

Topic 12 – Spectroscopy

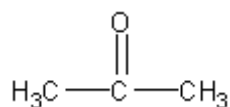
Revision Notes

1) Infrared spectroscopy

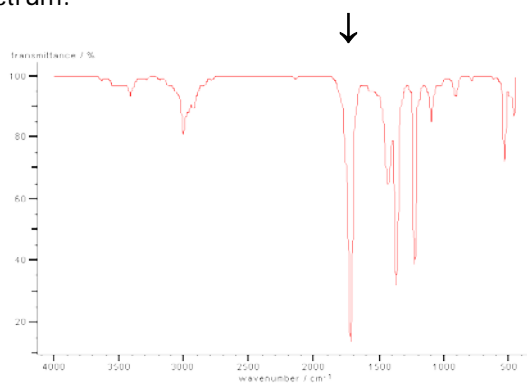
- The bonds in organic molecules absorb certain frequencies of infrared radiation.
- The frequencies that are absorbed can be used to identify the presence of certain bonds.
- The absorptions you need to know are:

- C=O 1680 - 1750 cm⁻¹
- OH in alcohols 3230 - 3550 cm⁻¹
- OH in carboxylic acids 2500 - 3300 cm⁻¹ (broad peak)
- C-O 1000 - 1300 cm⁻¹

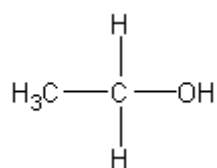
Example 1 – propanone



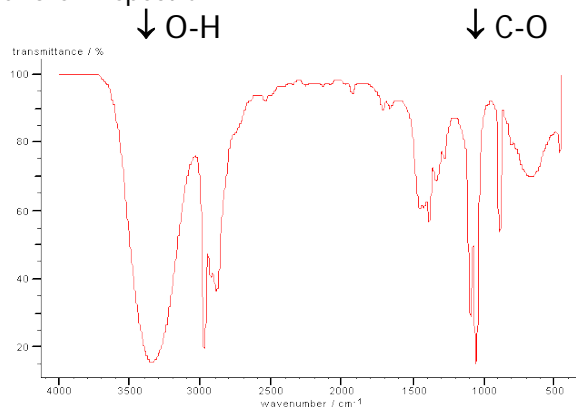
Of the absorptions mentioned above, only the C=O peak will be present in propanone's IR spectrum:



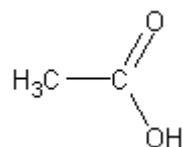
Example 2 – ethanol



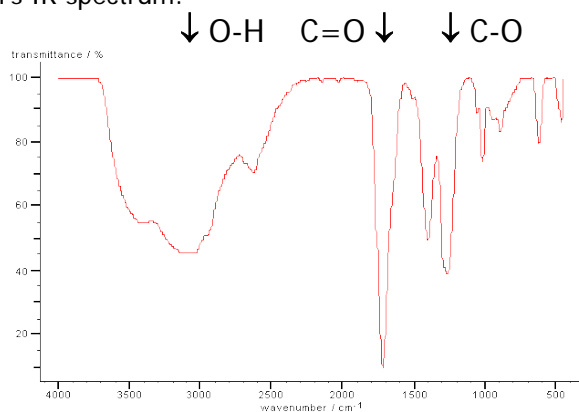
Of the absorptions mentioned above, the -OH in alcohols and the C-O peaks will be present in ethanol's IR spectrum:



Example 3 – Ethanoic acid



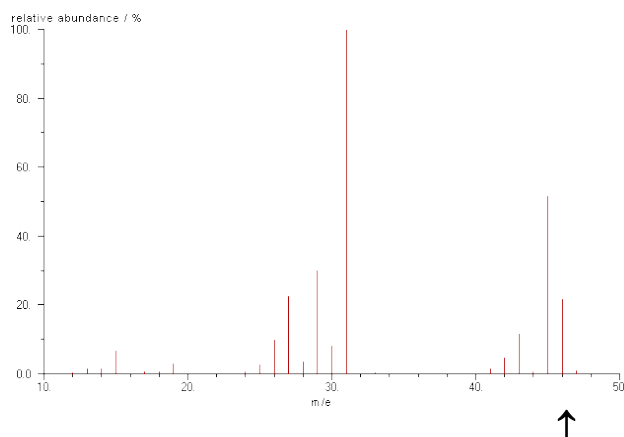
Of the peaks mentioned above, the –OH in acids, the C=O and the C-O peaks will be present in ethanol's IR spectrum:



2) Mass spectrometry

In a mass spectrum for a compound, the peak furthest to the right (or highest m/z) is called the molecular ion peak and it gives the molar mass of the compound.

Example – ethanol



The molar mass of ethanol is 46. The molecular ion peak is indicated by the arrow.

3) NMR spectroscopy

a) Introduction

- NMR stands for nuclear magnetic resonance
- It can be used on the nuclei of atoms that contain an odd number of protons and neutrons e.g. ^{13}C and ^1H
- NMR involves the interaction of materials with low-energy radio waves

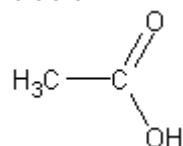
- NMR is the same technology as that use in magnetic resonance imaging (MRI) to obtain diagnostic information about internal structures in body scanners
- In NMR, the position of each peak is measured from the peak produced by a standard substance called tetramethylsilane, TMS, which is $(\text{CH}_3)_4\text{Si}$
- Solvents for running NMR spectra must not contain H atoms so deuterated solvents, such as CDCl_3 , are used

b) Proton NMR

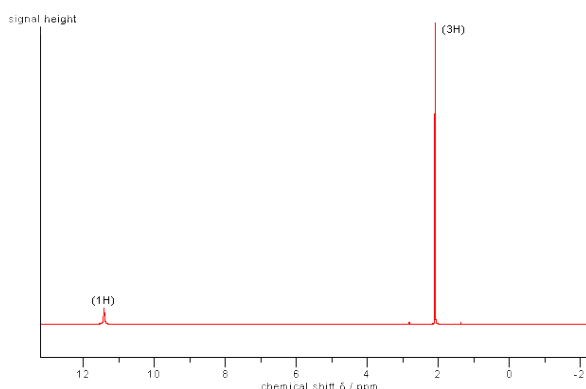
The peaks in a proton NMR spectrum give the following information about the hydrogen nuclei in an organic compound:

- The number of peaks shows the number of different types of proton
- The ratio of the areas under the peaks gives the number of protons of each type
- The distance along the axis (chemical shift) shows the environment of each type of proton (see data sheet)
- The splitting pattern shows how many neighbouring protons there are
- D_2O can be used to identify OH groups

Example 1 – Ethanoic acid



- Two different types of H so two peaks
- Size of peaks in ratio 3:1
- $-\text{COCH}_3$ at δ 2.0-2.9 and COOH at δ 11.0-11.7
- No splitting as H's not on adjacent atoms

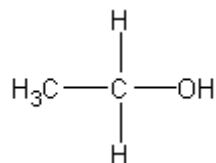


Peak splitting

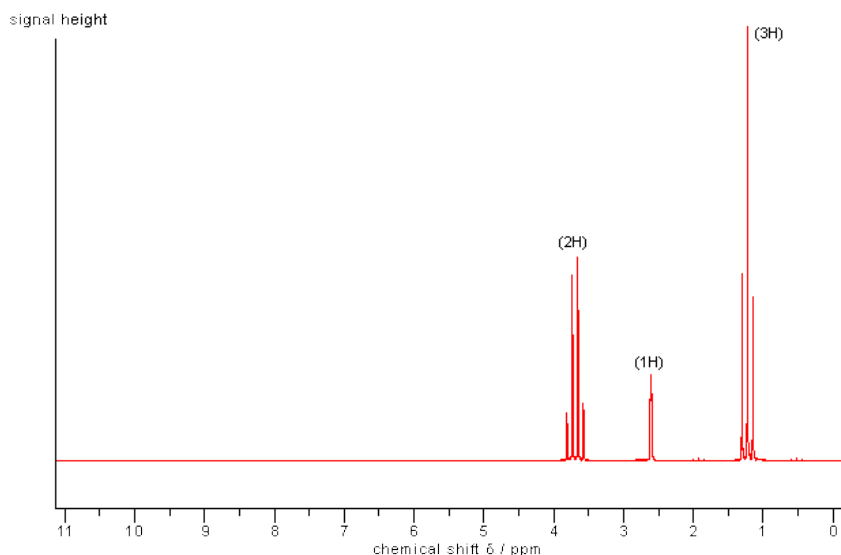
- 1) A peak will be split if there are H's on the next C or O.
- 2) Splitting follows the 'n+1' rule
- 3) 1H splits an adjacent peak into two (a doublet), 2H's split an adjacent peak into three (a triplet) and 3H's split an adjacent peak into four (a quartet)
- 4) If splitting occurs from both sides a more complicated pattern is produced (a multiplet)

- 5) In a doublet, the ratio of the areas under the peaks is 1:1. In a triplet, the ratio of the areas under the peaks is 1:2:1. In a quartet, the ratio of the areas under the peaks is 1:3:3:1

Example 2 – Ethanol



- Three different types of H so three peaks
- Size of peaks in ratio 3:2:1
- R-CH₃ at δ 0.7-1.6, -OCH₂R at δ 3.3-4.3 and R-OH at δ 1.0-5.5
- CH₃ peak split into triplet by 2Hs on next C
- CH₂ split into quartet by 3Hs on next C
- The OH peak is not split and does not split other peaks. Technically, this H is decoupled by fast proton exchange



Use of D₂O with O–H and N–H groups

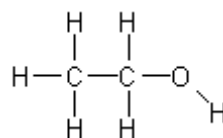
- Deuterium is an isotope of hydrogen that does not produce an NMR peak
- If an alcohol, carboxylic acid or amine is shaken with D₂O, the H of the O–H or N–H group is replaced by D and the peak disappears from the spectrum

b) Carbon-13 NMR

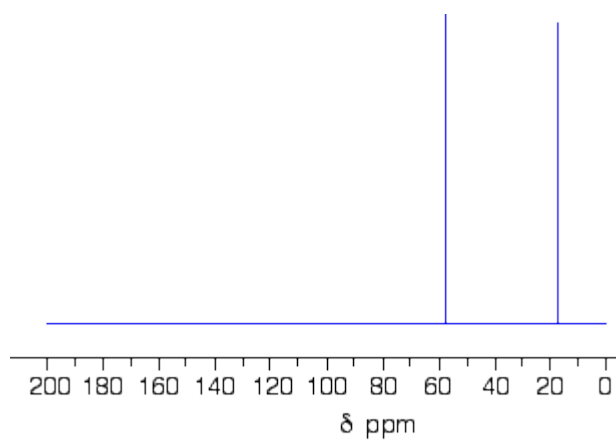
The peaks in a ¹³C NMR spectrum give the following information about the carbon nuclei in an organic compound:

- The number of peaks shows the number of different types of C
- The distance along the axis (chemical shift) shows the environment of each type of C (see data sheet)

Example 1 – Ethanol



- Two different types of C so two peaks
- **C-O** at δ 50-70 and **C-C** at δ 5-55



Source: <http://www.chemguide.co.uk/analysis/nmr/interpretc13.html>

Topic 13 – Chromatography

Revision Notes

1) Introduction

- Chromatography is an analytical technique for separating mixtures
- It separates the components of the mixture between a mobile phase and a stationary phase
- The mobile phase can be a liquid or a gas
- In thin-layer chromatography, TLC, the stationary phase is a solid In gas chromatography, GC, the stationary phase is either a liquid or solid on a solid support
- A solid stationary phase separates by adsorption
- A liquid stationary phase separates by relative solubility

1) Paper Chromatography

- Stationary phase is water adsorbed on paper
- Mobile phase is liquid solvent
- Separates by partition (relative solubility of solute between mobile and stationary phases)
- R_f values calculated from distance travelled by sample/distance travelled by solvent
- R_f values differ from solvent to solvent
- Components of mixture identified by comparing with known reference samples or using R_f values
- In two-way chromatography, the chromatogram is run in one solvent then rotated through 90° and run in a different solvent
- This is more effective than one-way chromatography because it is highly unlikely that 2 solvents have the same R_f values
- In the separation of amino acids, the spots are invisible and have to be shown up by adding ninhydrin or iodine (or by observing under u/v light)

2) Thin-layer Chromatography

- In TLC, the stationary phase is a thin layer of solid silica, SiO_2 , or alumina, Al_2O_3 coated onto a plate
- Stationary phase is silica/alumina
- Mobile phase is solvent
- A dry TLC plate separates by adsorption (solute molecules adsorbed onto stationary phase, rate of travel depends on solubility in mobile phase and strength of adsorption)
- A wet TLC plate separates by partition (water molecules adsorbed onto stationary phase act partially as stationary phase, solute molecules partitioned between stationary water phase and solvent)
- R_f values calculated from distance travelled by sample/distance travelled by solvent
- R_f values differ from solvent to solvent
- Components of mixture identified by comparing with known reference samples or using R_f values

3) Gas Chromatography, GC

- This is also called gas-liquid chromatography or GLC
- Mobile phase is a carrier gas e.g. nitrogen (which is inert)
- Sample mixture is injected into machine
- The retention time is the characteristic time it takes for a particular substance to pass through the system under set conditions
- The output is a graph of detector response (y-axis) against retention time (x-axis). This provides a spectrum of peaks for a sample representing the compounds present in a sample eluting from the column at different times
- Components of the mixture are identified by their retention times
- The use of retention times to identify substances is limited by the facts that similar compounds often have similar retention times and that unknown compounds have no reference retention times for comparison

4) GC-MS

- Gas chromatography can be combined with mass spectrometry
- Components separated by GC are directed into a mass spectrometer
- A computer can analyse a component's mass spectrum or compare it with a database for positive identification
- GC-MS is used in forensics, environmental analysis, airport security and space probes
- GC-MS is a far more powerful analytical technique than gas chromatography on its own