adjacent Protons | Splitting Pattern | Number of Peaks |
|----------------------------|-------------------|-----------------|
| 0 | Singlet | 1 |
| 1 | Doublet | 2 |
| 2 | Triplet | 3 |
| 3 | Quartet | 4 |

Course Code: SC202

Presented by

Course Instructor: **Dr Bhar Saha**
 Dept. of Science & Mathematics
 IIITG, Guwahati

NMR and CMR spectra of alcohols and ethers: H-bonding and Proton Exchange

NMR absorption by a hydroxylic proton (O-H) is shifted downfield due to hydrogen bonding. The degree of H-bonding depends on temperature, concentration and nature of the solvent. Therefore, the signal can be broadly based in the range of δ 1-5 ppm. It may sometimes be hidden by alkyl protons, but can be established through proton counting.

A hydroxylic proton generally gives a singlet in the NMR spectrum: its signal is not split by nearby protons, nor does it split their signals.

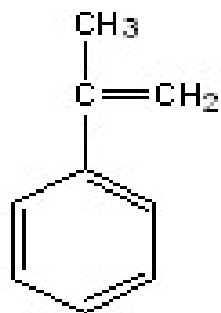
The oxygen of an alcohol or ether causes a downfield shift for the nearby protons due to inductive effect.

Course Code: SC202

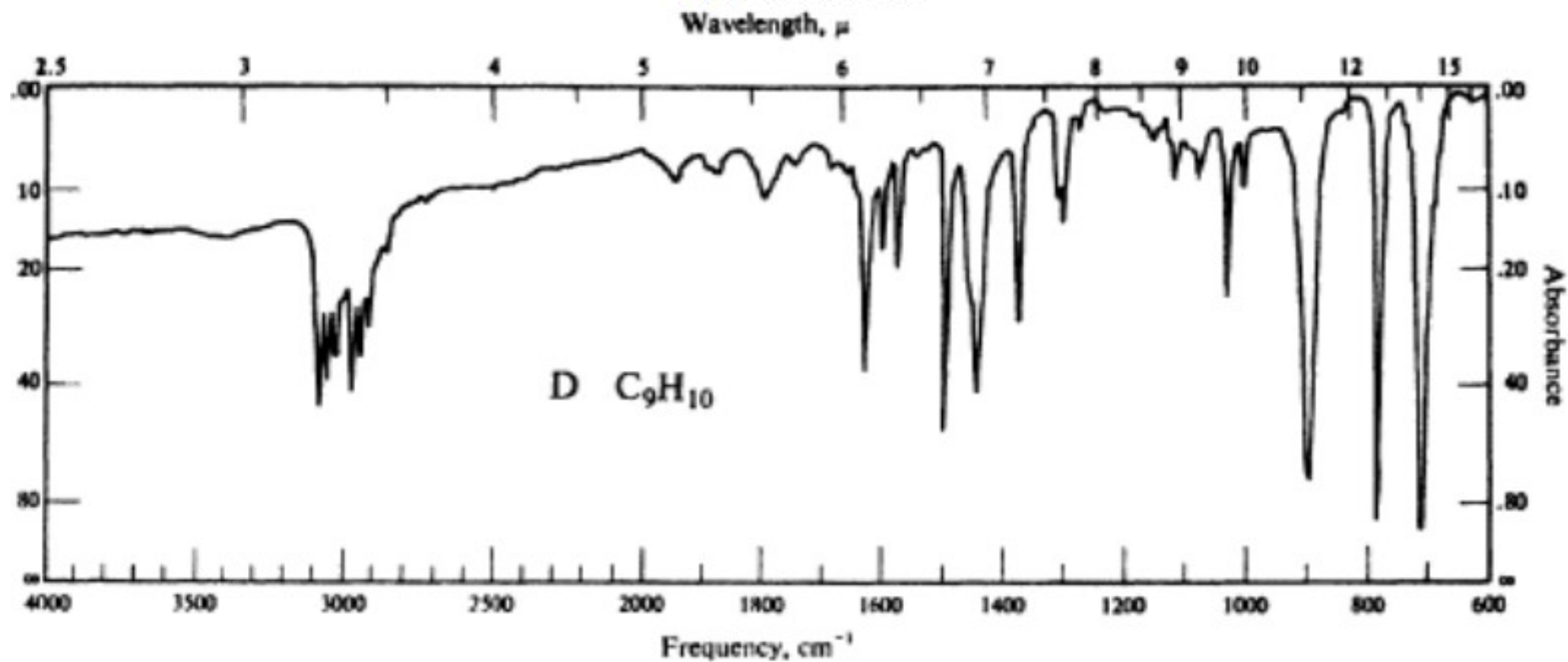
Presented by

Course Instructor: Dr Bhar Saha
Dept. of Science & Mathematics
IIITG, Guwahati

Example: IR Spectrum of compound



α -methylstyrene



Course Code: SC202

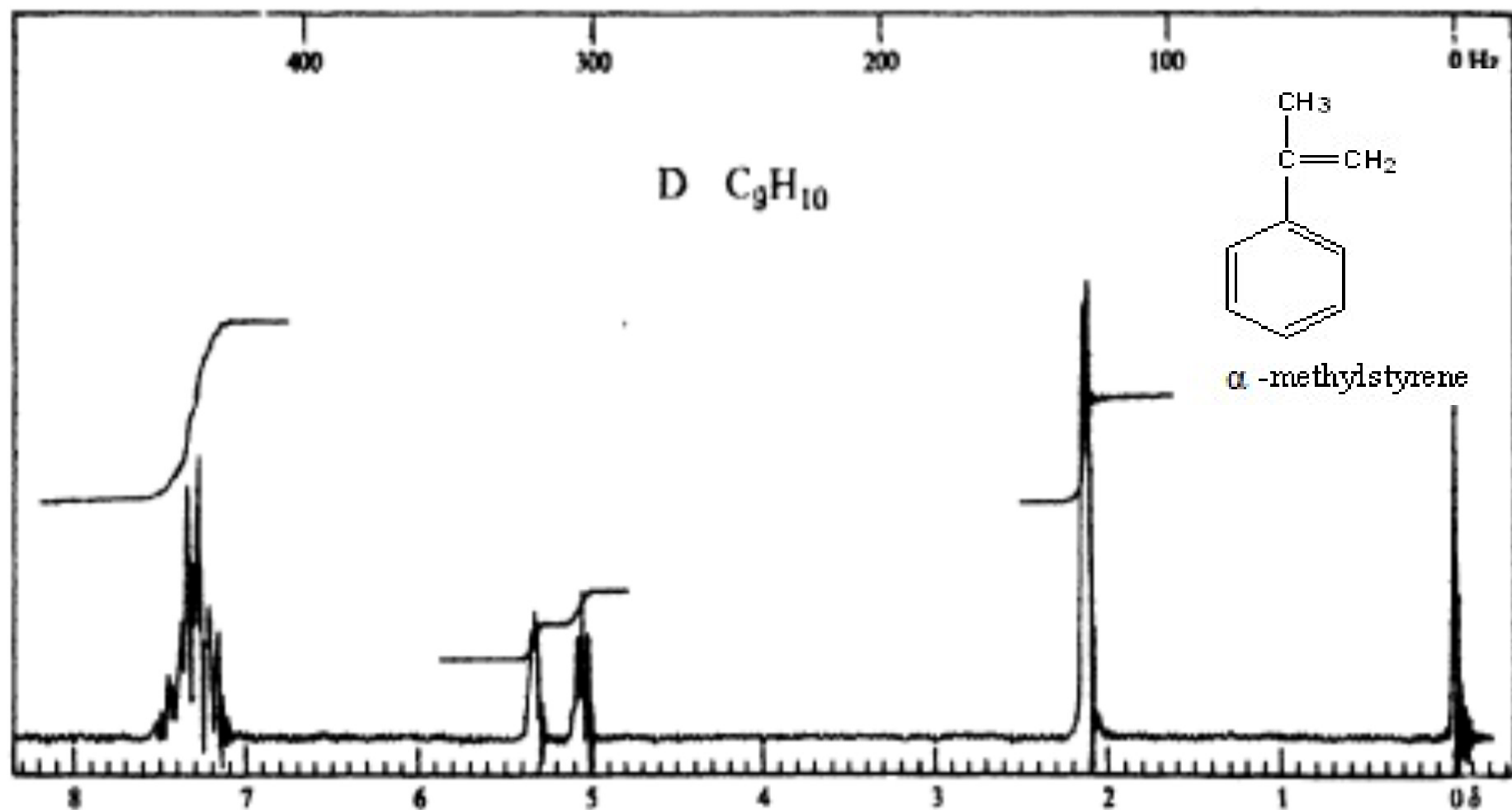
Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

IITG, Guwahati

NMR Spectrum of compound



Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha

Dept. of Science & Mathematics

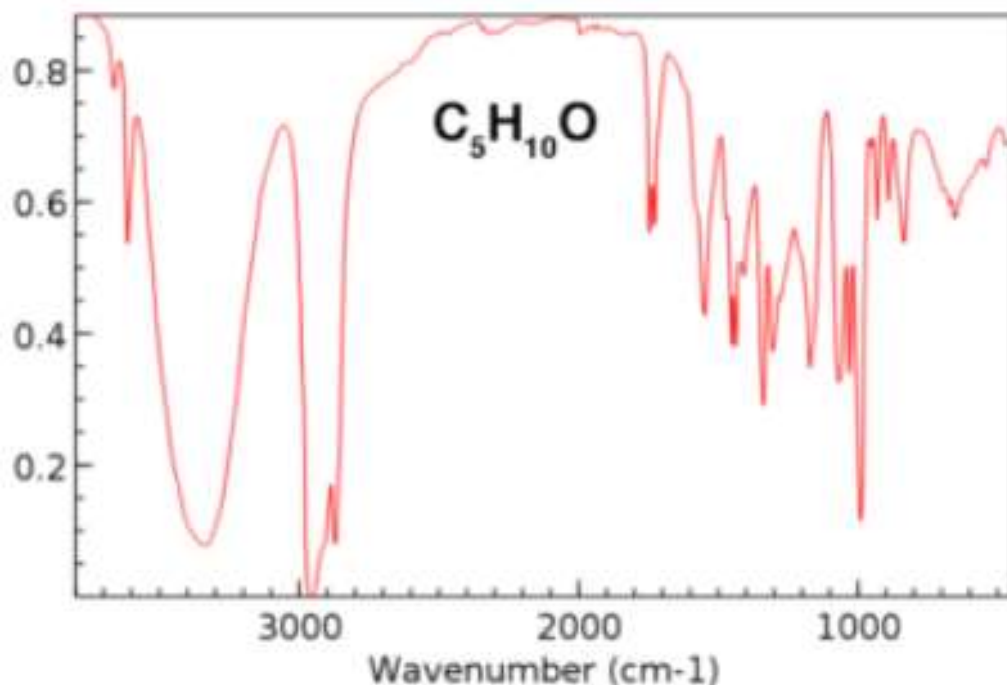
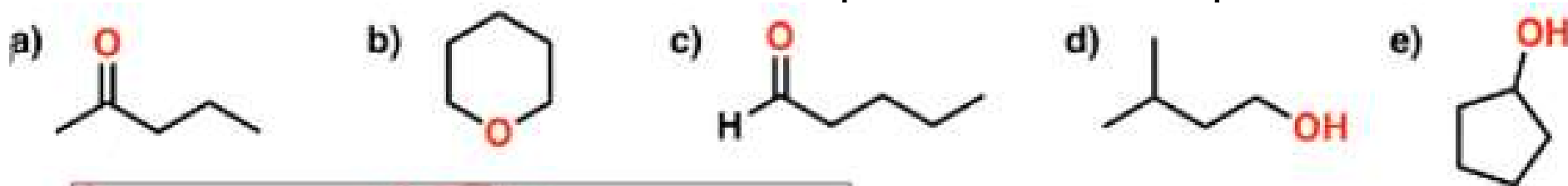
IIITG, Guwahati

Problems for practice:

1. Suggest the structure of the following compound by interpreting the given spectroscopic data:

IR: ν_{max} (cm^{-1}): 1745; ^1H NMR: δ (ppm): 1.20 (6H, d)
1.40 (2H, s)
1.50 (1H, septet)
3.67 (3H, s)

2. Which of these molecules best corresponds to the IR spectrum below:



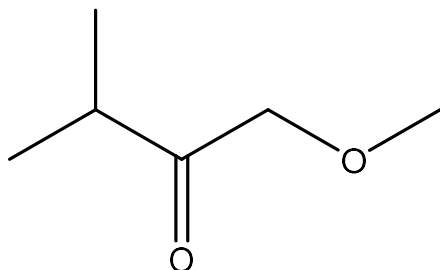
Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha
Dept. of Science & Mathematics
IIITG, Guwahati

Answers:

1.



2. *
- You're given the molecular formula, which is $C_5H_{10}O$. This corresponds to an **index of hydrogen deficiency (IHD)** of 1, so either a double bond or ring is present in the molecule. This immediately rules out d) whose IHD is zero and thus has a molecular formula of $C_5H_{12}O$.
 - Looking at the spectrum we see a broad peak at 3300 cm^{-1} and no dominant peak around 1700 cm^{-1} (That peak halfway down around 1700 cm^{-1} ? It's too weak to be a $C=O$.)
 - That broad peak at 3300 tells us that we have an alcohol (OH group). The only option that makes sense is e) (cyclopentanol) since it has both an OH group and an IHD of 1. It can't be b) since that molecule lacks OH.
 - a) and c) are further ruled out by the absence of $C=O$; B is ruled out by the presence of the OH at 3300 .

HD: *how many multiple bonds and rings are present in the structure OR how many molecules of H_2 need to be added to a structure in order to obtain the corresponding saturated, acyclic species.*

If you have a molecular formula, $C_cH_hN_nO_oX_x$, equation for IHD:

$$IHD = 0.5 * [2c + 2 - h - x + n]$$

Course Code: SC202

Presented by

Course Instructor: Dr Bhar Saha
Dept. of Science & Mathematics
IIITG, Guwahati

Alternatively,

E.F. [Empirical Formula] for

Alkanes/ subs. Cycloalkane: C_nH_{2n+2}

Alkenes/ Cycloalkanes: C_nH_{2n}

Alkynes/ Cycloalkenes: C_nH_{2n-2}

Course Code: SC202

Presented by

Course Instructor: **Dr Bhar Saha**

Dept. of Science & Mathematics

IIITG, Guwahati