

CHEM1102 Worksheet 4: Spectroscopy Workshop (1)

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 7. Spectroscopy Workshop (2) will follow in the week 5 tutorial.

Model 1: Infrared (IR) Spectroscopy

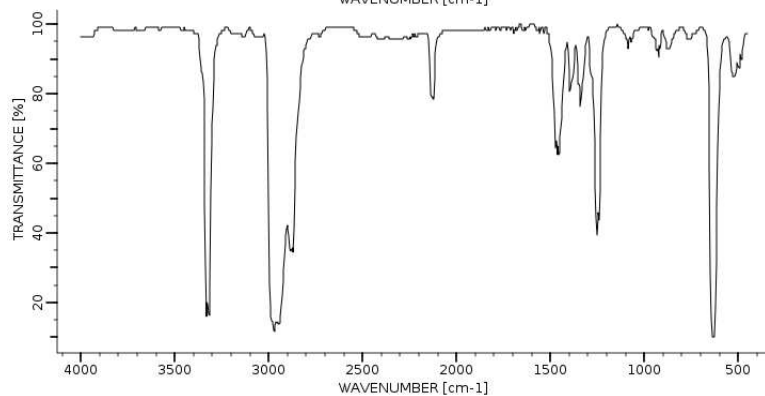
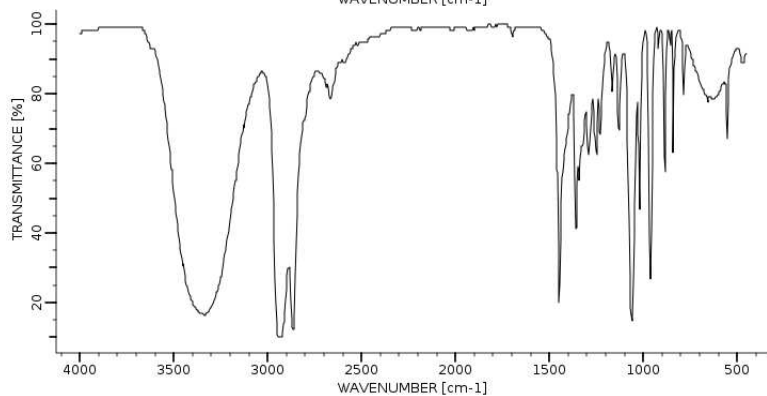
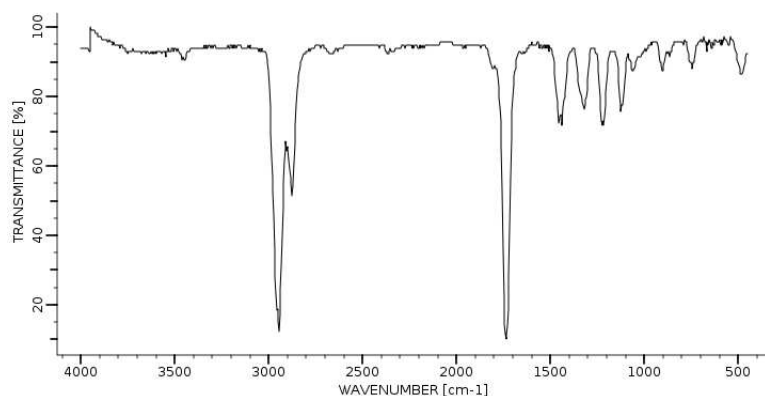
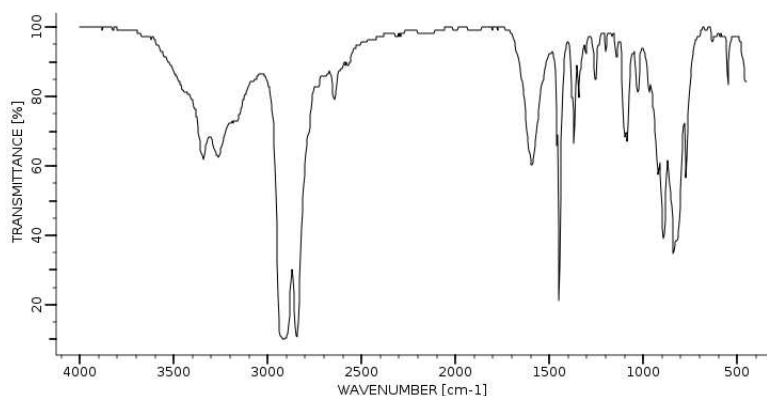
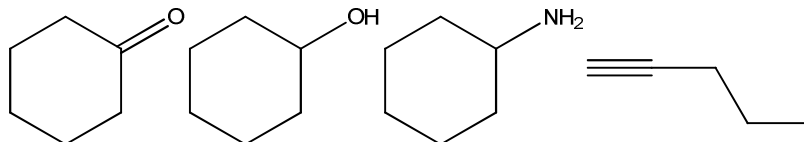
You have seen in lectures how bonds stretch and bend. A light wave of the correct frequency will be in resonance with a bond in motion and transfer its energy to this motion, like a parent pushing a swing. Light absorbed by the molecule in this manner falls in the infrared range. The frequencies at which 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

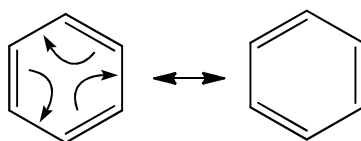
- Use the characteristic stretching frequencies to match the four compounds below to their IR spectrum.



Model 2: UV-Visible Spectroscopy

In Worksheet 3, you saw how a chain of double bonds, each separated by exactly one single bond could be drawn in different resonance forms. This pattern of double-single-double bonds is called *conjugation*.

Benzene is the classic example of a conjugated molecule.

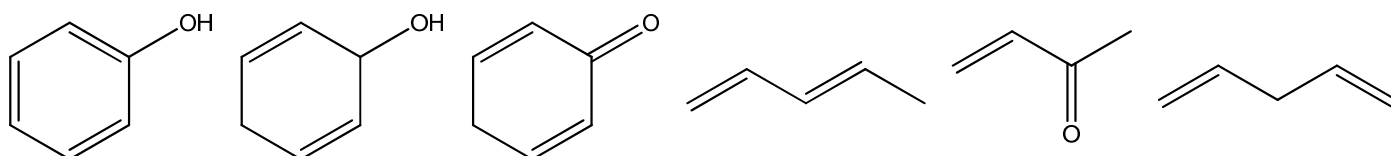


In CHEM1101, you learned about molecular orbitals. In conjugated molecules, the energy needed to excite an electron from the *highest occupied molecular orbital* (HOMO) to the *lowest unoccupied molecular orbital* (LUMO) is in the ultraviolet or even in the visible region of the spectrum.

For conjugated systems, this LUMO-HOMO energy difference falls in the UV-Vis range.

Critical thinking questions

1 Which of the molecules below are conjugated?



2. Circle the molecules above which would show a peak in the UV-Vis spectrum?

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



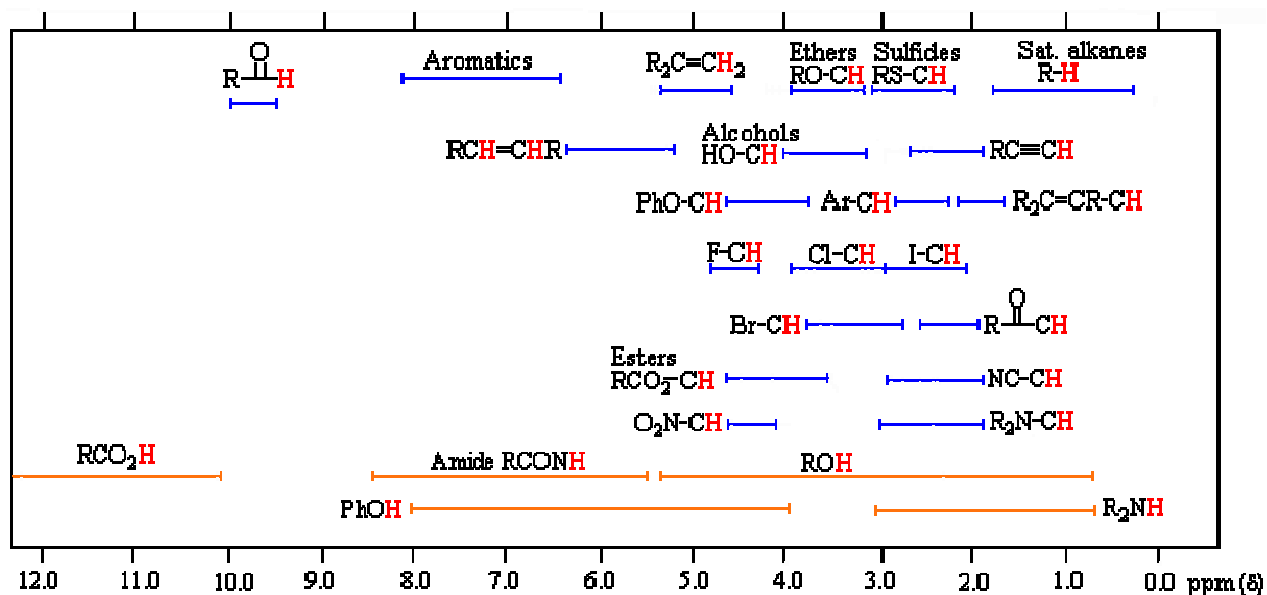
2. How many signals would you expect in the ^1H spectra for these compounds?

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

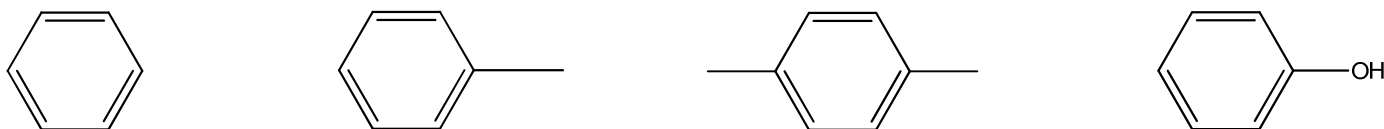
The chemical shift tells us what other atoms are nearby. If the ^1H is bonded, or near, to an electronegative atom like O, N or a halide, the electron density around the nucleus is lowered and its chemical shift is *increased*.

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).

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



3. Predict the *number* of signals and the approximate *chemical shifts* for the molecules below.



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

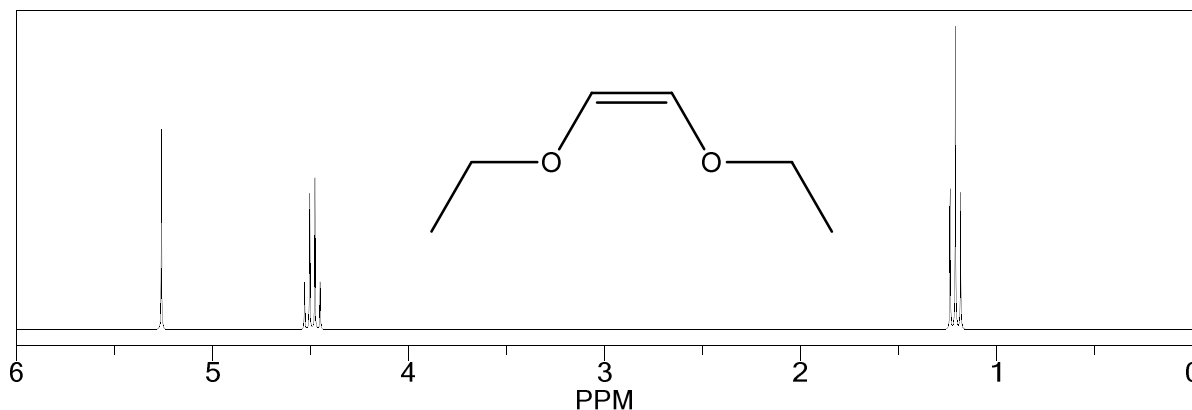
1. What is the relationship between the number of peaks into which a signal is split and the number of hydrogen atoms on the adjacent carbon atoms?
2. How many hydrogen atoms must there be on adjacent carbon atoms if the signal is a singlet?
3. The ^1H atoms on the central carbon atom in propane are 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

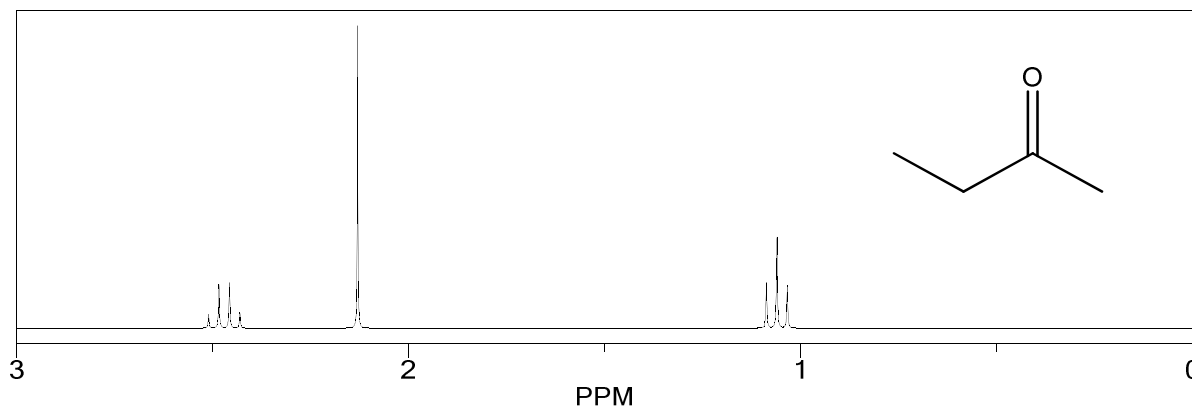
The height of a peak (specifically the *integral* of the area under the peak) is related to the number of protons it represents. If the ratio of the integrals of two peaks is 2:3, the ratio of protons represented by those peaks is also 2:3.

Critical thinking questions

1. Assign the peaks of the ^1H NMR spectrum of (*Z*)-1,2-diethoxyethane, shown below, and explain the spectrum in much details as you can, including the relative position 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.)

