

CHEM1611 Spectroscopy Workshop

This worksheet forms part of the 'Spectroscopy Problem Solving Assignment' which represents 10% of the assessment of this unit. You should use the support material on eLearning alongside this worksheet and your lecture notes. The assignment is assessed through online quizzes and must be completed by the end of week 12.

Model 1: 1. Infrared (IR) Spectroscopy

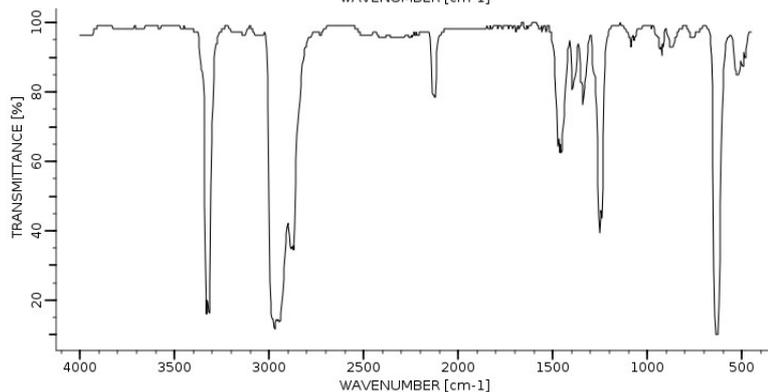
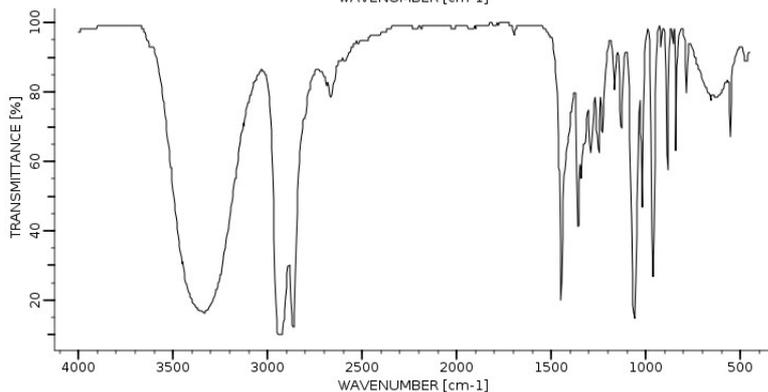
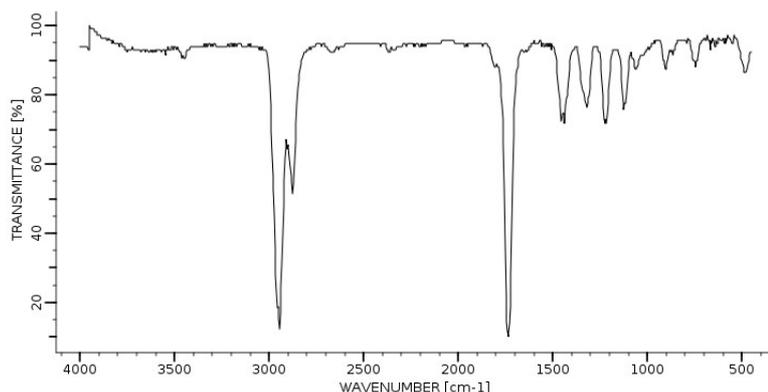
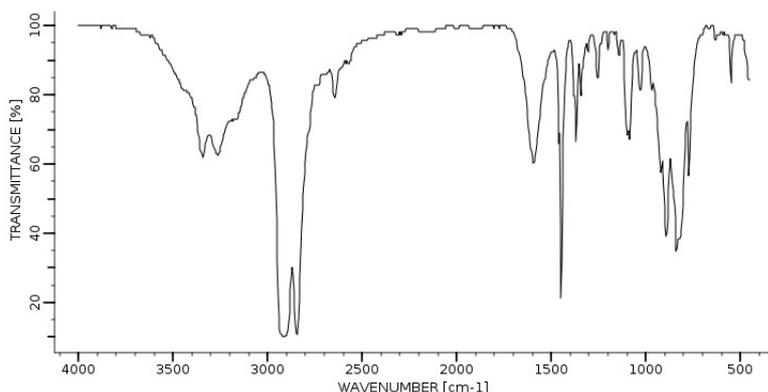
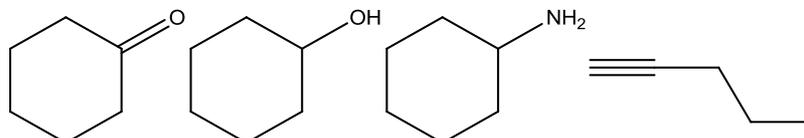
You have seen in lectures how bonds stretch and bend. A light wave of the correct frequency will be in resonance with a bond in motion and transfer its energy to this motion, like a parent pushing a swing. Light absorbed by the molecule in this manner falls in the infrared range. The frequencies at which some bonds stretch is quite similar in different molecules so **IR spectroscopy can be used to identify bonds, and hence functional groups**, in a molecule.

The table below lists IR absorption frequencies for some common bonds found in organic molecules:

Bond	alcohol O-H	alkane C-H	carbonyl C=O	amine N-H	alkyne C≡C
Absorption Range (cm ⁻¹)	3200-3650 (strong, broad)	2840-3000 (strong)	1690-1760 (strong)	3100-3500	2100-2260

Critical thinking questions

- Use the characteristic stretching frequencies to match each of the four compounds below to its IR spectrum.

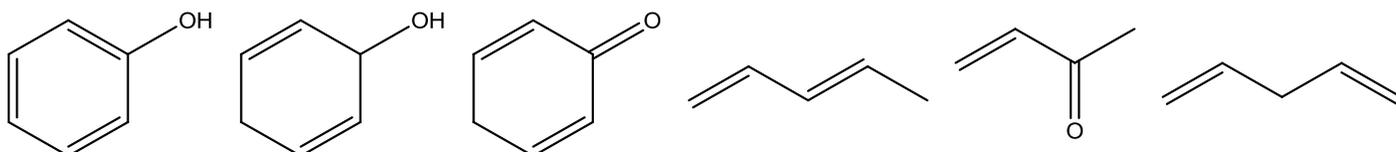


Model 2: UV-Visible Spectroscopy

Radiation in the ultraviolet (UV) and visible region of the electromagnetic spectrum has the correct energy to excite electrons in a filled molecular orbital into an empty molecular orbital of higher energy. In particular, **conjugated molecules** (those with alternating single and multiple bonds in at least part of the molecule), are able to absorb UV light >200 nm (which is the shortest wavelength that standard UV-Vis spectrometers can usually measure from). Given this information, which of the structures in Model 1 would show a peak in the UV-Vis spectrum?

Critical thinking questions

1 Which of the molecules below are conjugated?



- Circle the molecules above which would show a peak in the UV-Vis spectrum?
- How useful do you think a UV-Vis spectrum is in identifying organic molecules?

Model 3: ^1H NMR Spectroscopy - Chemical Shifts

NMR spectroscopy (most often ^{13}C and ^1H , other nuclei as well) is the **most powerful tool for identifying organic molecules**. This is due to its sensitivity. Each unique carbon or hydrogen will give rise to a specific **signal** (peak), with a characteristic **chemical shift** (position) in the NMR spectrum*.

Nuclei give rise to identical signals only when they are in the same **chemical environment**. This occurs when:

- they are attached to exactly the same atoms (e.g. the 4 hydrogen atoms of CH_4 are equivalent and give rise to only one peak)
- are related by symmetry (e.g. the two CH_3 groups in propane are equivalent).

Critical thinking questions

1. Circle each H environment in the molecules below. (*Hint: you should first draw them on!*)



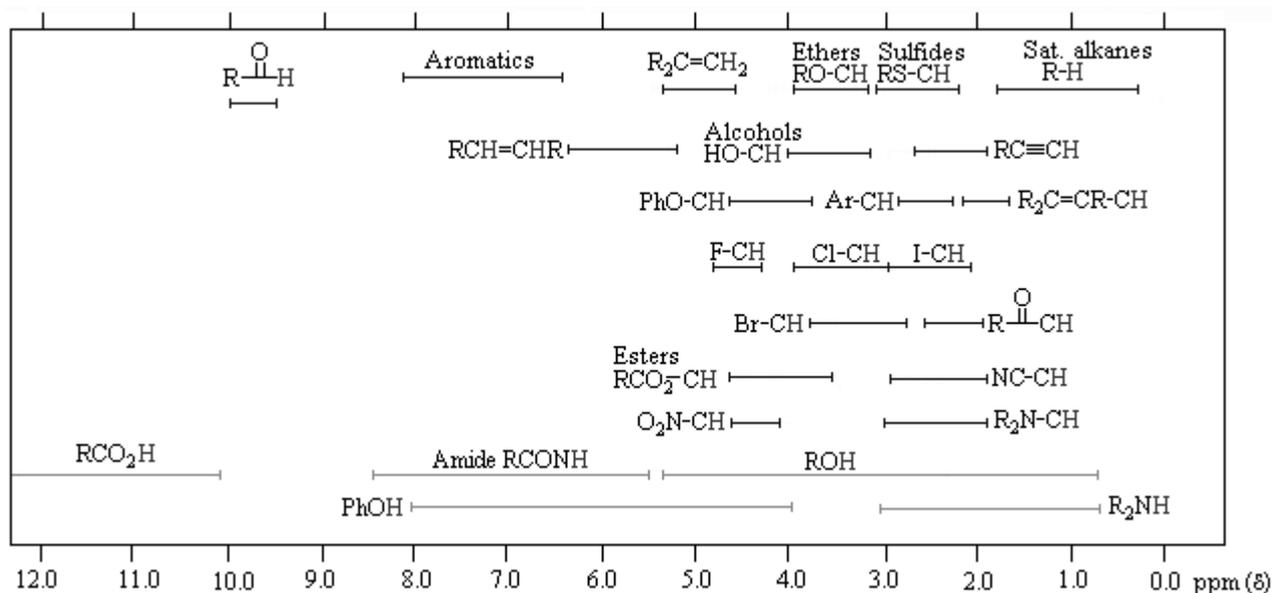
2. How many signals would you expect in the ^1H spectra for these compounds?

The chemical shift tells us what other atoms are nearby. If the ^1H is bonded, or near, to an electronegative atom like O, N or a halide, the electron density around the nucleus is lowered and its chemical shift is *increased*.

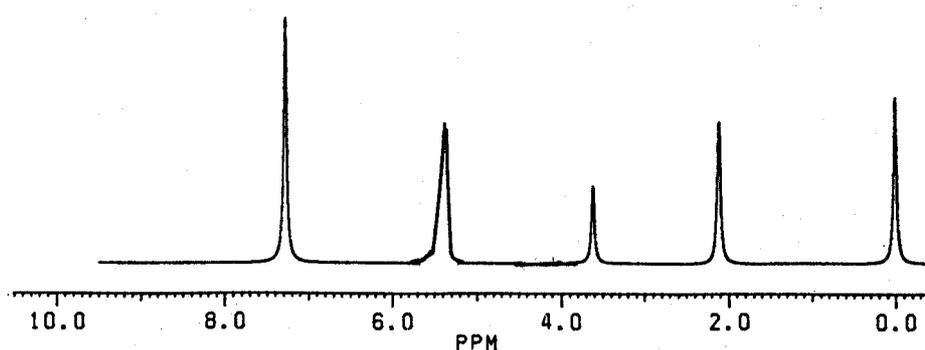
The *hybridization* of the carbon atom to which the ^1H is bonded is also important. A ^1H bonded to an sp^3 C atom (e.g. in an alkane) has a smaller chemical shift than a ^1H bonded to an sp^2 C atom (e.g. in an alkene or carbonyl).

* For a more in depth analysis of the material in Models 3 - 4, see the online resources on eLearning.

The figure below shows the characteristic chemical shifts (δ) for ^1H atoms in common groups, with R = alkyl and Ar = aromatic.



3. The ^1H n.m.r. spectrum of a mixture composed of differing concentrations of acetone (a), benzene (b), dimethyl ether (d), 1,1-dichloroethylene (e) and tetramethylsilane (t) is given below. Use the above list of chemical shifts to identify and label the signals due to each component of the mixture.



Model 4: ^1H NMR Spectroscopy - Coupling

^1H NMR spectra have an added level of complexity. A signal may be “split” by the presence of ^1H atoms on adjacent carbon atoms.

- the signal due to a ^1H next to a CH group appears as 2 peaks (*doublet* with relative heights 1:1)
- the signal due to a ^1H next to a CH₂ group appears as 3 peaks (*triplet* with relative heights 1:2:1)
- the signal due to a ^1H next to a CH₃ groups appears as 4 peaks (*quartet* with relative heights 1:3:3:1)

Note: equivalent protons do not split each other – i.e. a signal is not split by the protons giving rise to the signal. Hence, in the ^1H NMR spectrum for ethane, in which all of the hydrogen atoms are equivalent, consists of one signal which is a singlet.

Critical thinking questions

1. What is the relationship between the number of peaks into which a signal is split and the number of equivalent hydrogen atoms on the adjacent carbon atoms?
2. How many hydrogen atoms must there be on adjacent carbon atoms if the signal is a singlet?

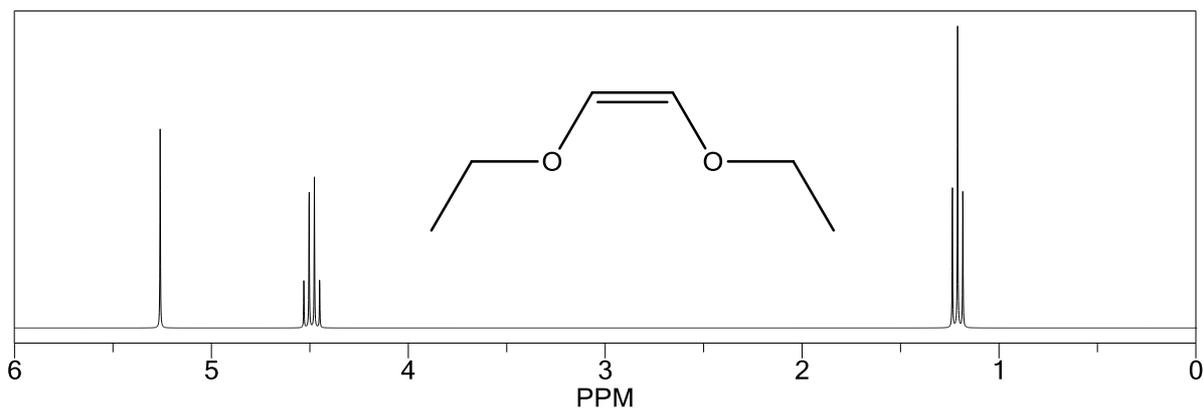
3. The ^1H atoms on the central carbon atom in propane are next to two $-\text{CH}_3$ groups. Into how many lines would you expect their NMR signal to be split?

Model 5: ^1H NMR Spectroscopy - Integration

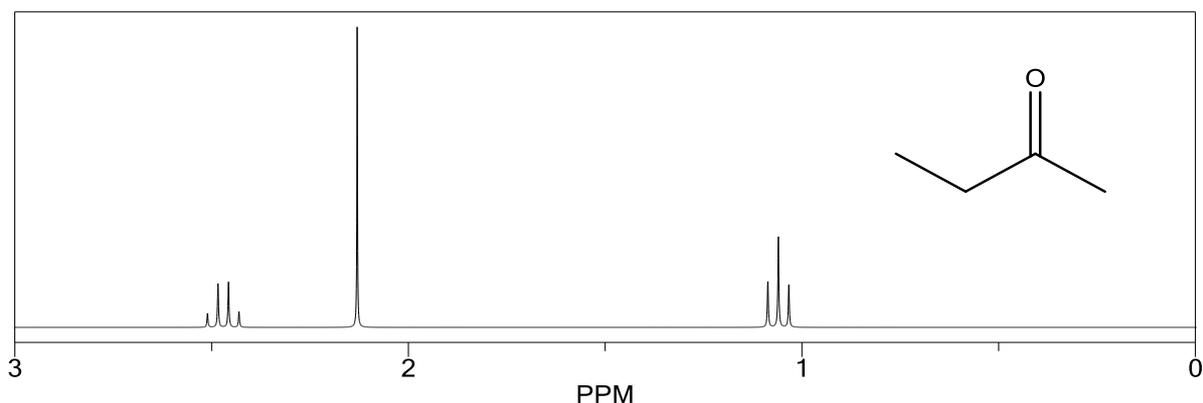
The *integral* of the area under the peak is related to the number of protons it represents. If the ratio of the integrals of two peaks is 2:3, the ratio of protons represented by those peaks is also 2:3.

Critical thinking questions

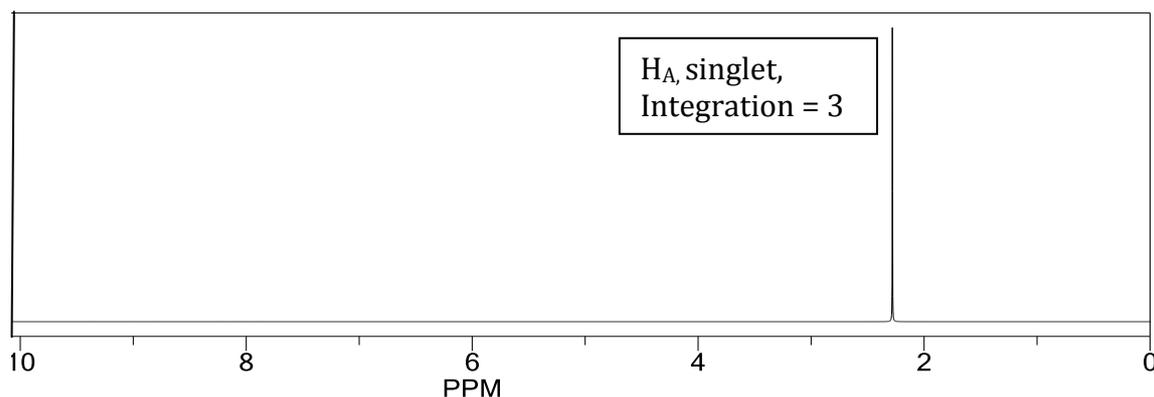
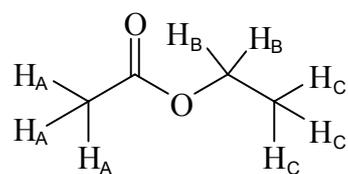
1. Assign the peaks of the ^1H NMR spectrum of (Z)-1,2-diethoxyethylene, shown below, and explain the spectrum in as much detail as you can, including the relative positions of the signals, the splitting and the relative sizes of the peaks.



2. Repeat this exercise for butanone



3. Sketch the resonances you would expect to observe for protons H_B and H_C in the ^1H NMR spectrum of the compound opposite. Ensure that the approximate chemical shifts, as well as peak splittings and signal integrations are incorporated in your answer. (The resonance for H_A is provided as a guide.)



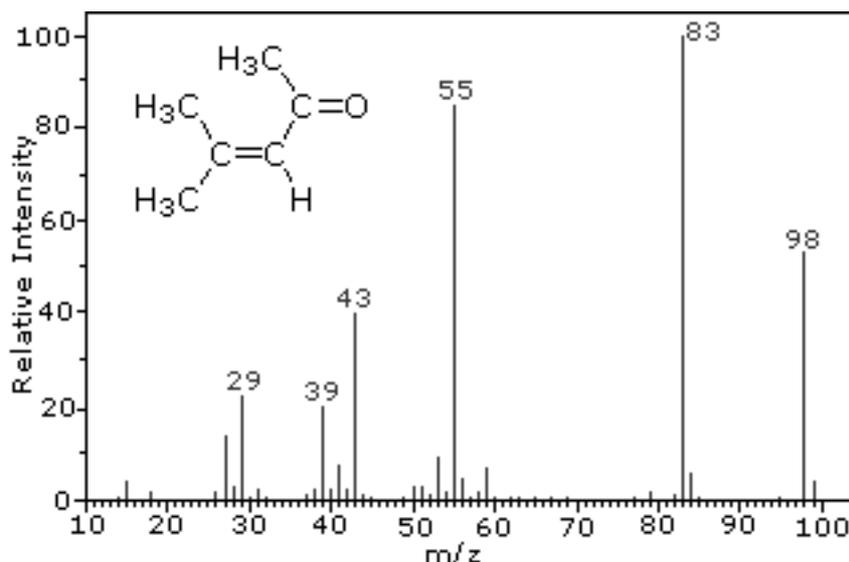
Model 6: Mass Spectrometry

Mass spectrometry allows us to determine the molecular weight of a compound. However, it is a high energy technique, and molecules will often break up into smaller fragments. These fragments can further help in the identification of the compound.

For example, a CH_2CH_3 group has a mass of 29, so a peak at 29 or a difference of 29 in the mass of two peaks might indicate the presence of a CH_2CH_3 group.

Critical thinking questions

1. Identify as many peaks as possible in the mass spectrum of 4-methylpent-3-en-2-one.



2. A compound containing carbon, hydrogen and nitrogen displays a molecular ion peak in its mass spectrum at m/z 41 and a fragment ion at m/z 15. Give the structure of a compound which is consistent with these data.

Model 7: Combined Use of Mass Spectrometry and IR, UV-Visible and NMR Spectroscopy to Identify Unknown Compounds.

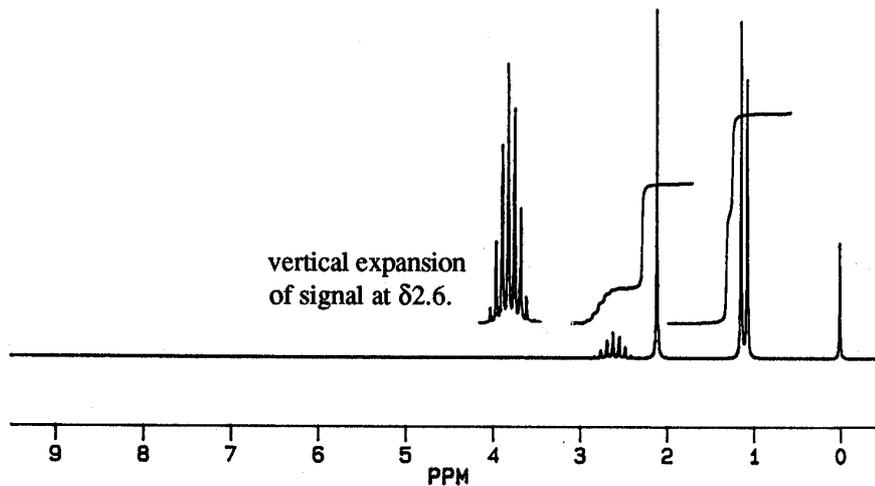
Commonly, all of these techniques are used to identify an unknown or newly synthesized compound as unambiguously as possible. The compound must be consistent with each spectrum. Each technique has its own strengths:

- mass spectrometry – helps to identify the molecular mass and, through the fragment pattern, can also be used to identify groups that are present (such as $-\text{CH}_3$, $-\text{C}_6\text{H}_5$ or $-\text{COCH}_3$).
- UV – Visible spectroscopy – identifies the presence / absence of conjugation such as aromatic rings
- IR spectroscopy – identifies the presence of common bonds, especially $\text{C}=\text{O}$ and $\text{O}-\text{H}$
- NMR – identifies types of atoms present (chemical shifts), relative numbers of each atom type (integration) and which groups are bonded together (coupling).

When performing this task, it is common to go through each piece of evidence to identify the parts of the molecule and to put them together. This can be a cyclical procedure with each spectrum examined more than once.

Critical thinking questions

1. A compound has a strong absorption near 1720 cm^{-1} in its infrared spectrum and a parent ion at m/z 86 in its mass spectrum. Its ^1H n.m.r. spectrum is given below. Give a structure consistent with these data.



2. A compound has a strong absorption in the infrared spectrum near 1700 cm^{-1} and molecular ions at m/z 166 and 168 in a 1:1 ratio in its mass spectrum. The ^1H NMR spectrum is given below. Give a structure consistent with these data.

