

CHEM1002 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 the quiz in the week 5 tutorial.

Model 1: Infrared (IR) Spectroscopy

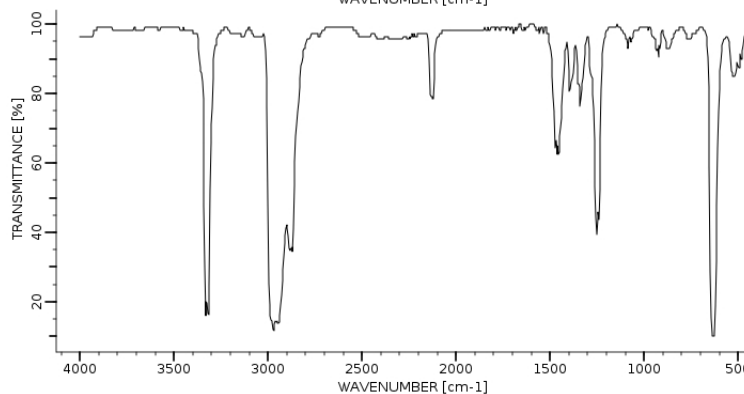
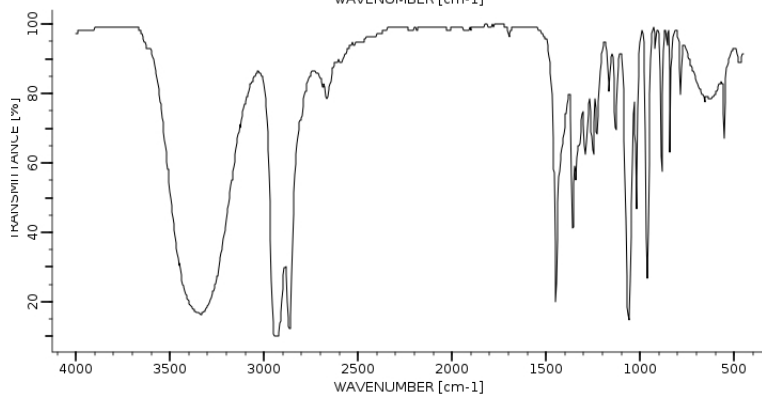
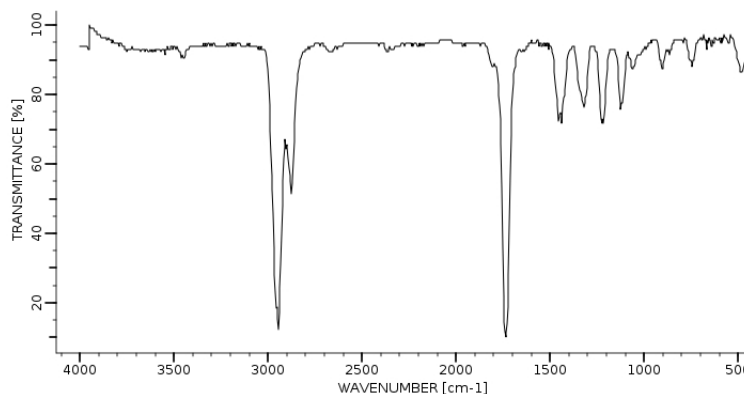
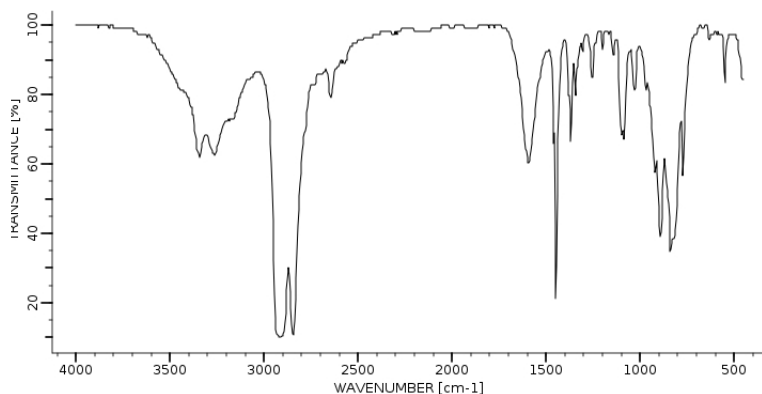
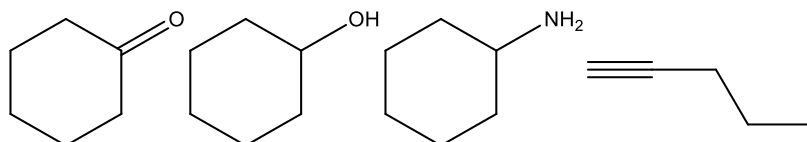
You have seen in lectures how bonds stretch and bend. A light wave of the correct frequency will be in resonance with a bond in motion and transfer its energy to this motion, like a parent pushing a swing. Light absorbed by the molecule in this manner falls in the infrared range. The frequencies at which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

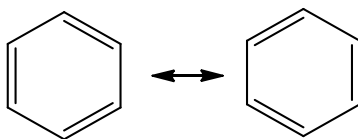
- Use the characteristic stretching frequencies to match each of the four compounds below to its IR spectrum.



Model 2: UV-Visible Spectroscopy

In Lecture 20 of CHEM1001, you saw that sometimes it is possible to draw two or more Lewis structures for a molecule. In organic chemistry, this occurs when there is a chain of double bonds, each separated by exactly one single bond. This pattern of double-single-double bonds is called *conjugation*.

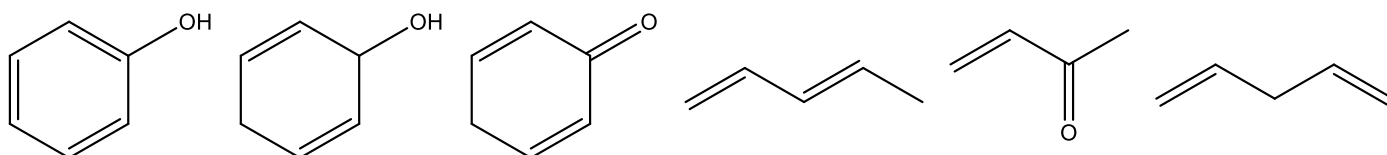
Benzene is the classic example of a conjugated molecule. Both of the Lewis structures below are possible:



Normally, the energy required to excite an electron in a molecule is very large and corresponds to ultra-violet or even higher energy light. For this reason, most compounds do not absorb visible light and are white in colour. However, for conjugated systems, the energy required to excite one of the π electrons falls in the UV-visible range. This means that the molecules absorb light in the UV-visible range leading to coloured molecules such as carotene, found in oranges, and curcumin, found in turmeric.

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: ^{13}C NMR Spectroscopy – Number of Signals

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 if they are in the same **chemical environment**. This occurs when:

- they are attached to exactly the same atoms (e.g. the 6 carbon atoms of benzene 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

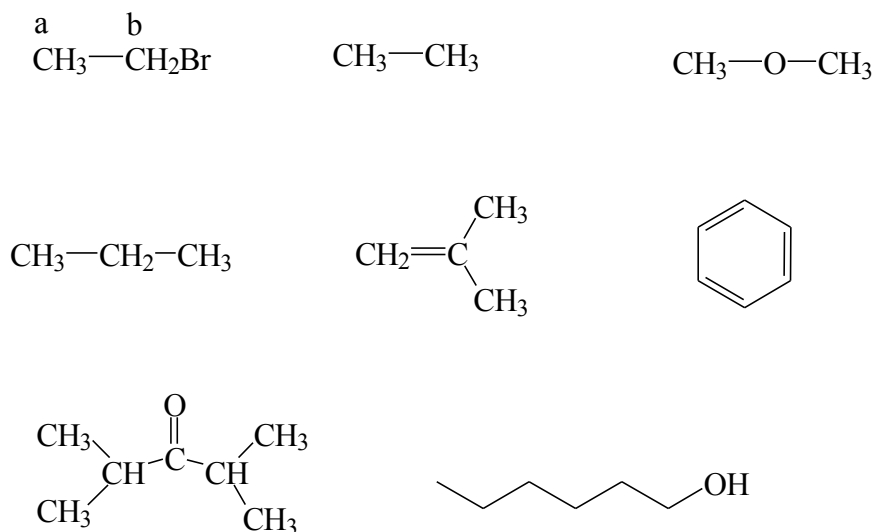
1. Indicate each C environment in the molecules below.



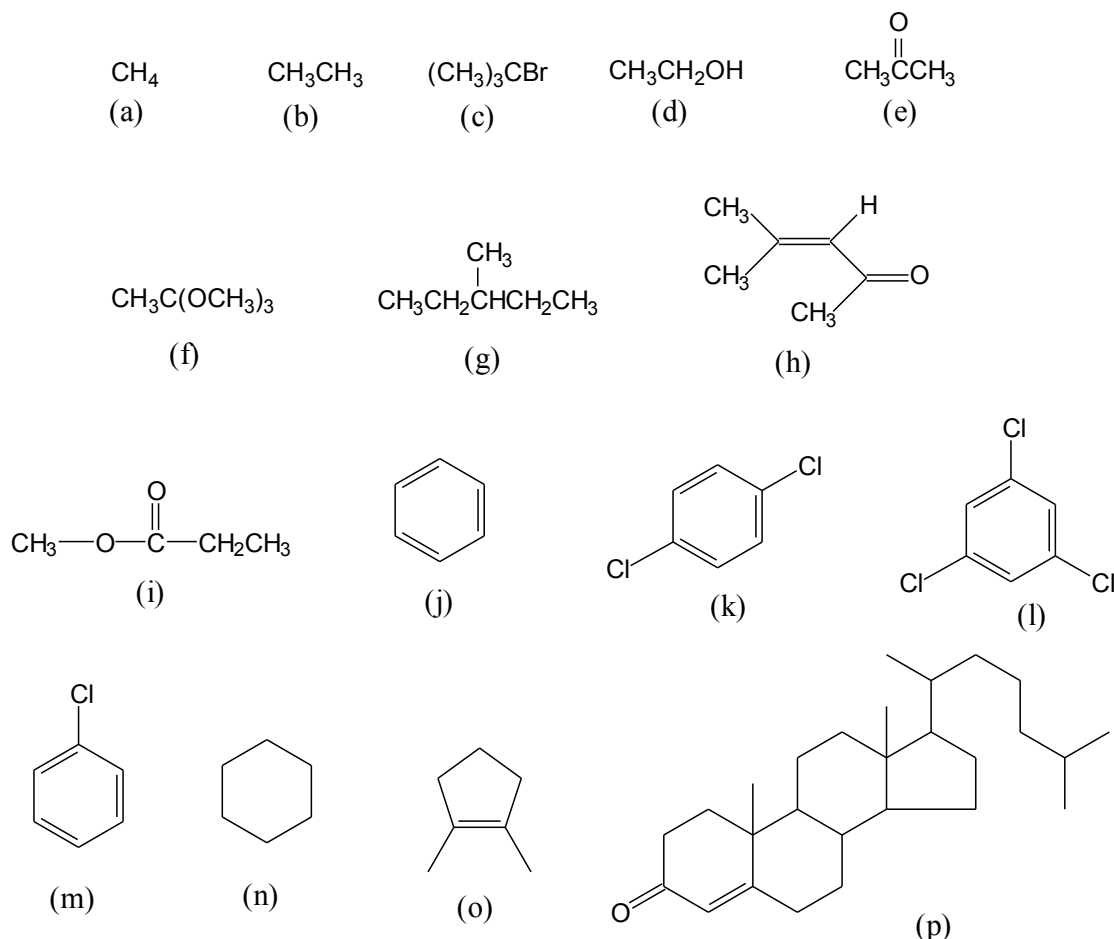
2. How many signals would you expect in the ^{13}C spectra for these compounds?

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

3. By using the letters a, b, c, *etc.*, label the equivalent sets of carbon atoms in the following compounds. The first compound has been done as an example.



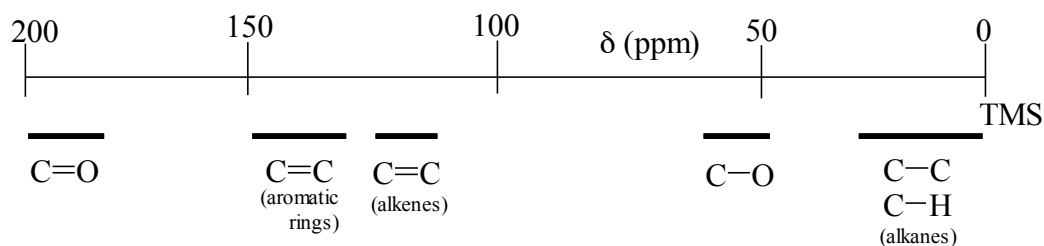
4. How many signals would you expect to find in the ^{13}C NMR spectrum of the following compounds?



Model 4: ^{13}C NMR Spectroscopy – Chemical Shifts

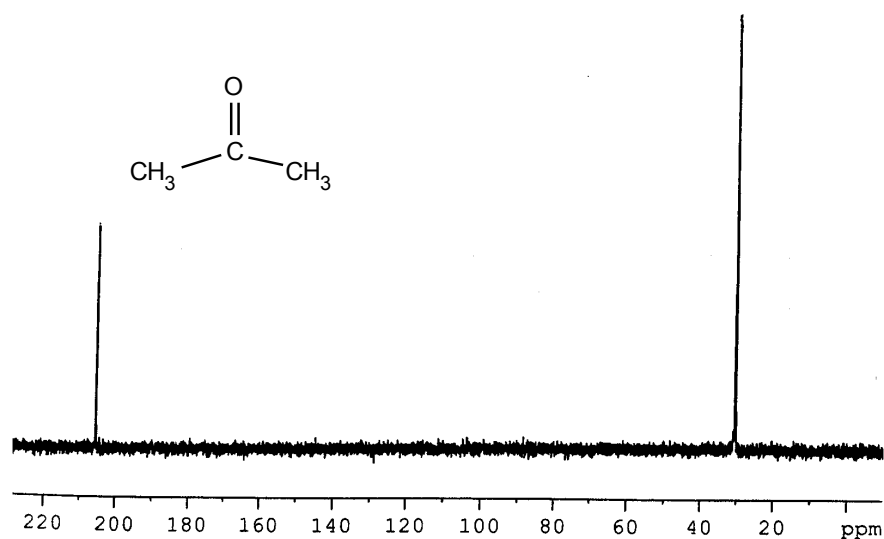
The “chemical shift” is the position of the signal or peak in the ^{13}C NMR spectrum. It tells us what other atoms are nearby. If the ^{13}C atom is bonded, or near, to an electronegative atom like O, N or a halide, the electron density around the nucleus is lowered and its chemical shift is *increased*. The *geometry and bonding arrangement* of the carbon atom is also important. A *tetrahedral C* atom (i.e. one making 4 single bonds) has a smaller chemical shift than a *trigonal planar C* atom (i.e. one making one double bond).

The figure below shows the characteristic chemical shifts (δ) for ^{13}C atoms in common groups.

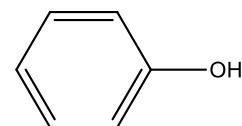
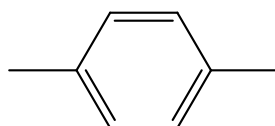
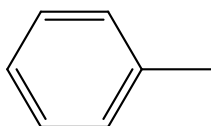


Critical thinking questions

1. The ^{13}C NMR spectrum of acetone is given below. Give the chemical shifts of the signals due to (a) carbonyl carbon and (b) methyl groups.



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



3. A compound has the molecular formula $\text{C}_3\text{H}_8\text{O}$ and has the ^{13}C NMR spectrum given below. Give a structure for this molecule.

