

WHAT IS SPECTROSCOPY?

- Atoms and molecules interact with electromagnetic radiation (EMR) in a wide variety of ways.
- Atoms and molecules may absorb and/or emit EMR.
- Absorption of EMR stimulates different types of motion in atoms and/or molecules.
- The patterns of absorption (wavelengths absorbed and to what extent) and/or emission (wavelengths emitted and their respective intensities) are called '*spectra*'.
- The field of **spectroscopy** is concerned with the interpretation of *spectra* in terms of atomic and molecular structure (and environment).

Light & the Electromagnetic Spectrum



Wavelength in centimeters



About the size of...



CLASS PROBLEMS

- Electromagnetic waves travel at the speed of light ($2.998 \times 10^8 \text{ m s}^{-1}$) in a vacuum. How many waves pass per second for:
Blue light (wavelength = 400 nm) Green light (wavelength = 500 nm)
Yellow light (wavelength = 600 nm) Red light (wavelength = 700 nm)
- How many waves are there per cm for blue, green, yellow and red light?
- For a particular wavelength of infrared radiation, the number of waves passing per second is 9×10^{13} . What is the wavelength and the wavenumber?
- Work out the energy in J and kJ mol⁻¹ for all the different types of EMR mentioned on this slide.
- What is the difference in energy in kJ mol⁻¹ between 400 nm and 500 nm and between 500 nm and 600 nm?

Avogadro constant

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

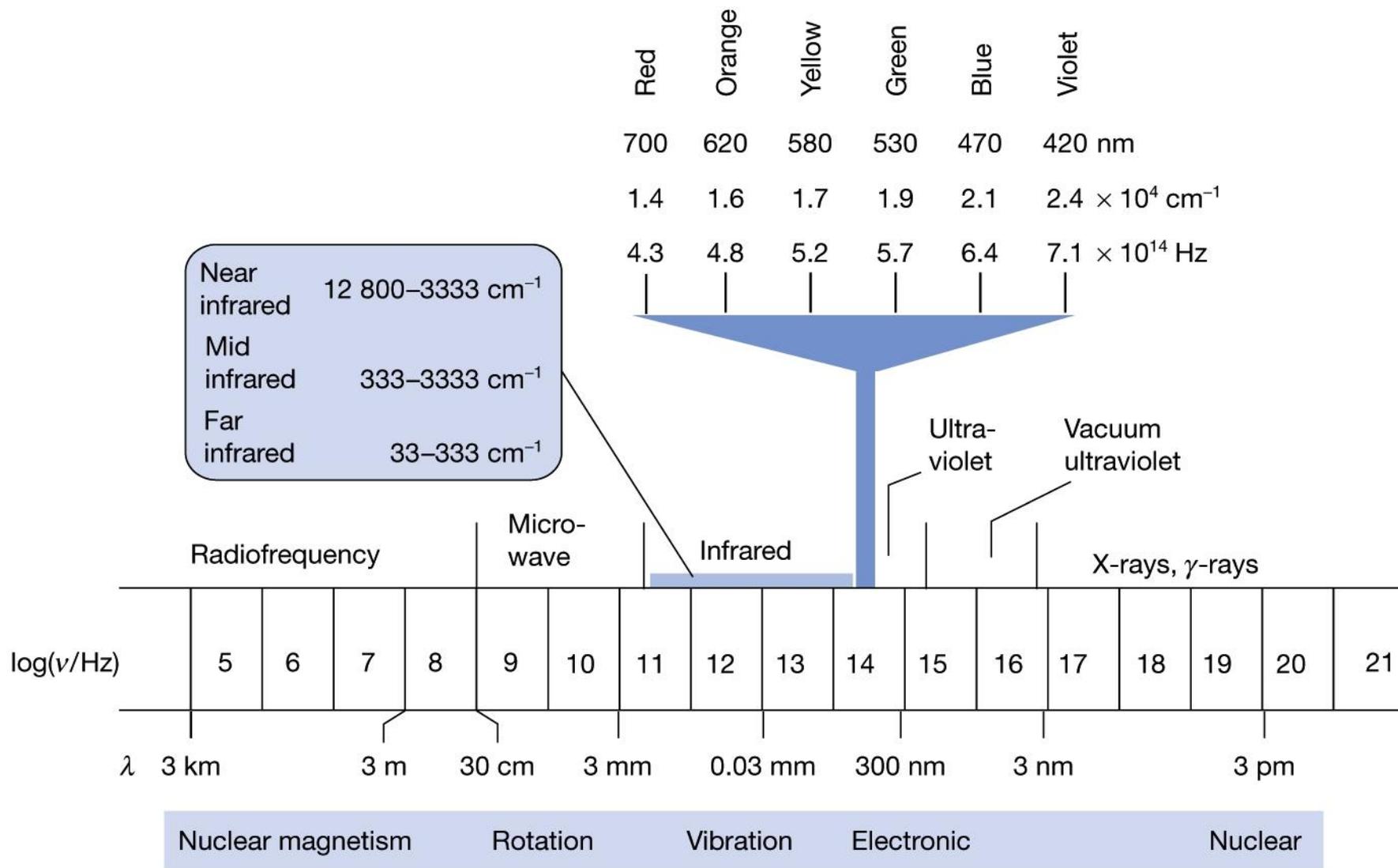
Planck constant

$$h = 6.626 \times 10^{-34} \text{ J s}$$

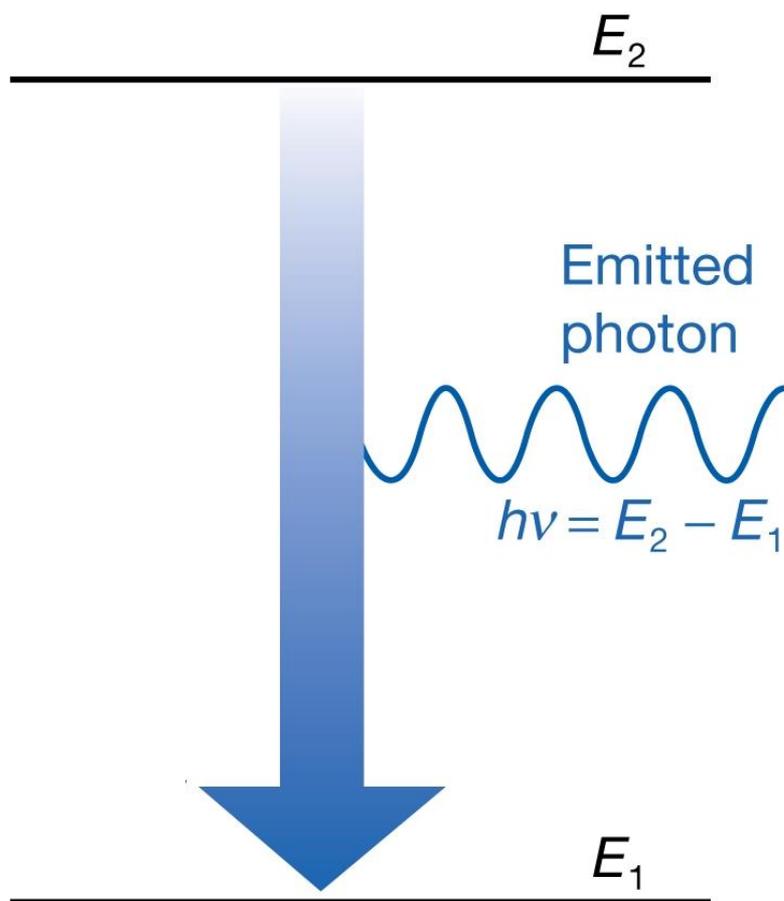
Velocity of light (vacuum)

$$c = 2.998 \times 10^8 \text{ m s}^{-1}$$

THE ELECTROMAGNETIC SPECTRUM



THE ENERGIES OF ELECTROMAGNETIC WAVES



$$c = \lambda \nu \quad \bar{\nu} = \frac{1}{\lambda}$$

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

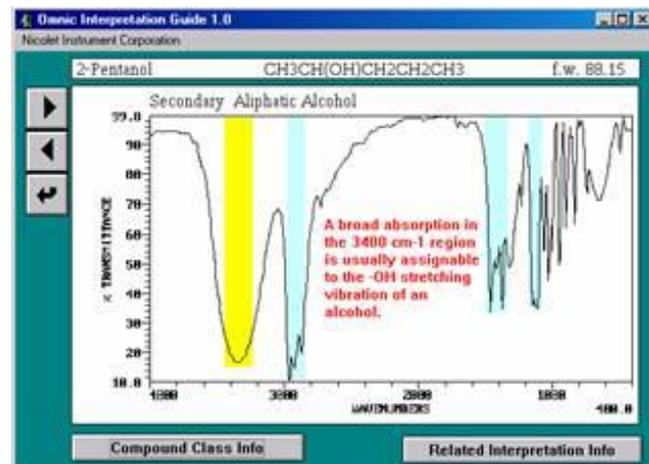
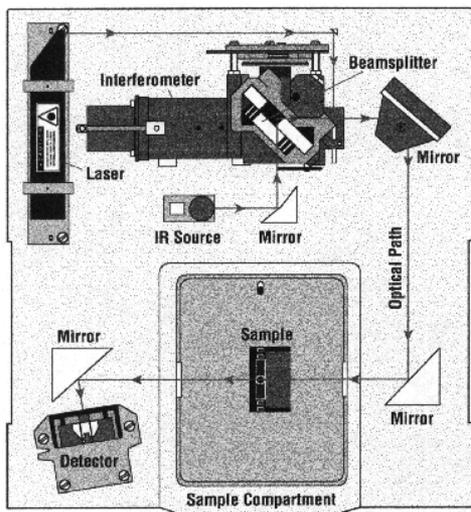
$$E = N_A h\nu = N_A h \frac{c}{\lambda} = N_A hc\bar{\nu}$$

λ

$\bar{\nu}$ (nu-bar) represents wavenumber, the number of wavelengths in 1 cm

INFRARED SPECTROSCOPY

- Infrared radiation stimulates molecular vibrations.
- Infrared spectra are traditionally displayed as %T (percent transmittance) versus wavenumber ($4000\text{-}400\text{ cm}^{-1}$).
- Useful in identifying presence or absence of functional groups.



INFRARED ABSORPTION BANDS

POSITION	 REDUCED MASS  BOND STRENGTH (STIFFNESS)	LIGHT ATOMS HIGH FREQUENCY STRONG BONDS HIGH FREQUENCY
STRENGTH	 CHANGE IN 'POLARITY'	STRONGLY POLAR BONDS GIVE INTENSE BANDS
WIDTH	 HYDROGEN BONDING	STRONG HYDROGEN BONDING GIVES BROAD BANDS

INFRARED (VIBRATIONAL) SPECTROSCOPY

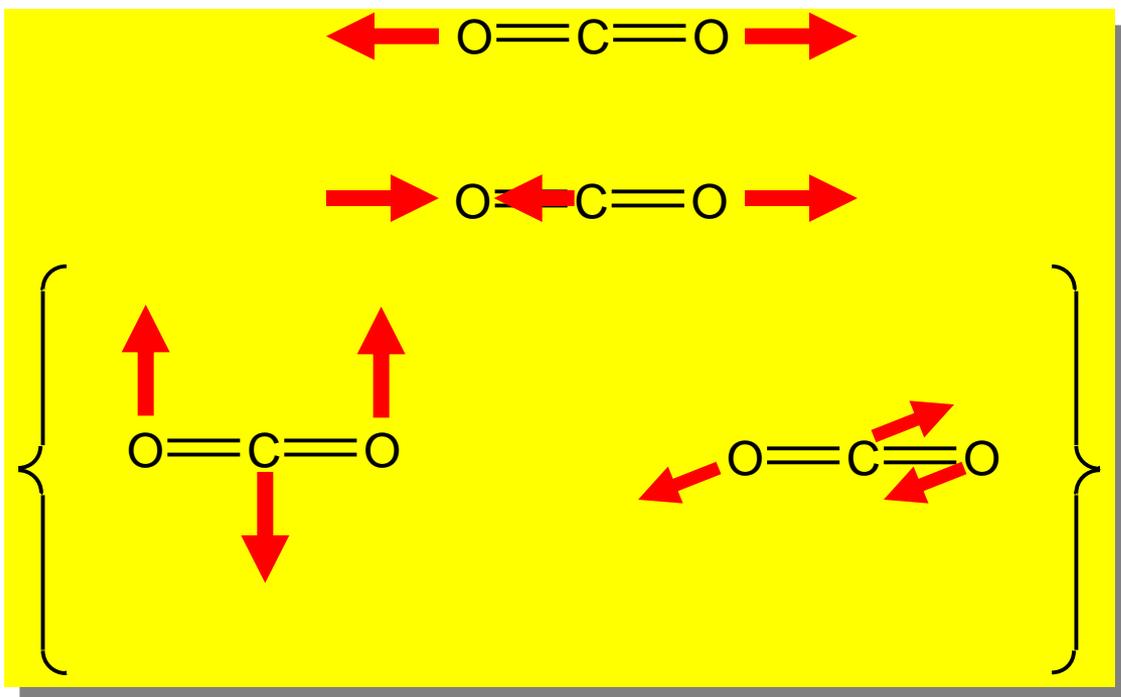
Bond →	C-H	C-D	C-O	C-Cl
$\bar{\nu}/\text{cm}^{-1}$ →	3000	2200	1100	700
Bond →	C≡O	C=O	C-O	
$\bar{\nu}/\text{cm}^{-1}$ →	2143	1715	1100	

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{f}{\mu}}$$
$$\mu = \frac{m_a m_b}{m_a + m_b}$$

- Only vibrations that cause a change in 'polarity' give rise to bands in IR spectra

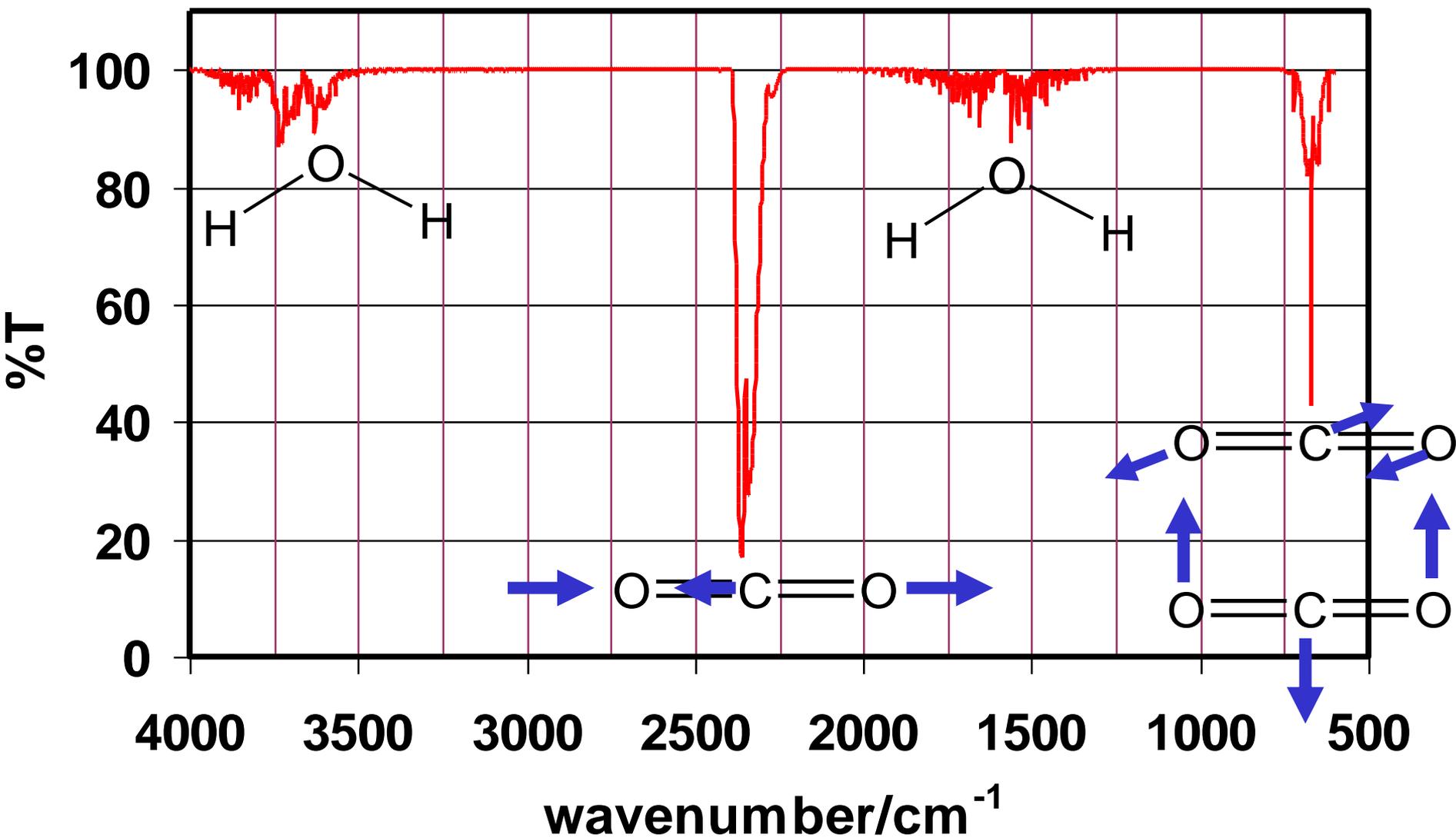
INFRARED (VIBRATIONAL) SPECTROSCOPY

- Only vibrations that cause a change in 'polarity' give rise to bands in IR spectra – which of the vibrations for CO_2 are infrared active?

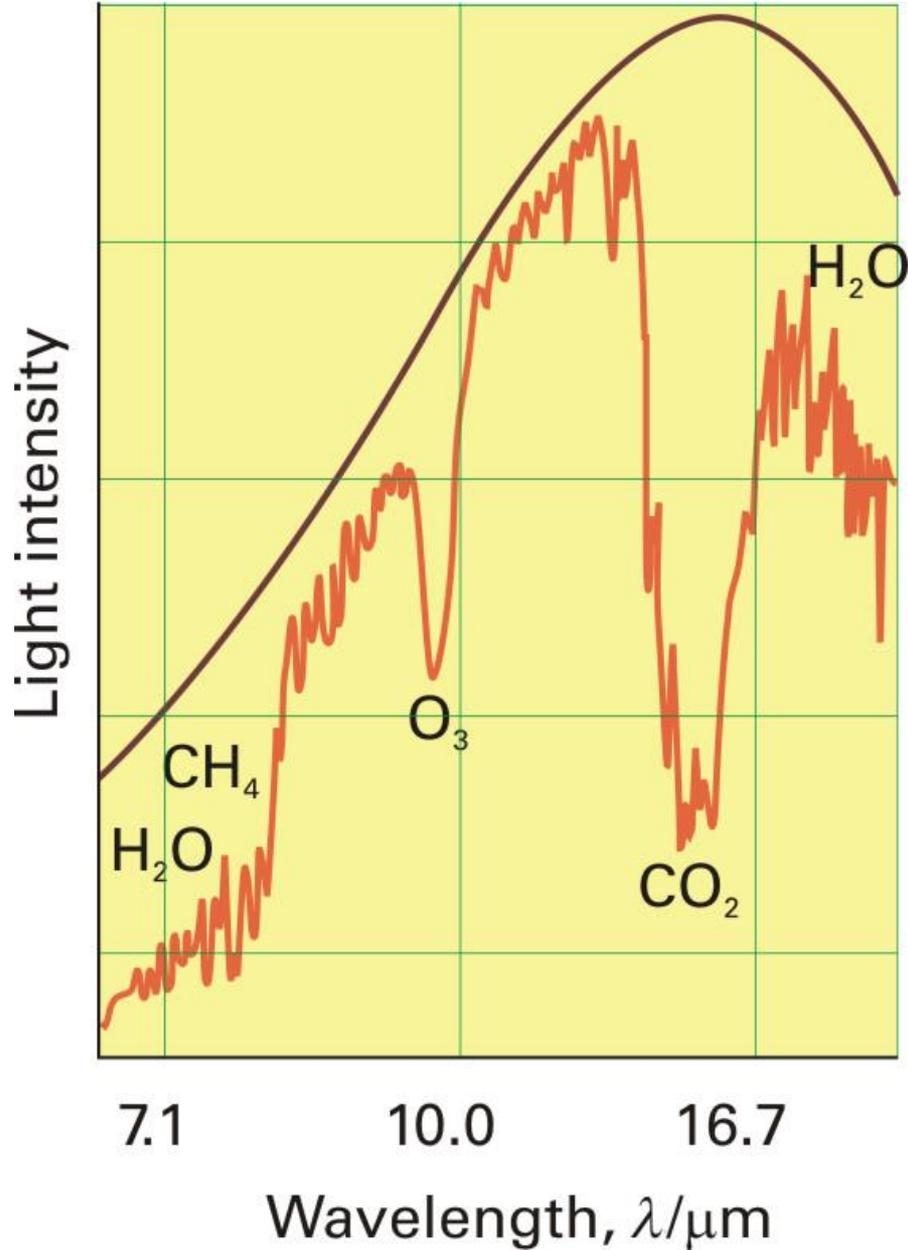


- Symmetric stretch
- Asymmetric stretch
- Bending (doubly degenerate)

INFRARED SPECTRUM OF DAVE McGARVEY'S BREATH



GLOBAL WARMING



- See Atkins Box 19.1, p 500
- ‘The intensity of infrared radiation that would be lost from the Earth in the absence of greenhouse gases is shown by the smooth line. The jagged line is the intensity of the radiation actually emitted. The maximum wavelength of radiation absorbed by each greenhouse gas is indicated.

REGIONS OF THE INFRARED SPECTRUM

4000-3000 cm ⁻¹	3000-2000 cm ⁻¹	2000-1500 cm ⁻¹	1500-1000 cm ⁻¹
O-H N-H C-H	C≡C C≡N	C=C C=O	C-O C-F C-Cl deformations
increasing energy			
			
increasing frequency			
			

INTERPRETATION OF INFRARED SPECTRA

- An element of judgement is required in interpreting IR spectra but you should find that it becomes relatively straightforward with practice.
- It is often possible to assign the peaks in the 1600-3600 cm^{-1} region by consulting tables or databases of IR spectra. When making an assignment, give both the type of bond and the type of vibration, e.g. O-H stretch or C-H bending vibration.
- The most useful regions are as follows:
 - 1680-1750 cm^{-1} : C=O stretches feature very strongly in IR spectra and the type of carbonyl group can be determined from the exact position of the peak.
 - 2700-3100 cm^{-1} : different types of C-H stretching vibrations.
 - 3200-3700 cm^{-1} : various types of O-H and N-H stretching vibrations.
- Too many bonds absorb in the region of 600-1600 cm^{-1} to allow confident assignment of individual bands. However, this region is useful as a fingerprint of a molecule, *i.e.* if the spectrum is almost identical to an authentic reference spectrum then the structure can be assigned with some confidence.

INFRARED ABSORPTION BANDS

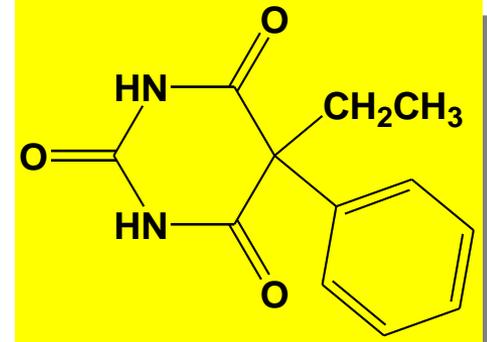
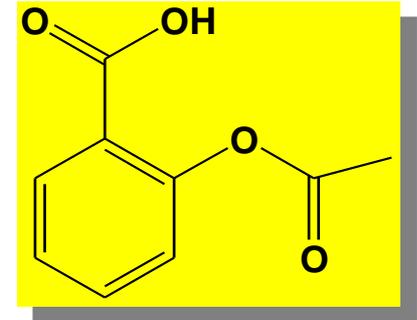
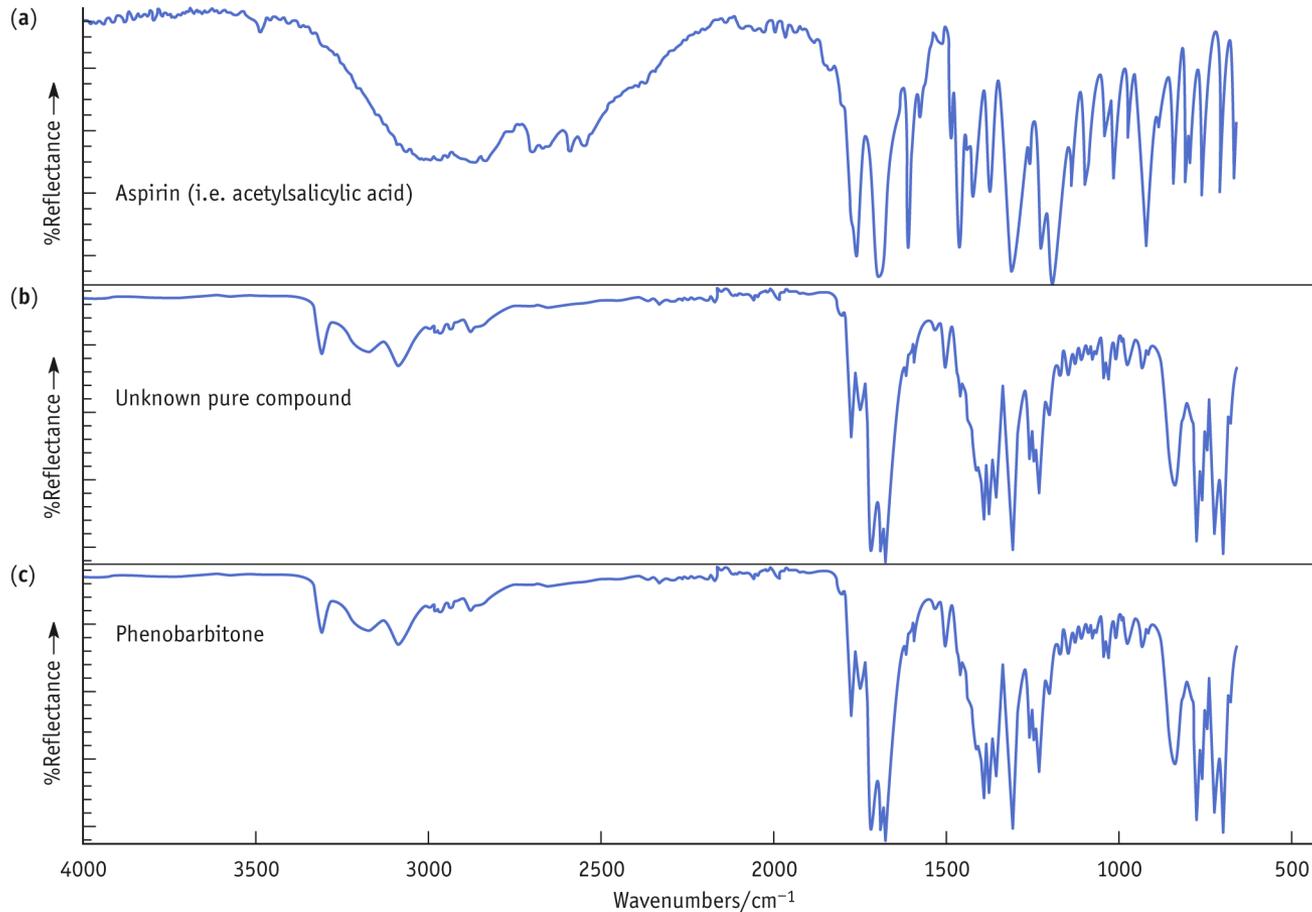
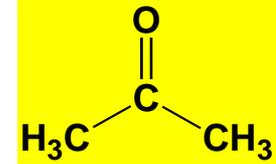
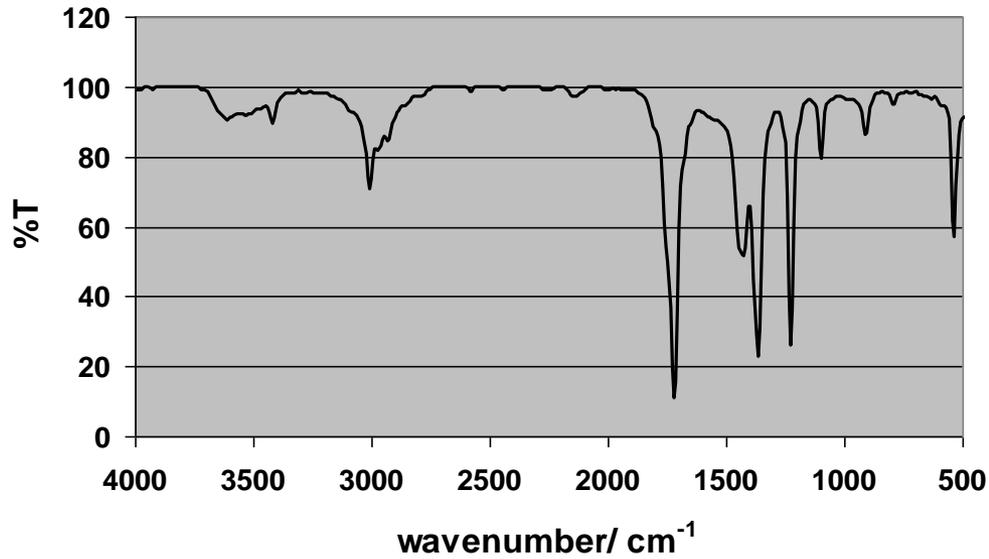


Figure 7.10 The infrared spectra of (a) aspirin, (b) an unknown compound and (c) phenobarbitone

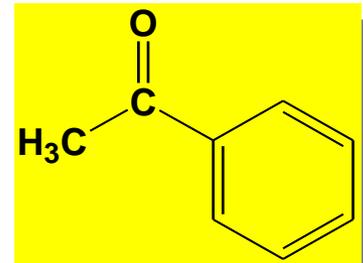
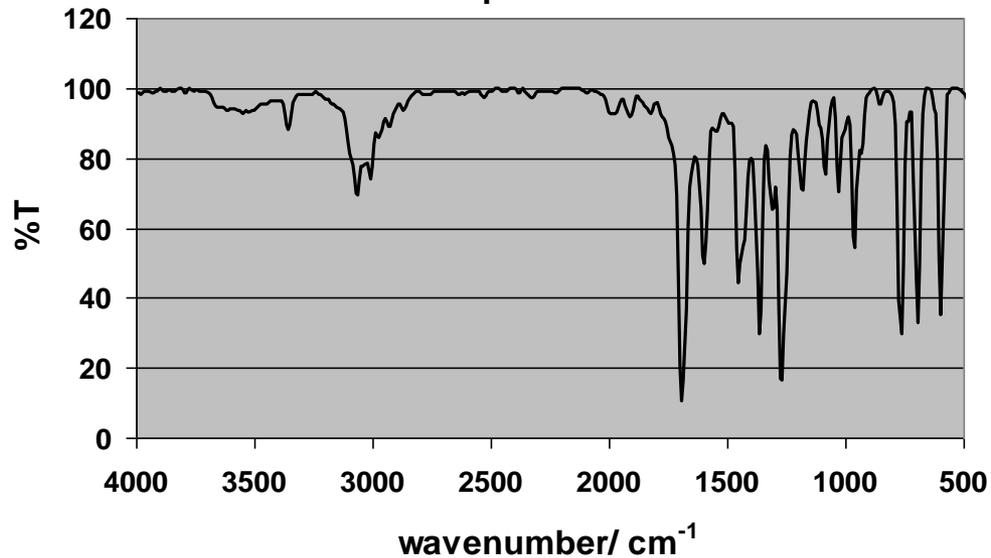
Recorded by Jayne Francis, Staffordshire University, UK.

INFRARED SPECTRA

Acetone

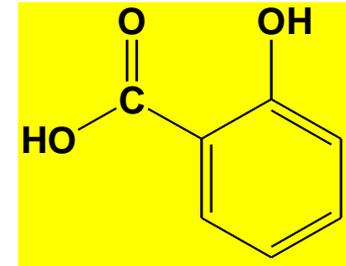
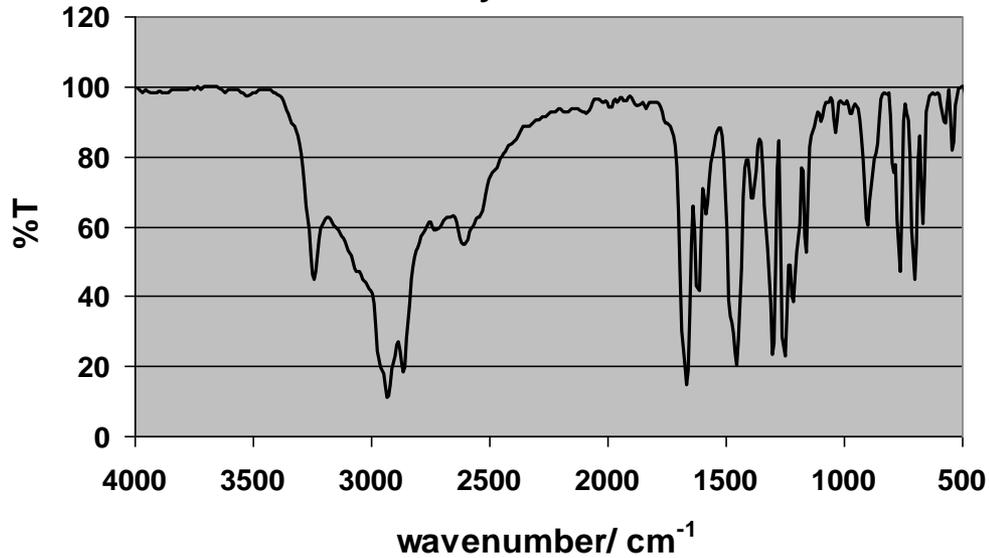


Acetophenone

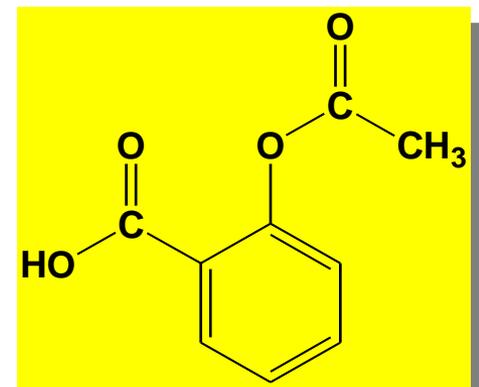
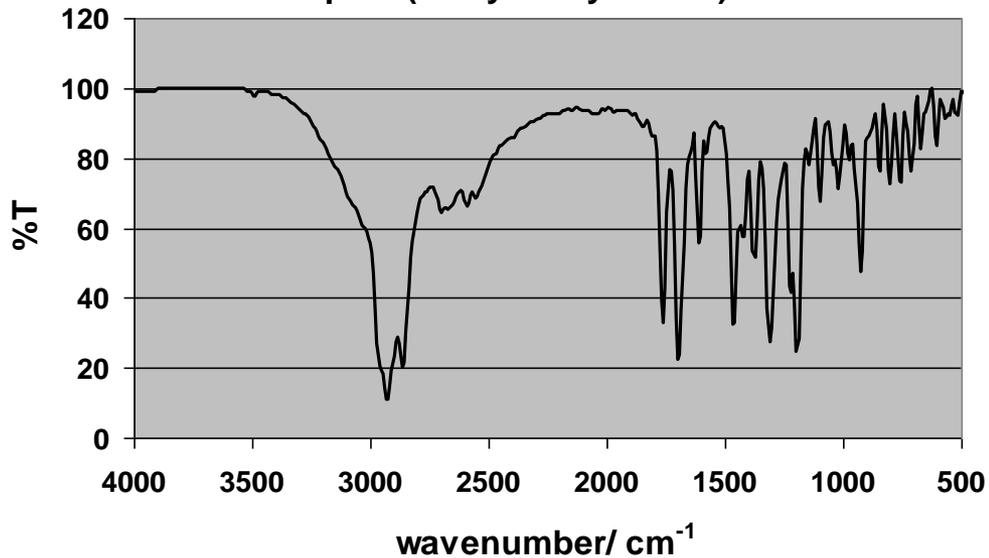


INFRARED SPECTRA

Salicylic acid

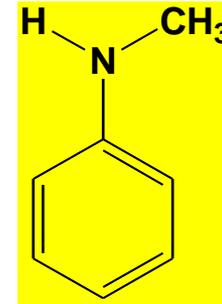
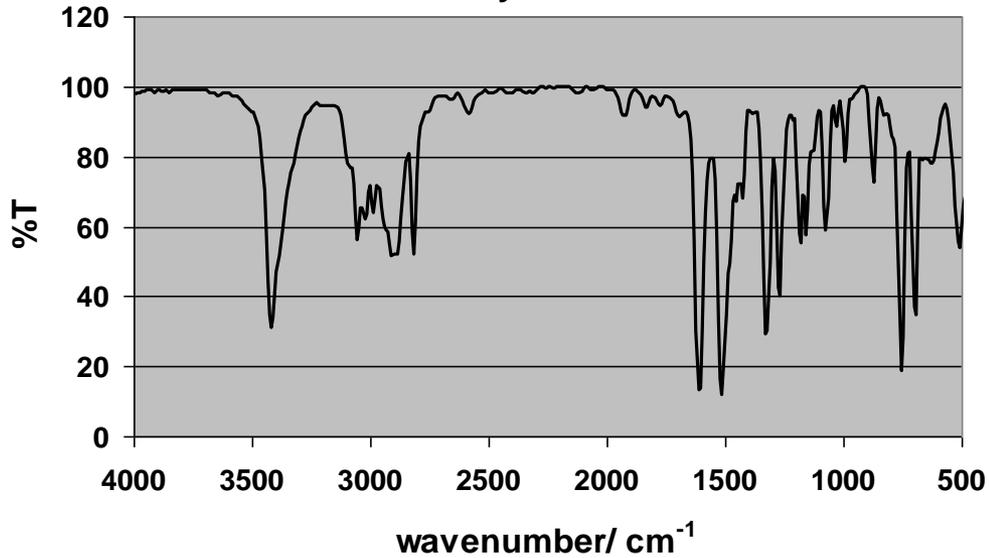


Aspirin (acetylsalicylic acid)

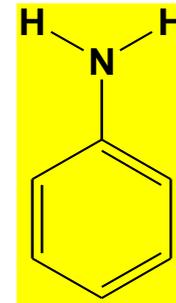
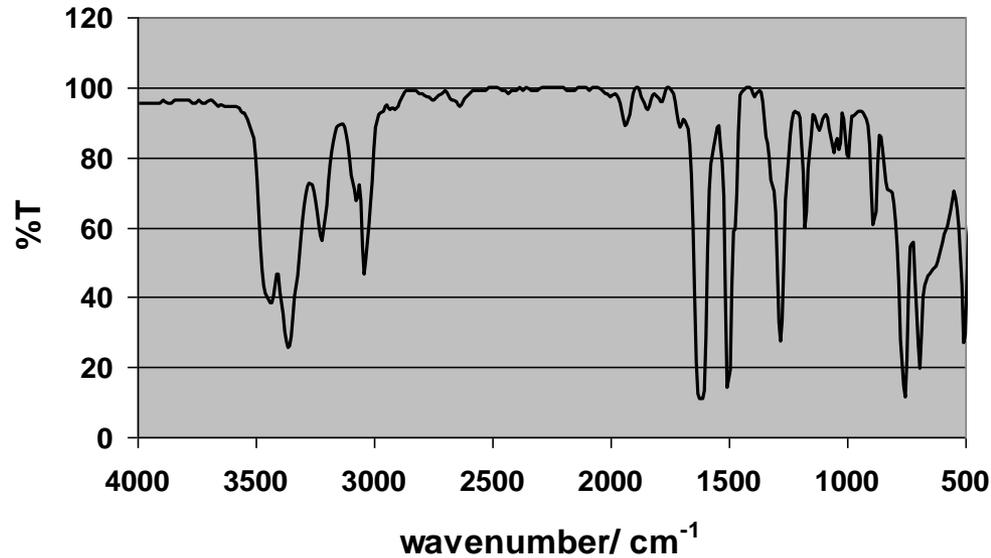


INFRARED SPECTRA

N-methylaniline

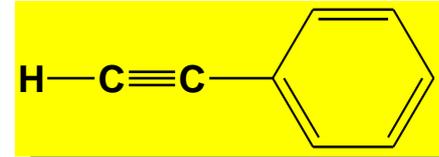
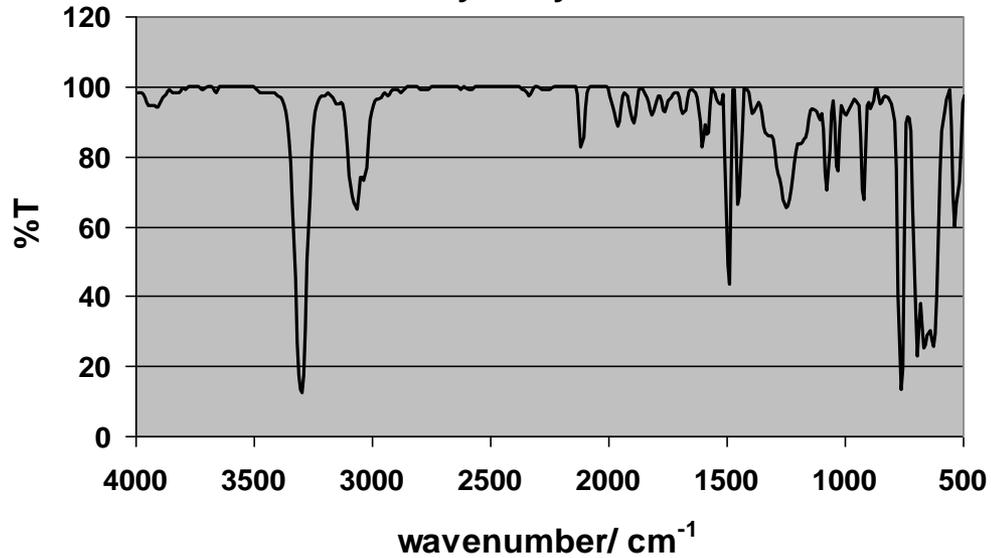


Aniline



INFRARED SPECTRA

Phenylacetylene



Phenol

