

# INFRARED SPECTROSCOPY : ANALYTICAL TECHNIQUES

Analytical techniques are used to separate, purify, identify and analyse compounds

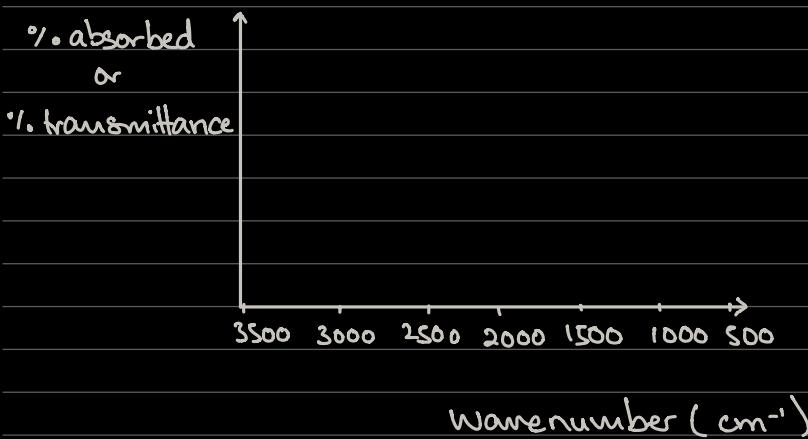
• IR spec is used to identify compounds

- An infrared spectrum is produced when a compound absorbs certain wavelengths of light in the infrared region of the electromagnetic spectrum and transmits other wavelengths.
- Some frequencies or wavelengths are absorbed, and a detector measures the % transmittance of light that passes through the compound
- An IR spectrum shows either % absorbance or % transmittance against wavenumbers

↳ inverse of wavelength,  $\frac{1}{\lambda}$

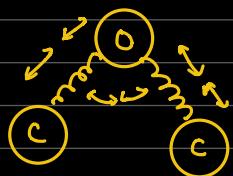
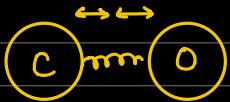
$$\text{Energy} \propto \frac{1}{\lambda}$$

- Higher energy absorbed  $\rightarrow$  shorter wavelengths absorbed
- Lower energy absorbed  $\rightarrow$  longer wavelengths absorbed



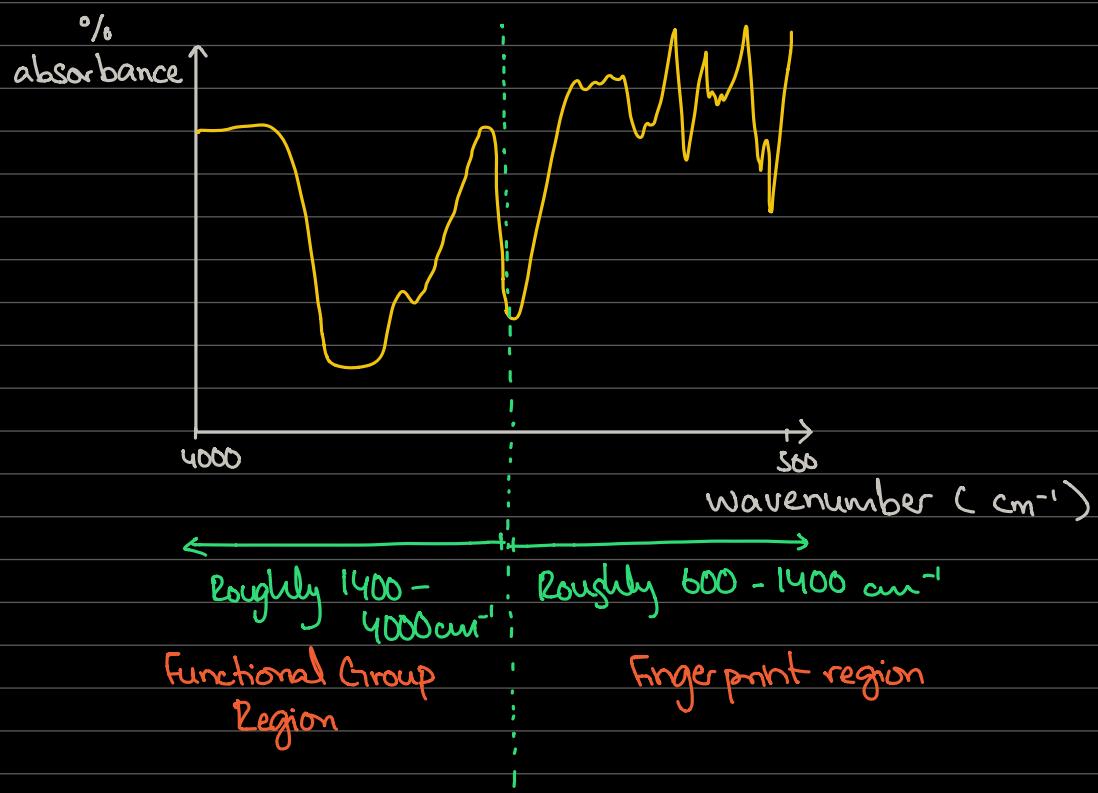
- The infrared energy absorbed by the compound is transferred to the bonds within the compound.
- The energies in infrared radiation correspond to the energies involved in bond vibration

Bond Vibrations  
Bond Stretching      Bond Bending



- The nuclei of atoms can vibrate backwards and/or forwards around an average position
- The energy involved in this vibration depends on the length of the bond and the mass of the bond
- This means that different bonds will vibrate in a different way involving different amounts of energy
- An exact amount of energy can make the bond vibrate into a higher state and this amount of energy varies from bond to bond

### IR SPECTRUM



- The more useful information is provided in the functional group region as it identifies the functional group(s) present in the molecule.
- Compounds that are polar are "IR active" and show up as peaks in the functional group region
- The fingerprint region is more complex and is unique for every compound

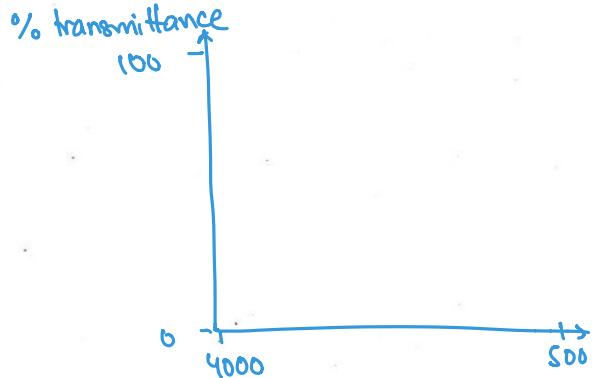
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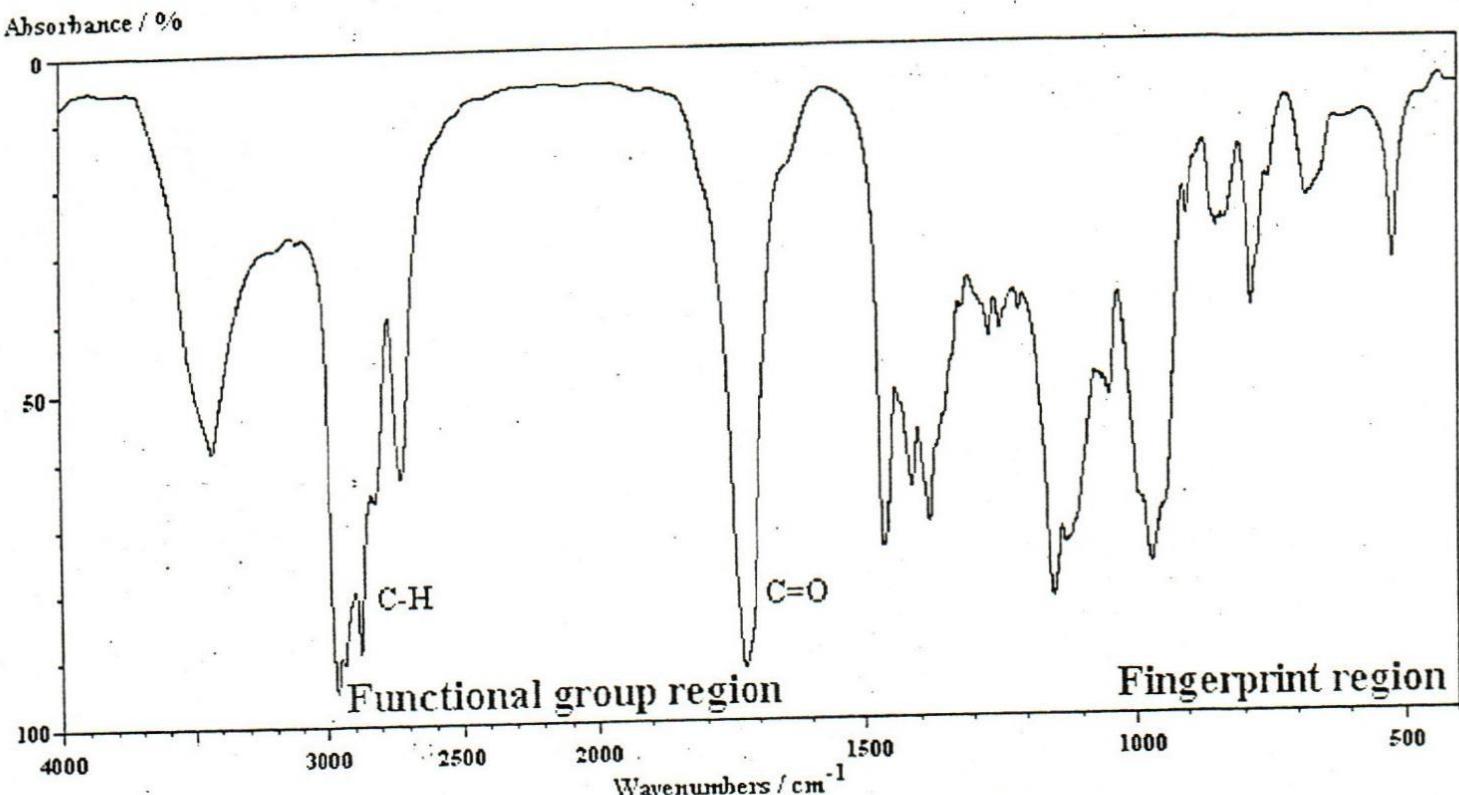
**Infra Red Spectroscopy**

Both are valid  
IR spectrums



↳ This is the one that's  
more frequently given in questions



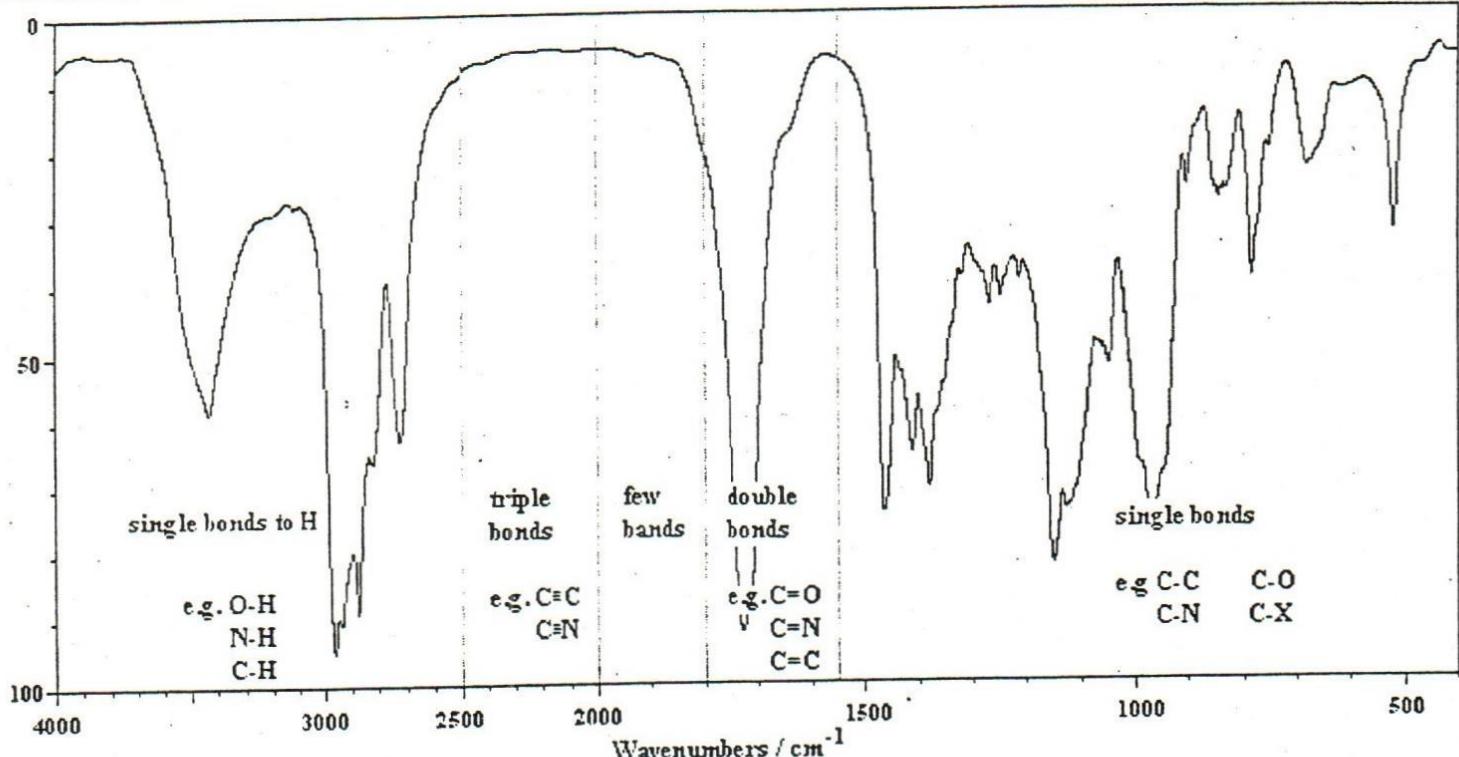


- Most of the information that is used to interpret an IR spectrum is obtained from the ***functional group region***.
- In practice, it is the polar covalent bonds than are IR "active" and whose excitation can be observed in an IR spectrum.
- In organic molecules these polar covalent bonds represent the ***functional groups***.
- Hence, *the most useful information obtained from an IR spectrum is what functional groups are present within the molecule* (NMR spectroscopy typically gives the hydrocarbon fragments).
- Remember that some functional groups can be "viewed" as combinations of different bond types. For example, an ester,  $\text{CO}_2\text{R}$  contains both  $\text{C}=\text{O}$  and  $\text{C}-\text{O}$  bonds, and both are typically seen in an IR spectrum of an ester.
- In the ***fingerprint region***, the spectra tend to be more complex and much harder to assign.

### MOST IMPORTANT THING TO REMEMBER.....

When analysing an IR spectrum *avoid the temptation to try to assign every peak*.  
 The ***fingerprint region***, however, can be useful for helping to confirm a structure by direct comparison with a known spectra.

Absorbance / %



## Infra-Red (IR) Spectroscopy

Important absorptions:

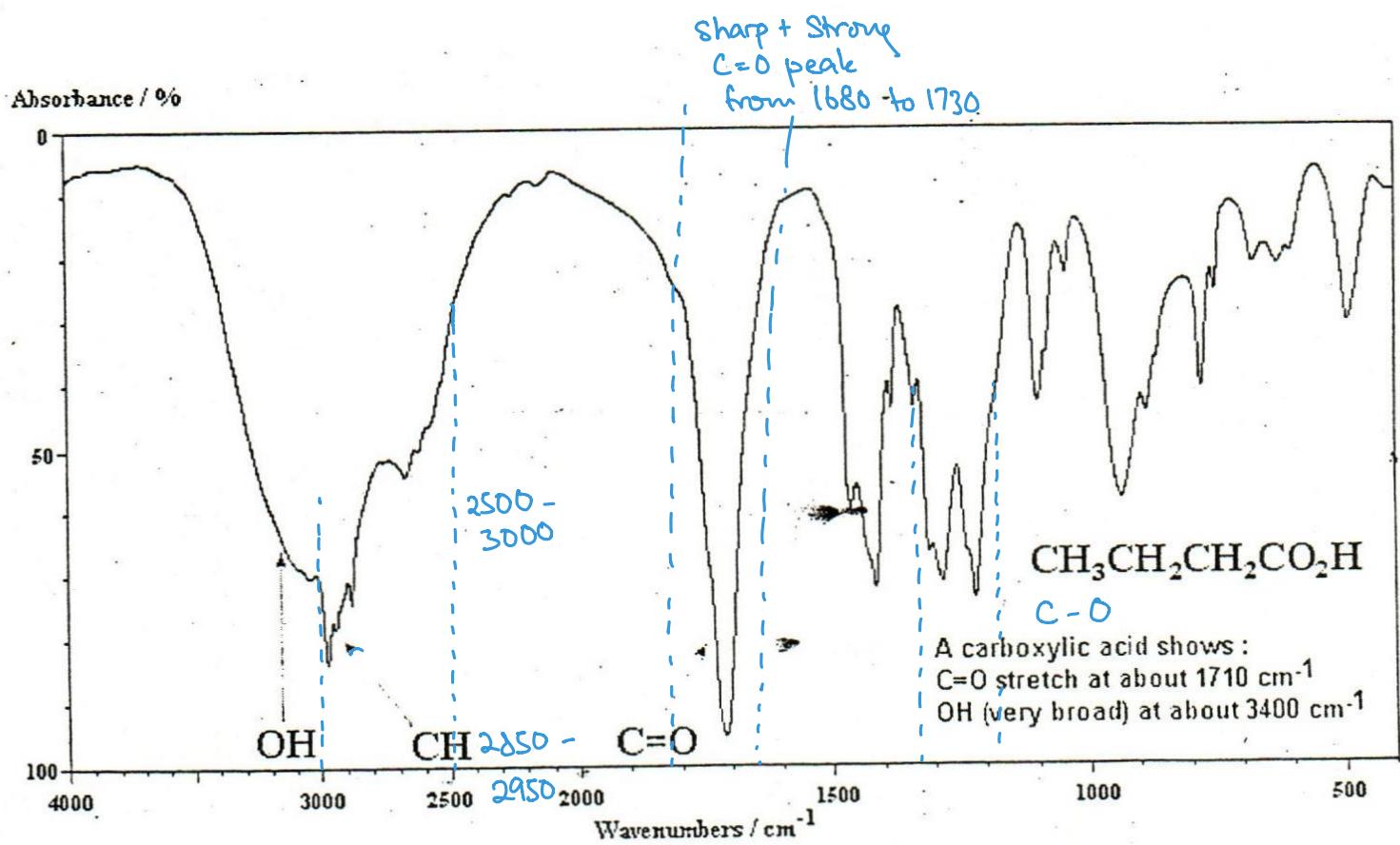
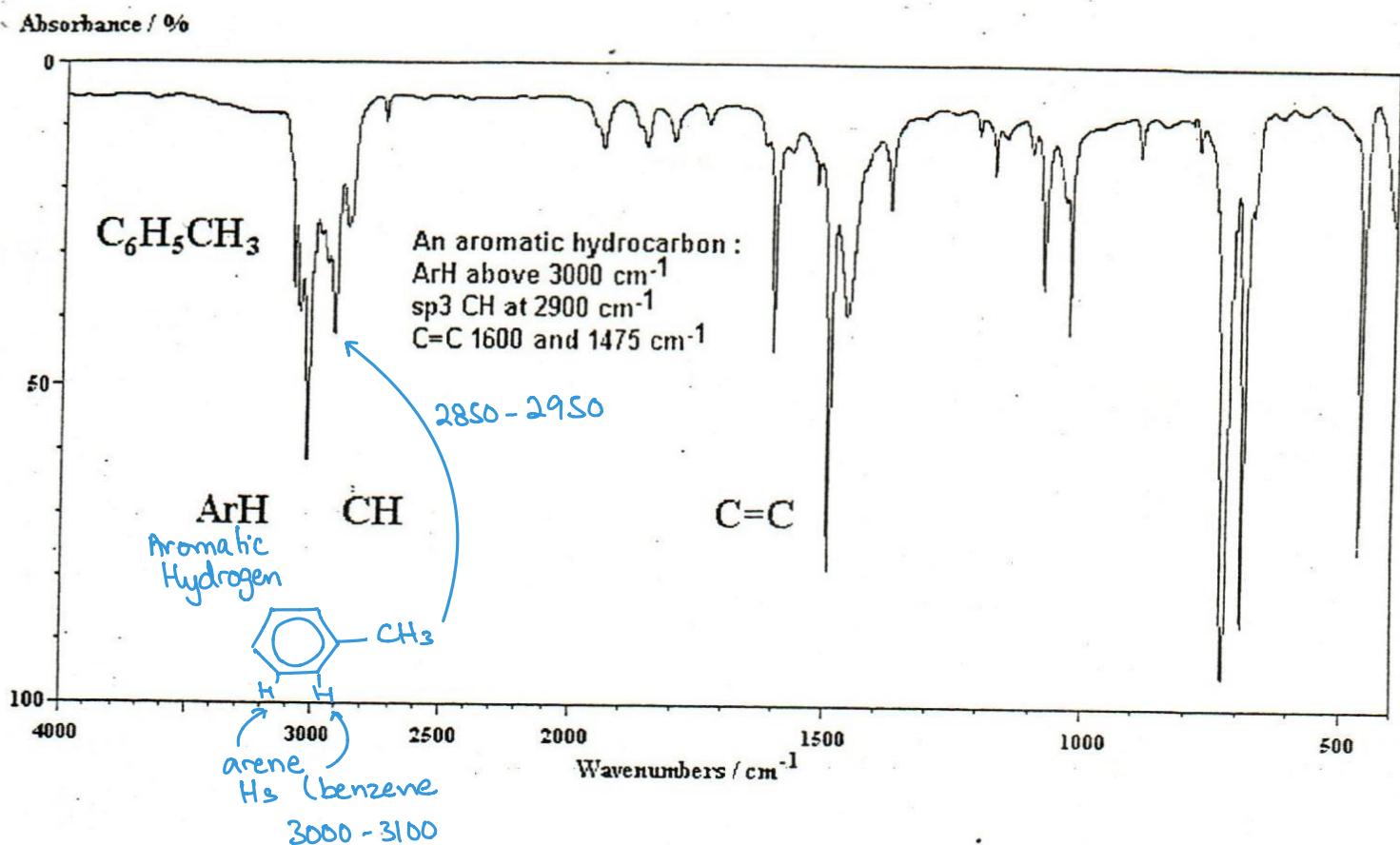
The more important absorptions that you should probably learn to recognize, in order of importance are:

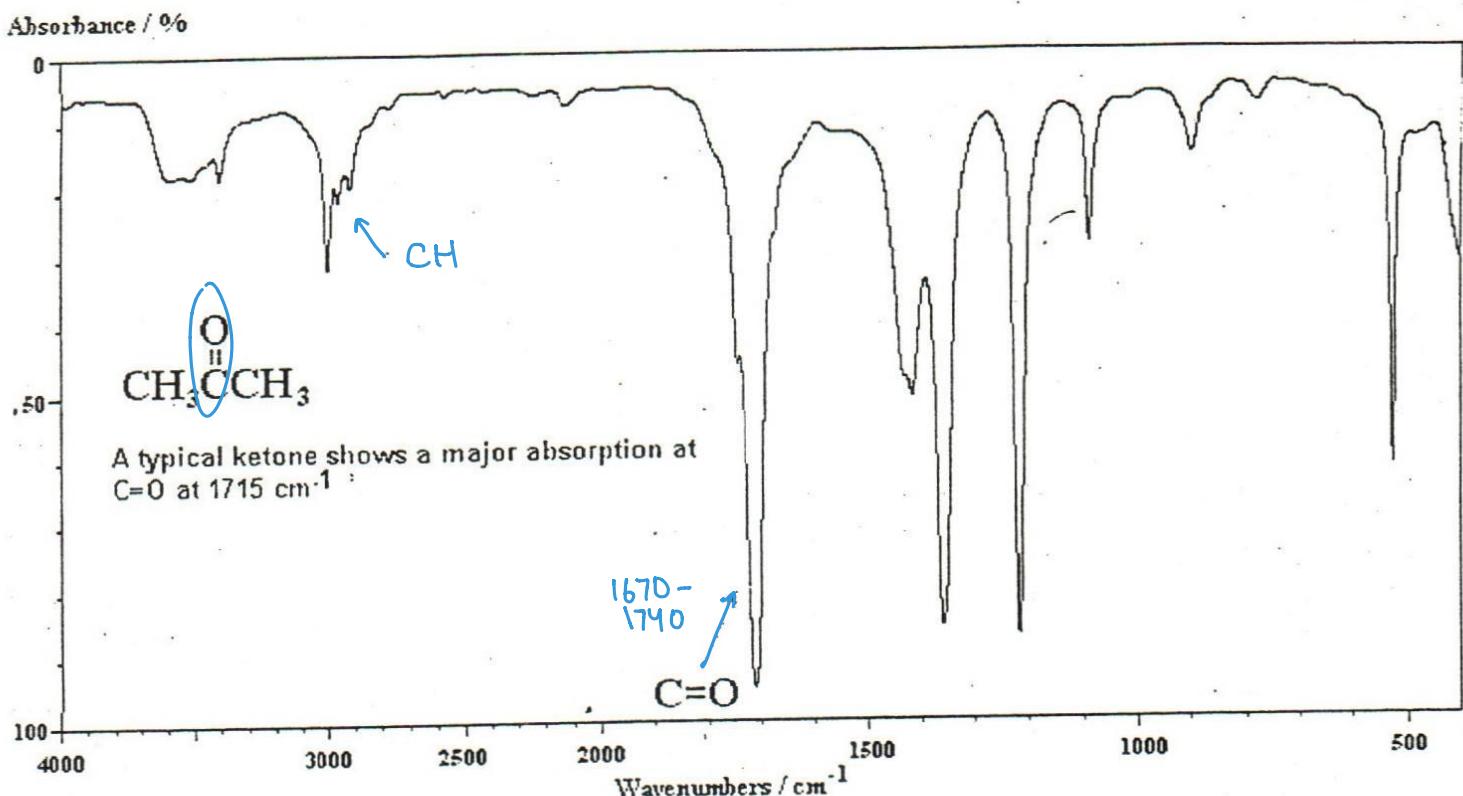
| Bond  | Base Value | Strength / Shape         | Comments  |
|-------|------------|--------------------------|---|
| 1 C=O | 1715       | s, "finger"              | Exact position depends on type of carbonyl  |
| 2 O-H | 3600       | s, brd                   | Broad due to H bonding  |
| 3 N-H | 3500       | m                        | Can tell primary from secondary   |
| 4 C-O | 1100       | s                        | Also check for OH and C=O   |
| 5 C=C | 1650       | w alkene<br>m-s aromatic | Alkene w due to low polarity<br>Aromatic usually in pairs                                   |
| 6 C≡C | 2150       | w, sharp                 | Most obvious in terminal alkynes  |
| 7 C-H | 3000       | s                        | As hybridisation of C changes sp <sup>3</sup> -sp <sup>2</sup> -sp, the frequency increases |
| 8 C≡N | 2250       | m, sharp                 | Characteristic since little else around it  |

If you know these, then you can identify most of the functional groups of interest. Note that it is rarely useful to look for C-C since the large majority organic molecules will have them.

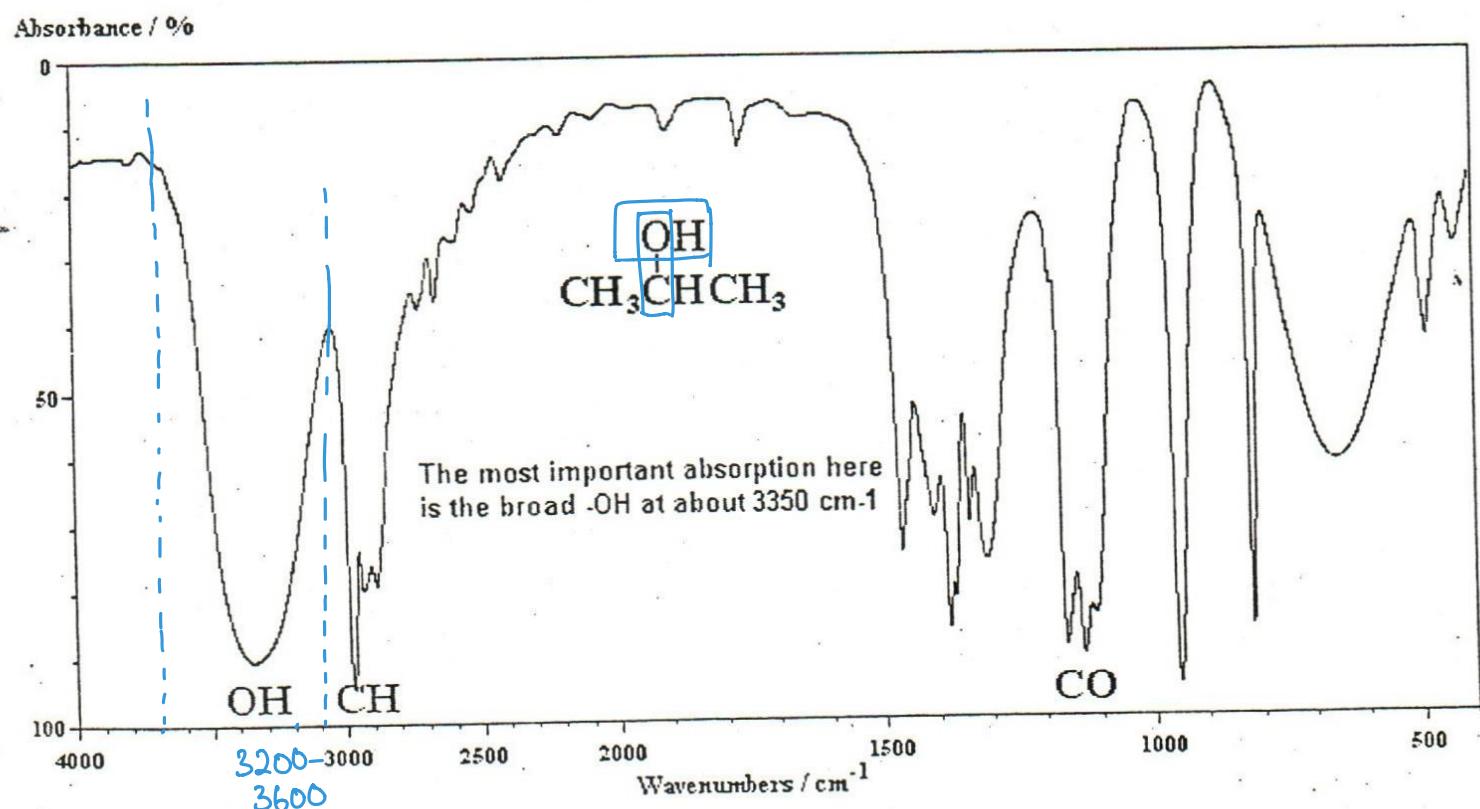
You should also be aware that the exact substitution pattern of a particular bond causes shifts in the position of the absorption and, therefore, ranges of values are typically given in most tables.

It is possible to rationalize the shifts of absorbances based on electronic effects due to proximal groups,

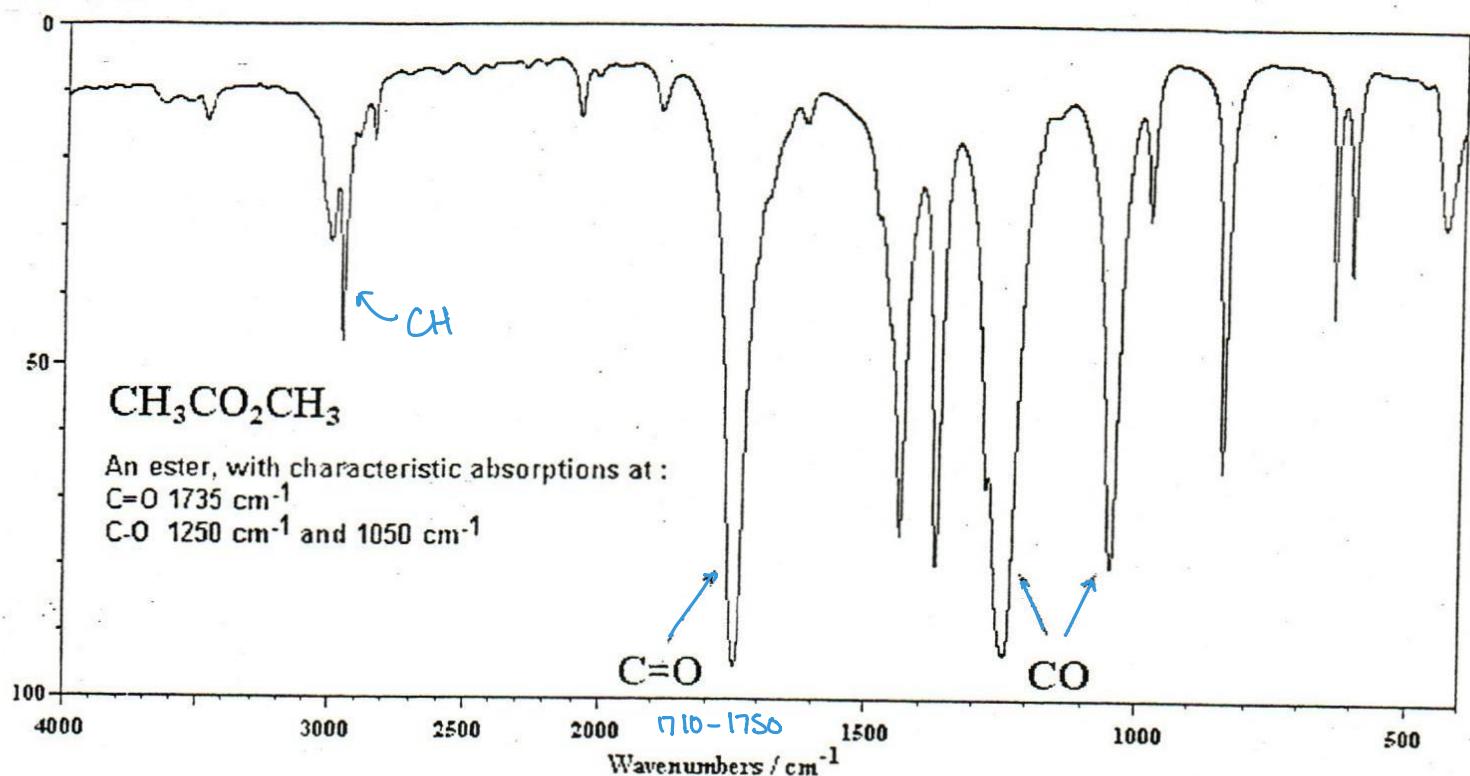




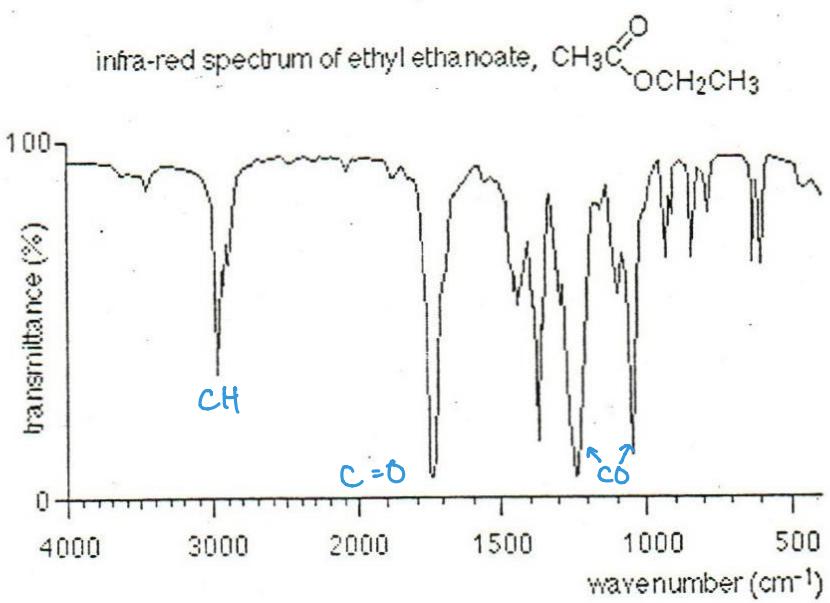
The characteristic absorption of the alcohol, 2-propanol, is the broad band due to the hydrogen bonded -OH group.



Absorbance / %

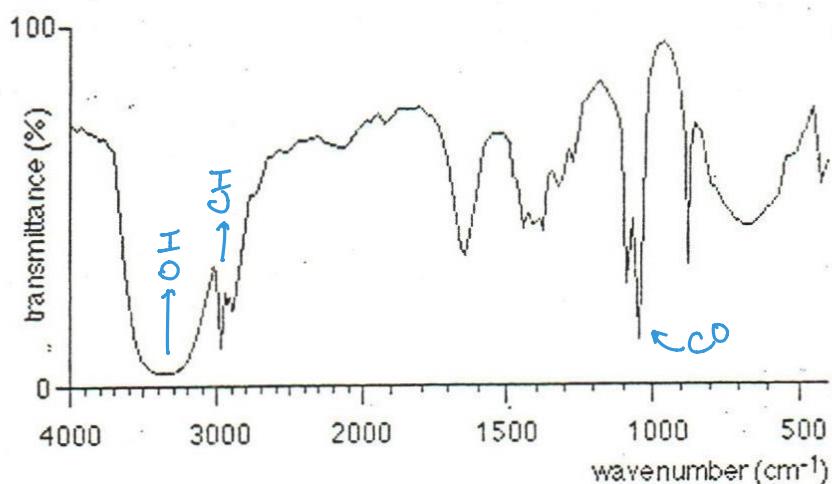


### Ethyl ethanoate

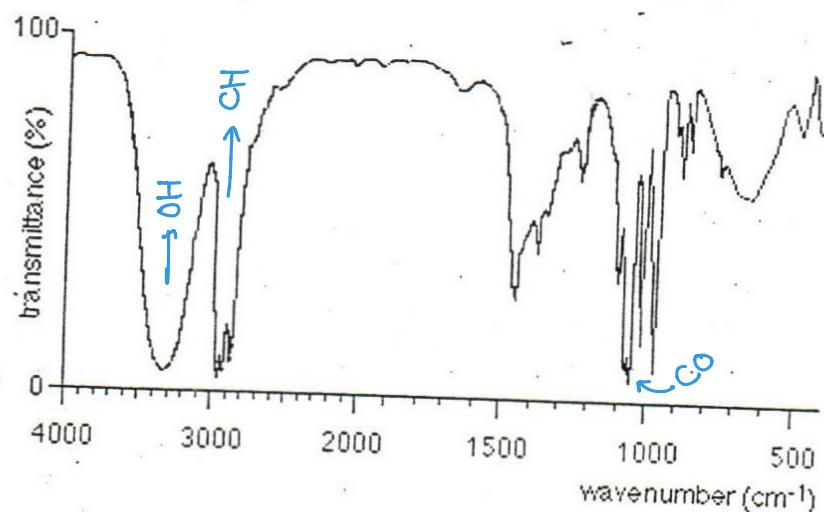


## Ethanol

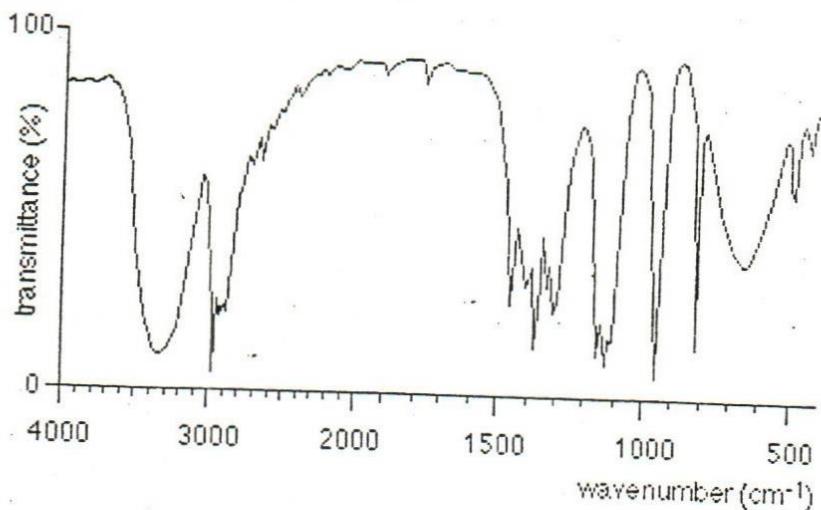
infra-red spectrum of ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$



infra-red spectrum of propan-1-ol,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

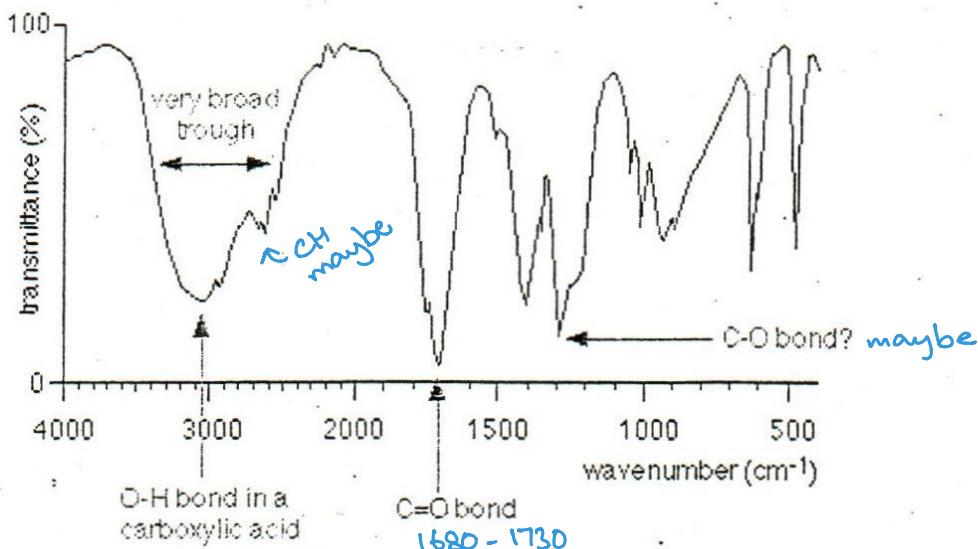


infra-red spectrum of propan-2-ol,  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$



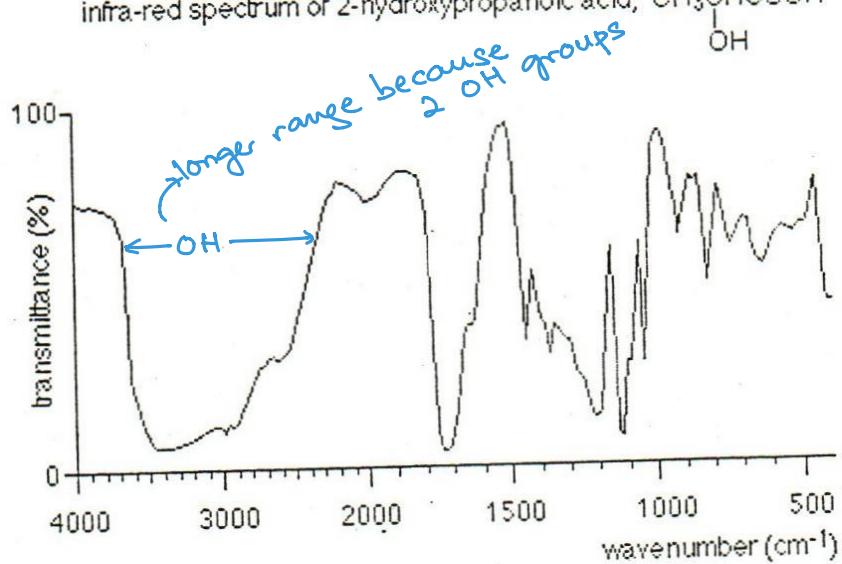
infra-red spectrum of ethanoic acid,  $\text{CH}_3\text{COOH}$

CH peak is overlapped within the broad OH peak of the acid

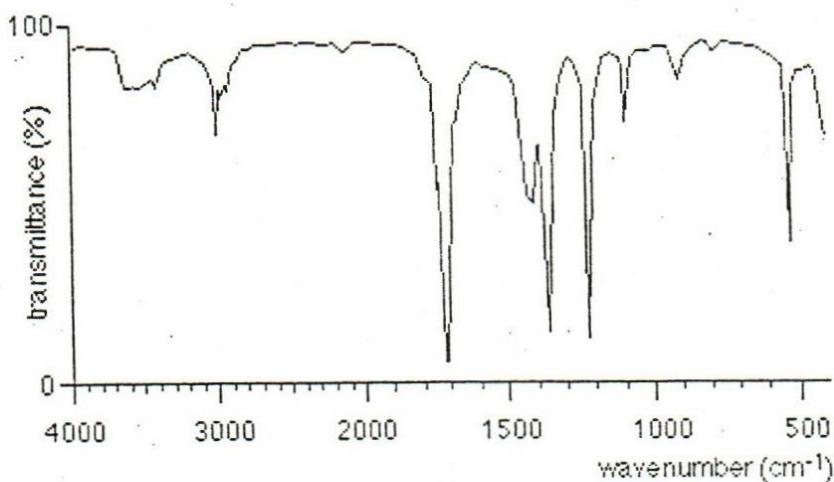


### 2-hydroxypropanoic acid (lactic acid)

infra-red spectrum of 2-hydroxypropanoic acid,  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$

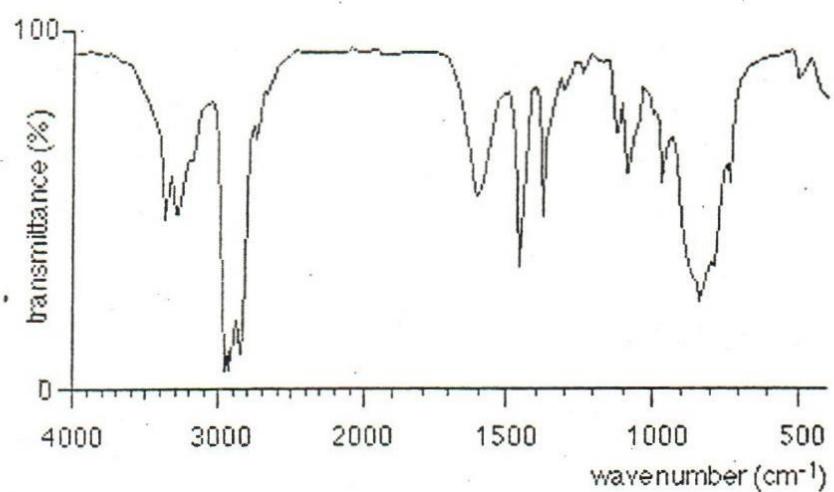


infra-red spectrum of propanone,  $\text{CH}_3\text{C}(=\text{O})\text{CH}_3$



## 1-aminobutane

infra-red spectrum of 1-aminobutane,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

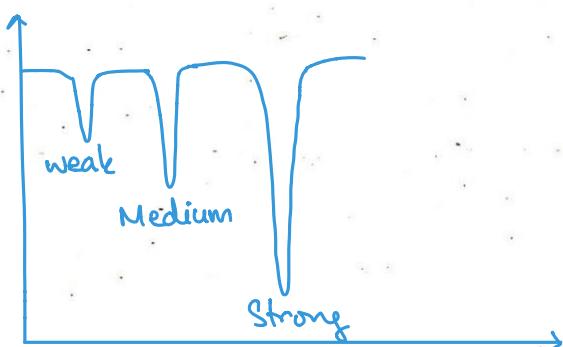


## 8 Characteristic infra-red absorption frequencies for some selected bonds

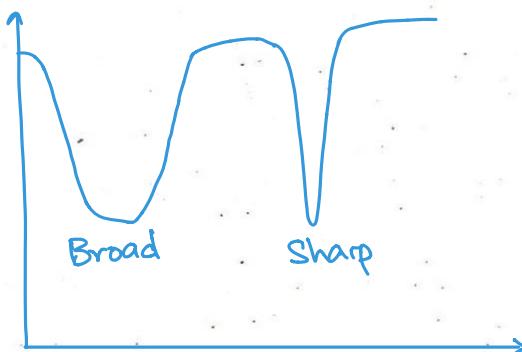
*Only bond identifiable in the fingerprint region*

| Bond | Functional groups containing the bond   | Absorption range (in wavenumbers)/cm <sup>-1</sup> | Appearance of peak (s = strong, w = weak) |
|------|---|--|---|
| C-O  | alcohols, ethers, esters  | 1040-1300  | s   |
| C=C  | aromatic compounds, alkenes   | 1500-1680  | w unless conjugated                       |
| C=O  | amides<br>ketones and aldehydes<br>carboxylic acids<br>esters                         | 1640-1690<br>1670-1740<br>1680-1730<br>1710-1750   | s<br>s<br>s<br>s                          |
| C≡C  | alkynes   | 2150-2250  | w unless conjugated                       |
| C≡N  | nitriles  | 2200-2250  | w   |
| C-H  | alkanes, CH <sub>2</sub> -H<br>alkenes/arenes, =C-H                                   | 2850-2950<br>3000-3100                             | s<br>w                                    |
| N-H  | amines, amides  | 3300-3500  | w   |
| O-H  | carboxylic acids, RCO <sub>2</sub> -H<br>H-bonded alcohol, RO-H<br>free alcohol, RO-H | 2500-3000<br>3200-3600<br>3580-3650                | s and very broad<br>s<br>s and sharp      |

*weak vs. strong*



*broad vs. sharp*

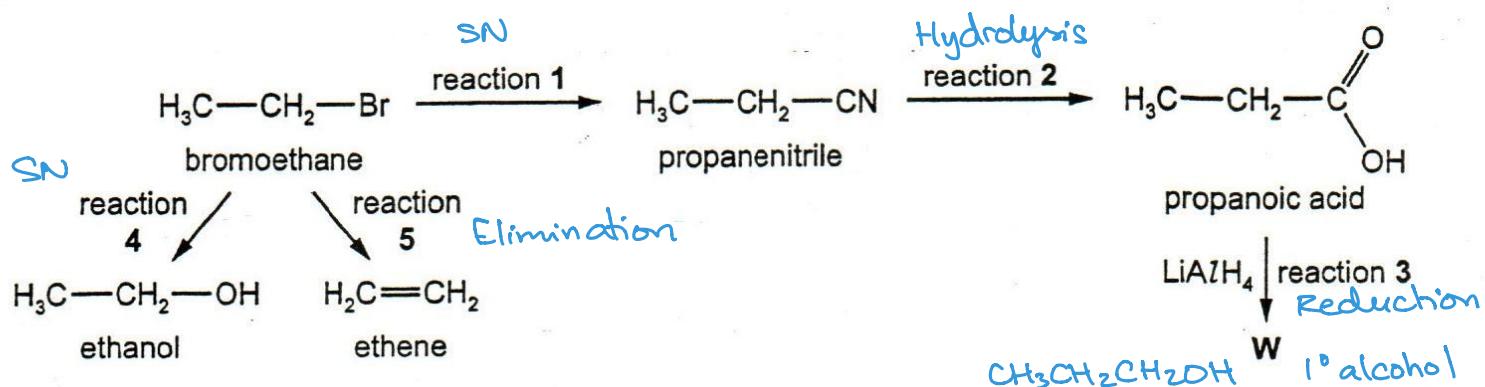


*Broad → Absorbing over a wider range of wavenumbers*

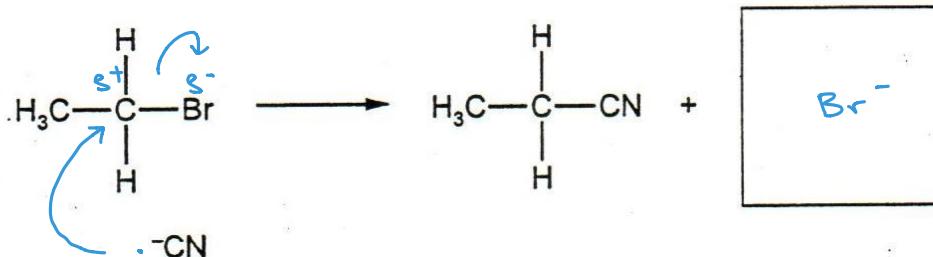
*Sharp → Absorbing over a small range of wavenumbers*



1 A reaction sequence is shown.



- (a) Complete the diagram to show the mechanism of reaction 1. Include all necessary charges, partial charges, lone pairs and curly arrows.

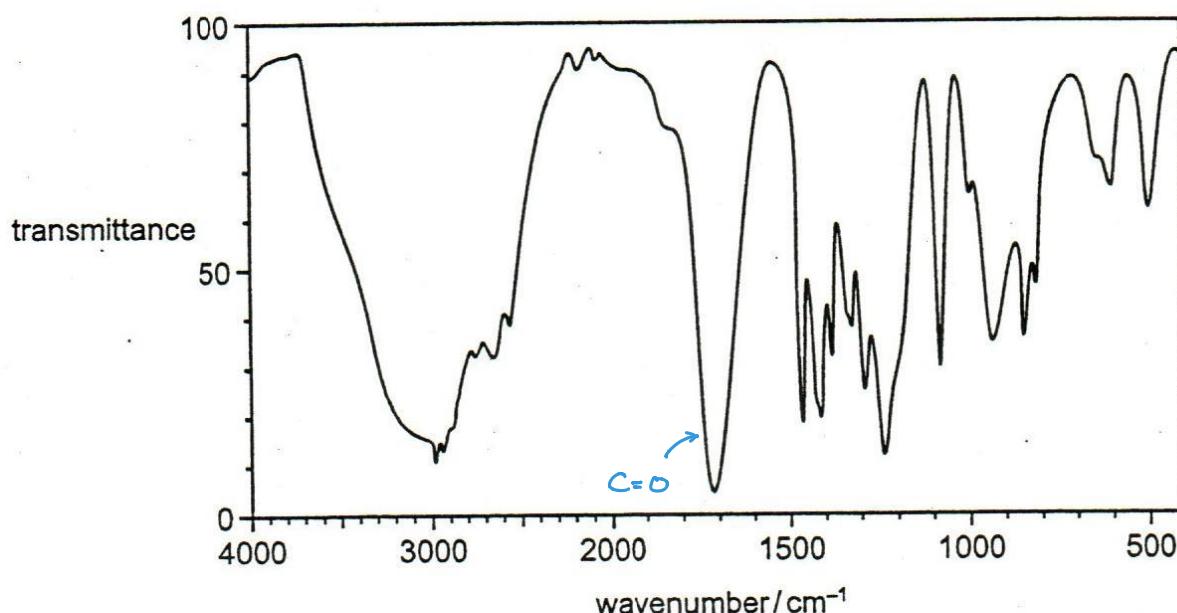


[2]

- (b) (i) Give the name of the type of reaction involved in reaction 3.

..... Reduction ..... [1]

The infra-red spectrum of the propanoic acid produced by reaction 2 is shown.



- (ii) Describe and explain the main difference between the infra-red spectrum of W and that of propanoic acid.

The peak at  $1680 - 1730 \text{ cm}^{-1}$  will not be present in W's infrared spectrum, as W is an alcohol [2]

2 This question is about molecules with molecular formula  $C_4H_8O_2$ .

- (a) Give the structural formulae of the pair of **chain** isomers with the formula  $C_4H_8O_2$  that are carboxylic acids.



[2]

- (b) (i) Give the structural formulae of a pair of **positional** isomers with the formula  $C_4H_8O_2$  that are esters.



[2]

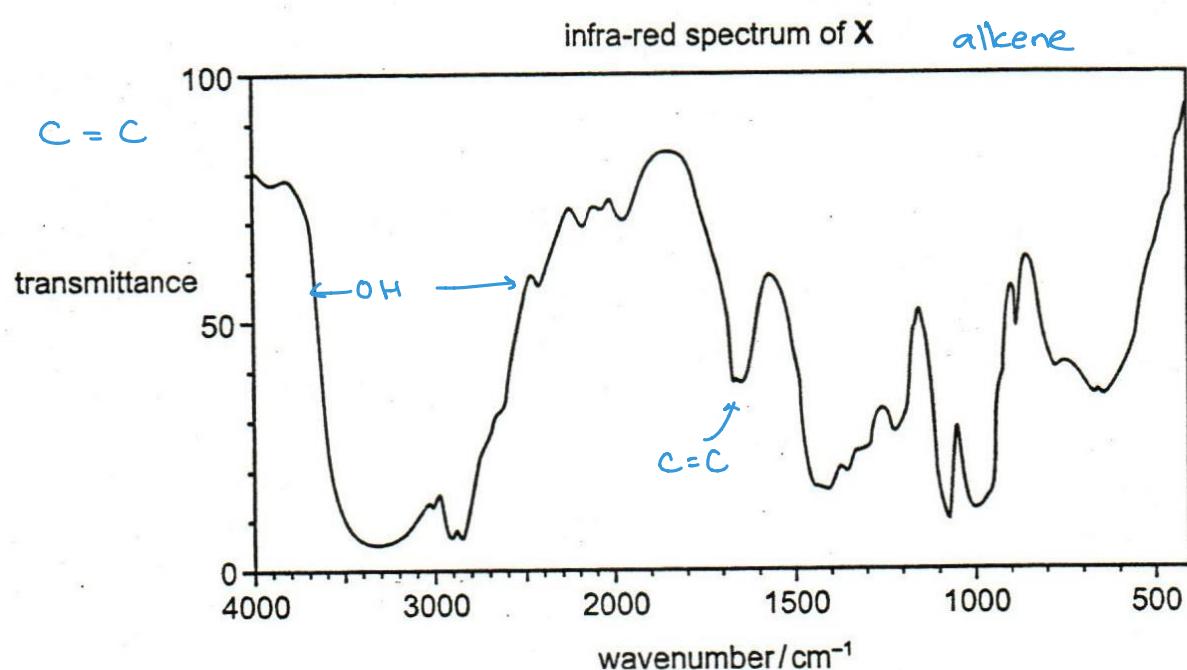
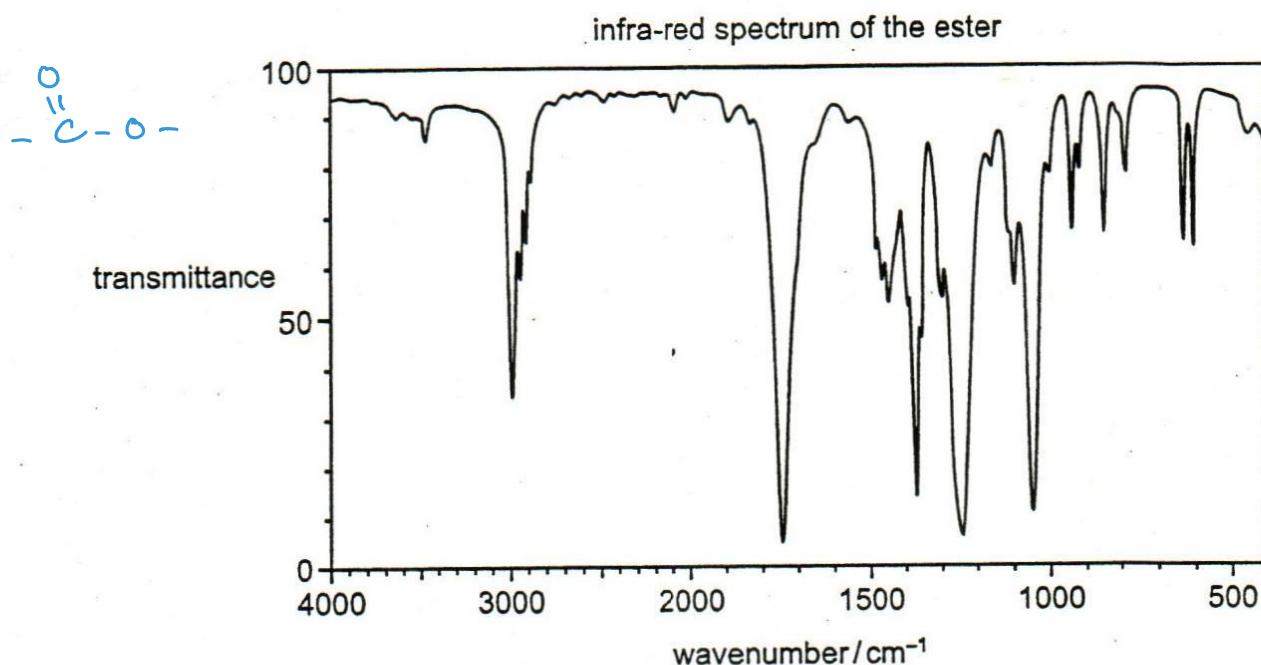
- (ii) Give the reagents and conditions needed to produce one of your esters in (i).

..... propanoic acid + methanol, reagent : conc.  $H_2SO_4$  .....

..... Conditions : Heat under reflux ..... [2]

(c) The infra-red spectra of one of the esters and of another isomer, X, are shown.

X decolourises bromine water and is not an ester or an acid.



Explain the differences between these two spectra, with particular reference to the peaks with wavenumbers above 1500  $\text{cm}^{-1}$ .

Absorbance peak seen at  $1710 - 1750 \text{ cm}^{-1}$  due to  $\text{C}=\text{O}$  in the ester's spectrum. Peak at  $1500 - 1680 \text{ cm}^{-1}$  due to  $\text{C}=\text{C}$  in X's spectrum. Broad peak at  $3200 - 3650 \text{ cm}^{-1}$  due to  $\text{O}-\text{H}$  (X's spectrum)

[3]

[Total: 9]

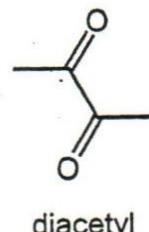
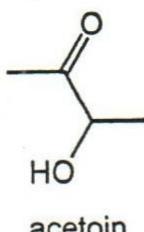
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AUGUST 2016

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June 2016  
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Turn over

- 3 Acetoin,  $\text{CH}_3\text{COCH}(\text{OH})\text{CH}_3$ , and diacetyl,  $\text{CH}_3\text{COCOCH}_3$ , are two of the compounds that give butter its characteristic flavour. Their skeletal formulae are shown.



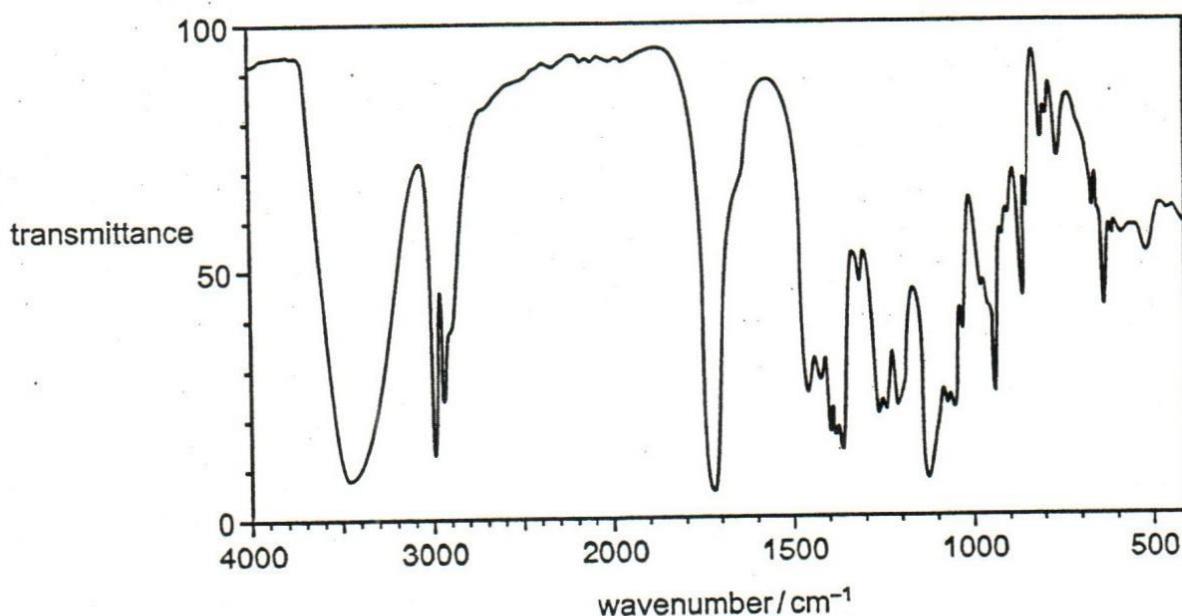
- (a) Give the systematic name for acetoin.

..... [1]

- (b) Identify the reagents and conditions necessary for the conversion of acetoin into diacetyl.

..... [2]

- (c) The infra-red spectrum for acetoin is shown.



- (i) Explain the main features of this spectrum, with reference to the peaks with wavenumbers greater than 1500 cm<sup>-1</sup>.

.....  
 .....  
 .....  
 .....  
 ..... [3]

- (ii) State and explain how the infra-red spectrum for diacetyl would differ from the infra-red spectrum for acetoin.

.....  
.....  
.....

[2]



