

# Measurement and Data Processing. DP Chemistry HL2/SL2





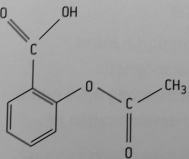
## Degree of Unsaturation or Index of Hydrogen Deficiency:

This technique can be used to determine the number of rings or multiple bonds ( $\pi$ ) in a molecule.

- A double bond is counted as one degree of unsaturation
- A triple bond is counted as two degrees of unsaturation
- A ring is counted as one degree of unsaturation
- An aromatic ring is counted as four degrees of unsaturation

The IHD can be determined two ways:

- From the structure
- From the molecular formula

Compound	Structure	Number of rings, double bonds, and triple bonds	IHD
benzene		<ul style="list-style-type: none"><li>• one ring</li><li>• three double bonds (in Kekulé structure)</li></ul>	4
cyclobutane		<ul style="list-style-type: none"><li>• one ring</li></ul>	1
cyclohexane (chair conformation)		<ul style="list-style-type: none"><li>• one ring</li></ul>	1
cyclopentadiene		<ul style="list-style-type: none"><li>• one ring</li><li>• two double bonds</li></ul>	3
2-acetoxybenzoic acid (aspirin)		<ul style="list-style-type: none"><li>• one ring</li><li>• five double bonds</li></ul>	6
ethyne	$\text{H} - \text{C} \equiv \text{C} - \text{H}$	<ul style="list-style-type: none"><li>• one triple bond</li></ul>	2

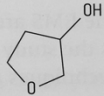
In order to deduce the IHD for the generic molecular formula  $\text{C}_c\text{H}_h\text{N}_n\text{O}_o\text{X}_x$ , where X is a halogen atom (F, Cl, Br, or I), we can use the following expression:

$$\text{IHD} = (0.5)(2c + 2 - h - x + n)$$

For  $\text{C}_4\text{H}_8\text{O}_2$ :  $c = 4$   $h = 8$   $n = 0$   $o = 2$   $x = 0$

$$\text{IHD} = (0.5)(8 + 2 - 8 - 0 + 0) = 1$$

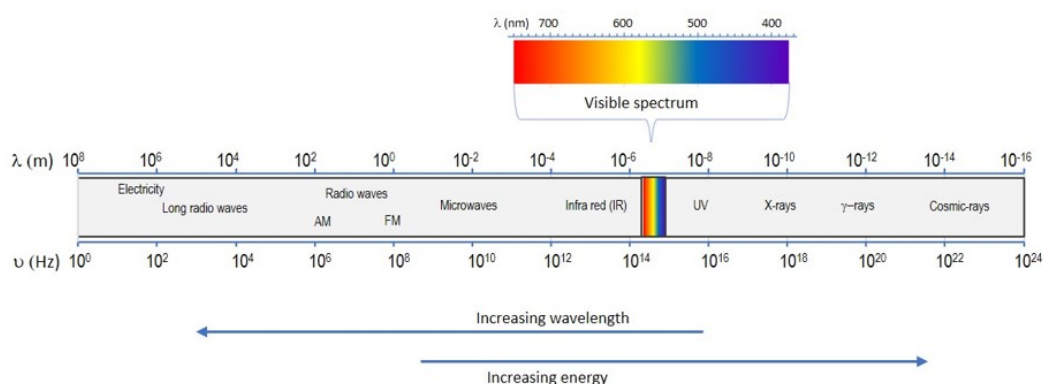
Therefore the molecule contains either one double bond or one ring. There are several isomers of  $\text{C}_4\text{H}_8\text{O}_2$ . There are three illustrations on the following page.

Isomer of $C_4H_8O_2$	Structure	IHD
methyl propionate	$H_3C - O - \overset{\overset{O}{\parallel}}{C} - CH_2CH_3$	1
ethyl ethanoate	$H_3C - \overset{\overset{O}{\parallel}}{C} - O - CH_2CH_3$	1
tetrahydro-3-furanol		1

Let us take four compounds with different molecular formulas and deduce their IHD using the formula:

Molecular formula	IHD
$C_{17}H_{21}NO_4$ (cocaine)	8
$C_{27}H_{46}O$ (cholesterol)	5
$C_6H_7N$ (aniline)	4
$C_{15}H_{10}ClN_3O_3$ (clonazepam)	12

## Electromagnetic Spectrum (EMS):



The energy of the E/M spectrum,  $E$ , is directly related to the frequency,  $\nu$ , of the radiation as described by Planck's equation:

Where  $h = 6.63 \times 10^{-34} \text{ Js}$

$$E = h\nu = \frac{hc}{\lambda}$$

$E$  = energy of radiation (J)

$\nu$  = frequency of radiation (Hz or  $s^{-1}$ )

$\lambda$  = wavelength (m)

Various types of E/M radiation will influence chemicals in different ways:

- **X-rays** – very high ionizing energy that will cause electrons to be removed from the inner energy levels of atoms. Diffraction patterns lead to bond distances and bond angles. This is the basis for x-ray crystallography.
- **Visible and Ultraviolet Light** – this radiation gives rise to electronic transitions and this provides clues as to what the energies of the transitions are. This is the basis of UV-vis spectroscopy.

- **Infrared Radiation**- This heat radiation causes certain bonds in a molecule to vibrate (stretch and bend) giving clues as to what functional groups are present. This is the basis of IR spectroscopy.
- **Microwaves**- cause molecular rotations and provide information on bond length.
- **Radio waves**- can cause nuclear transitions in strong magnetic fields because radio waves can be absorbed by certain nuclei, which causes their spin states to change. NMR, Nuclear Magnetic Resonance Spectroscopy is a technique which follows this premise.

The three main forms of spectroscopy that are used to identify organic compounds are:

- **Infrared Spectroscopy (IR)**
- **Proton Nuclear Magnetic Resonance Spectroscopy ( $^1\text{H}$  NMR)**
- **Mass Spectroscopy (MS)**

### Infrared Spectroscopy:

IR is not energetic enough to cause electronic transitions, but it can be used to cause molecules to vibrate. The vibrational transitions correspond to different functional groups. The Spring Model is used as it considers each covalent bond as a spring. These bonds can be shrunk, stretched, bent and twisted. This can be described by Hooke's Law:

$$F \propto x \quad \text{or} \quad F = -kx$$

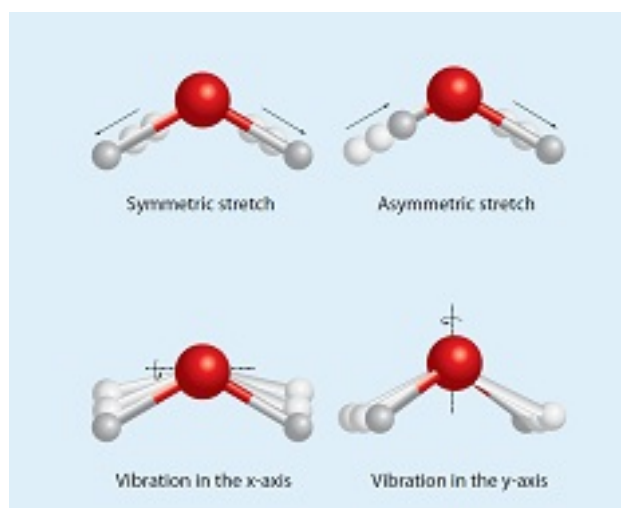
Expansion of the length of a spring ( $x$ ) from its equilibrium will be directly proportional to the force ( $F$ ) caused by the load applied to the spring. The frequency ( $\nu$ ) of the vibration can be related to the mass ( $m$ ) via the equation:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

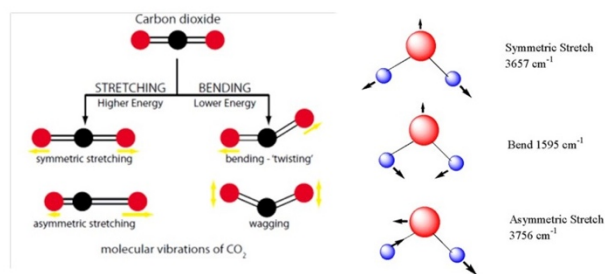
As you can see, lighter atoms vibrate at higher frequencies

and heavier atoms vibrate at lower frequencies. As you can imagine multiple bonds require more energy to stretch them. For HCl there is only one type of stretching. Look at the following table to see how bond strength relates to wavenumber:

Molecule	Bond Enthalpy / $\text{kJmol}^{-1}$	Wavenumber / $\text{cm}^{-1}$
H-Cl	431	2886
H-Br	366	2559
H-I	298	2230



### How does the greenhouse effect work?



Molecules absorb infrared energy through increased vibrations that change the molecule's dipole moment

Likewise, we can observe different types of absorption when molecules bend or stretch in symmetrical or asymmetrical ways.

H<sub>2</sub>O can stretch in three different ways with three different spectra:

- Asymmetric Stretch (3652 cm<sup>-1</sup>)
- Symmetric Stretch (3756 cm<sup>-1</sup>)
- Symmetric Bend (1595 cm<sup>-1</sup>)

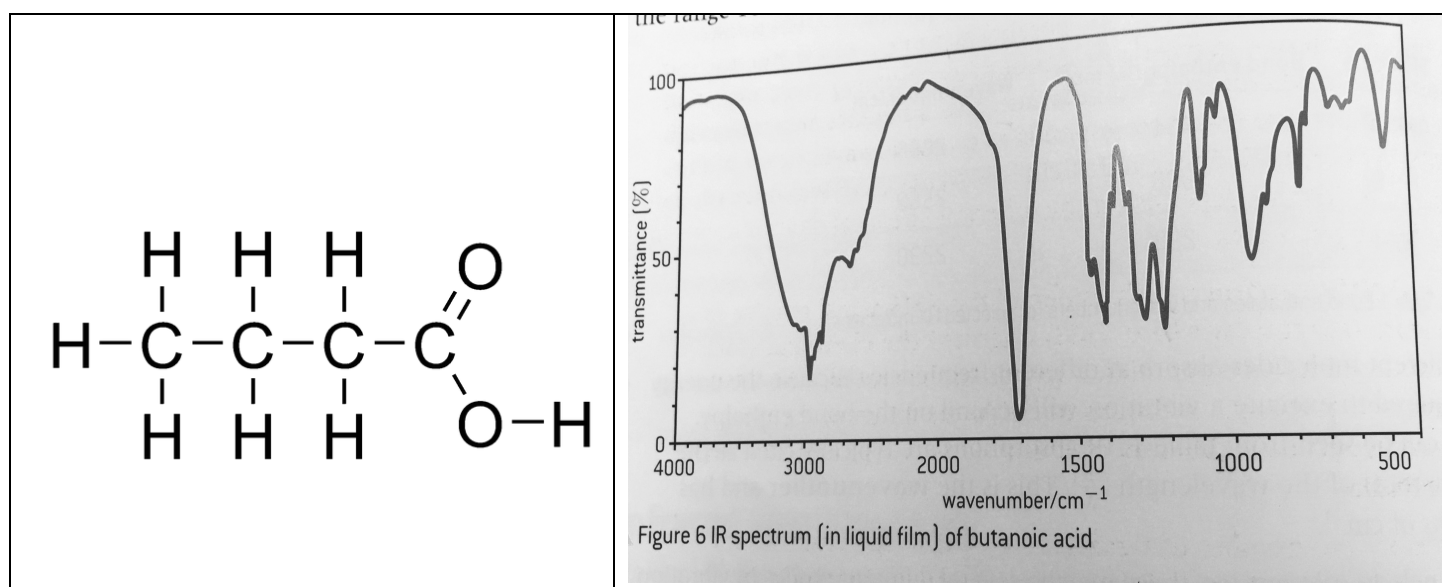
For a covalent bond to absorb IR radiation there needs to be a change in the molecular dipole moment.

Molecule	Polarity of Molecule	Absorption of IR Radiation
H-H	Non-polar	No (IR inactive)
O=O	Non-polar	No (IR inactive)
O=C=O	Non-polar	Symmetric stretch – NO (IR inactive)  Asymmetric stretch – YES (IR active @2349 cm <sup>-1</sup> )  Symmetric bend – Yes (IR active @ 667 cm <sup>-1</sup> )

The absorbance, A, of a sample can be related to the transmittance by the expression:

$$A = -\log_{10}T$$

An IR spectrum is a plot of % Transmittance, %T, vs the wavenumber in cm<sup>-1</sup>. %T ranges from 0 - 100%. IR spectra are useful in determining organic functional groups. The typical wavenumbers are provided in your data booklet.



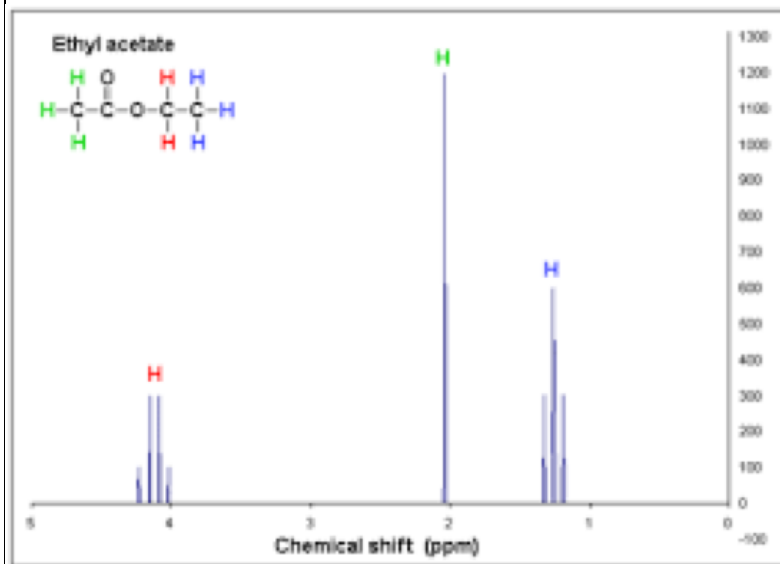
You will notice the following absorptions in Figure 6:

- There is a strong, broad peak from  $2500\text{--}3000\text{ cm}^{-1}$ , characteristic of an O-H bond.
- There is a strong peak in the range of  $1700\text{--}1750\text{ cm}^{-1}$ , characteristic of an C=O group.
- There is a peak from  $2850\text{--}3090\text{ cm}^{-1}$ , characteristic of the C-H bond.
- The range from  $300\text{--}1400\text{ cm}^{-1}$  represents complex vibrations, it is seen as the **fingerprint region**.

IR Spectroscopy is a supportive technique that mainly reveals organic functional groups and not the entire structure.

### **Proton Nuclear Magnetic Resonance ( $\text{H}^1$ NMR) Spectroscopy:**

This technique reveals information about the different chemical environments of hydrogen. This is a very important structural technique available to organic chemists. The nucleus of the hydrogen atom can exist in two different spin states (this is different than electron spin). When exposed to a powerful electromagnet, the nuclei can behave as tiny magnets. This will separate them by either aligning them with the magnetic field or against it. This results in two different energy levels. Nuclei aligning to the magnetic field are lower energy. Nuclei aligning against the magnetic field are higher energy. The difference between these two energy levels is  $\Delta E$ . Tetramethylsilane (TMS) is used as a calibration chemical. The position of the NMR signal for the unknown is measured relative to the TMS – this is known as the **chemical shift**. The chemical shift,  $\delta$ , is expressed as parts per million. The  $\delta$  assigned to TMS is assigned as zero. Your data booklet will show you different hydrogen environments and their representative shifts. The number of signals on a  $\text{H}^1$  NMR spectrum shows how many different chemical environments of hydrogen there are.



Type of proton	Chemical shift / ppm
	2.2–2.7
	1.8–3.1
	3.3–3.7
	3.7–4.8
	9.0–13.0*
	1.0–6.0*
	4.5–6.0
	4.0–12.0*
	6.9–9.0
	9.4–10.0

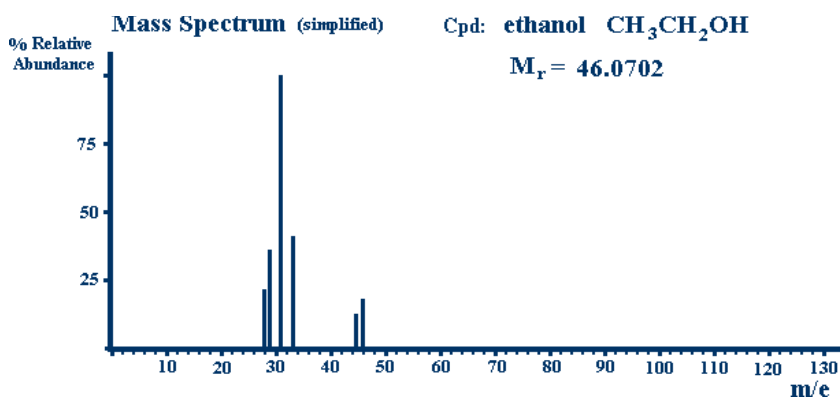
\*Signals from the hydrogen atoms in the —OH groups are very variable owing to hydrogen bonding.

### Mass Spectroscopy (MS):

In a mass spectrometer, extremely strong magnetic fields are applied to chemicals. Many of these chemicals will ionize and become a  $M^+$  ion.  $M + e' \rightarrow M^+ + 2e'$ . Due to the extreme magnetic fields some molecules will break up into smaller fragments that are ions. This **fragmentation pattern** provides insight into the organic functional groups present.

- $(M_r - 15)^+$  results from the loss of  $-CH_3$
- $(M_r - 17)^+$  results from the loss of  $-OH$
- $(M_r - 18)$  results from the loss of an  $H_2O$  molecule
- $(M_r - 28)^+$  results from the loss of  $CH_2=CH_2$  or  $C=O$
- $(M_r - 29)^+$  results from the loss of  $-CHO$  or  $-CH_2CH_3$
- $(M_r - 31)^+$  results from the loss of  $-OCH_3$
- $(M_r - 45)^+$  results from the loss of  $-COOH$

The following image is the mass spectra of ethanol.



The following image is the mass spectra of ethanoic acid

