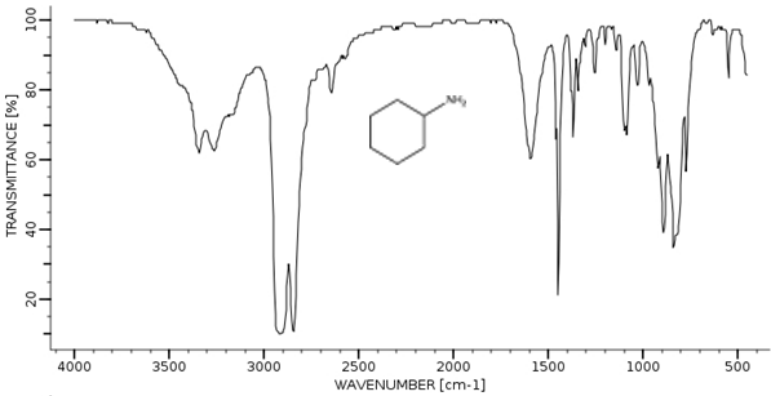
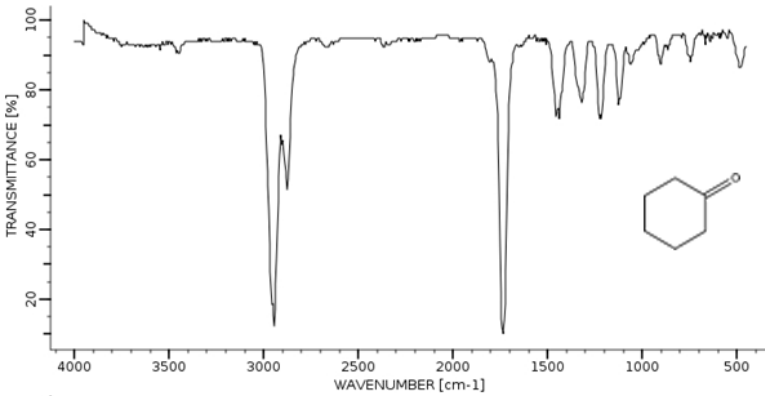
# CHEM1611 Spectroscopy Workshop – Answers to Critical Thinking Questions

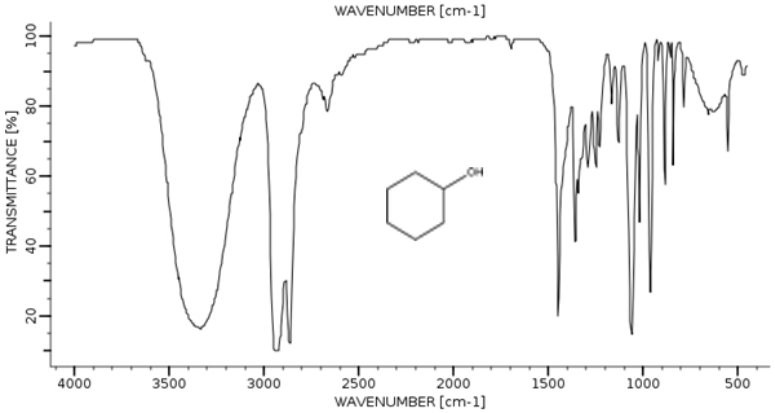
The worksheets are available in the tutorials and form an integral part of the learning outcomes and experience for this unit.

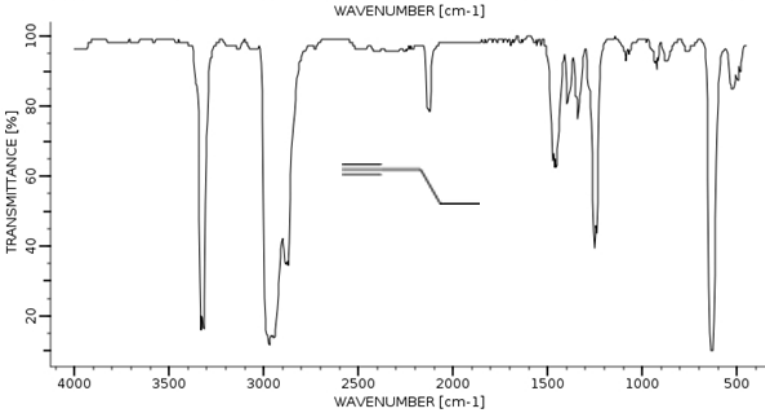
## Model 1: Infrared (IR) Spectroscopy

1. See below.



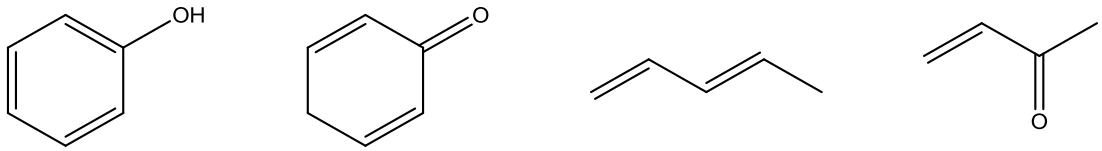




## Model 2: UV-Visible Spectroscopy

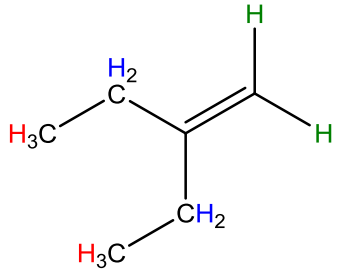
1. See below.

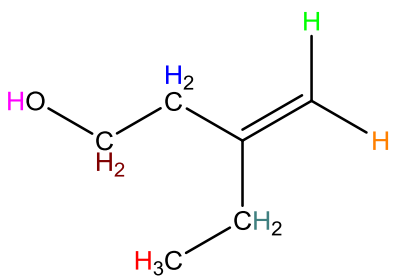



2. All of the above.
3. Restricted to the identification of conjugation.

## Model 3: $^1$H NMR Spectroscopy - Chemical Shifts

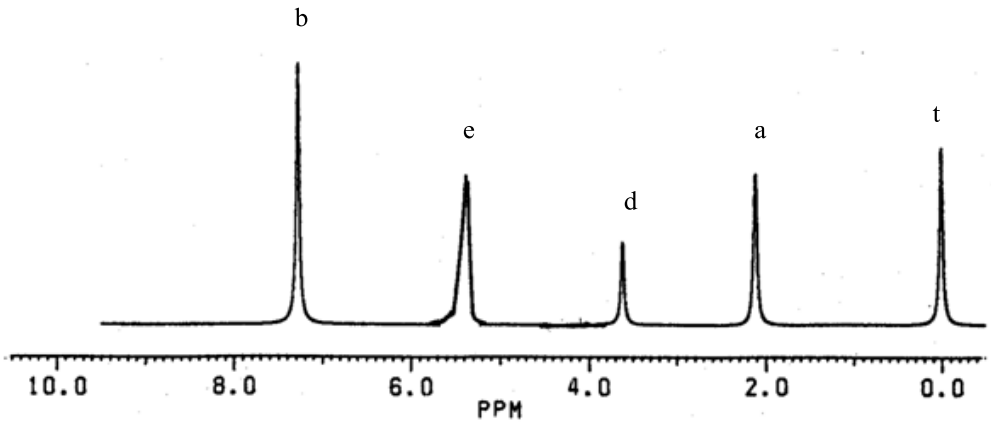
1. The molecule on the left has 3 types of H atom and the molecule on the right has 7 types of H atom.




2. The molecule on the left will give 3 signals and the molecule on the right will give 7 signals.

3.

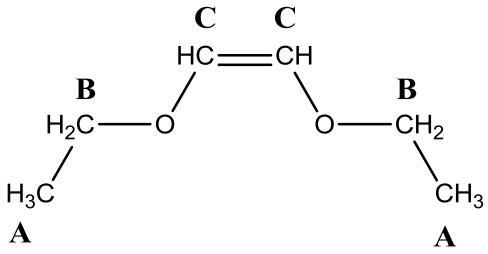



## Model 4: $^1$H NMR Spectroscopy - Coupling

1. Number of peaks = $n$ + 1 where $n$ is the number of hydrogen atoms on adjacent atoms which are not equivalent to the $^1$H giving rise to the signal.
2. None, or the adjacent hydrogen atoms are in the same environment (equivalent).
3. A septet with intensity ratio 1: 6 : 15 : 20 : 15 : 6 : 1.

## Model 5: $^1$H NMR Spectroscopy - Integration

1. There are 3 signals due to the 3 types of $^1$H environment: A, B and C.



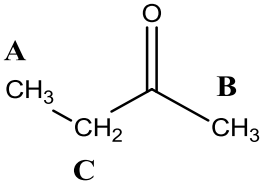

The signal at 1.3 ppm is due to the 6 $^1$H in environment A: relative integral = 3. The signal is split into a 1:2:1 triplet due to coupling to the 2 $^1$H on the neighbouring $CH_2$ group (B).

The signal at 4.5 ppm is due to the 4 $^1$H in environment B: relative integral = 2. The signal has a higher chemical shift than that for group A due to the presence of the electronegative O atom. The signal is split into a 1:3:3:1 quartet due to coupling to the 3 $^1$H on the neighbouring $CH_3$ group (A).

The signal at ~5.3 ppm is due to the 2 $^1$H in environment C: relative integral = 1. The signal has a higher chemical shift than that for group A or B as the $^1$H atoms are on a $sp^2$ C atom that is bonded to an electronegative O atom. There are no $^1$H on the neighbouring atoms, except the other equivalent $^1$H atom, so no splitting due to coupling is observed.

Note that the relative number of hydrogen atoms in each environment given by the integration is 3:2:1, but the actual number of hydrogen atoms is 6:4:2.

2. There are 3 signals due to the 3 types of $^1$H environment: A, B and C.



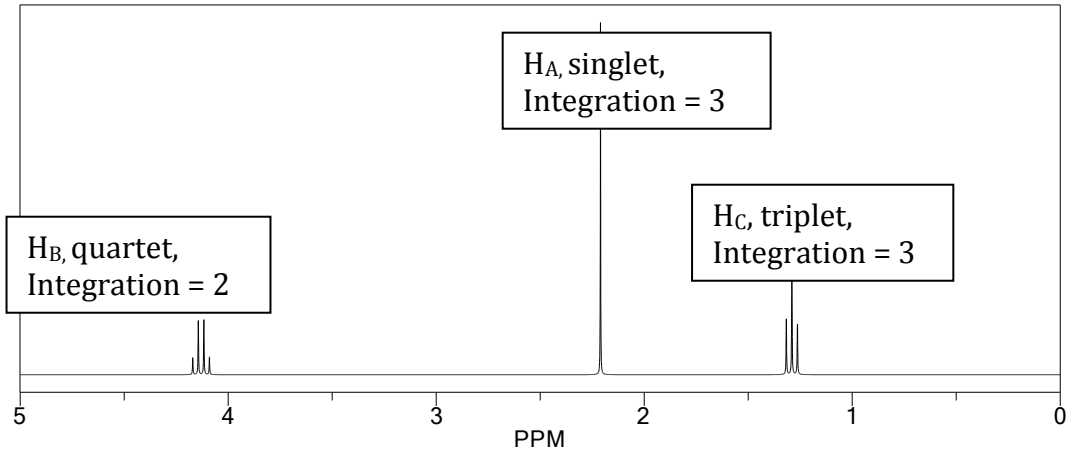

The signal at ~1.1 ppm is due to the 3 $^1$H in environment A: integral = 3. The signal is split into a 1:2:1 triplet due to coupling to the 2 $^1$H on the neighbouring $CH_2$ group (C).

The signal at 2.1 ppm is due to the 3 $^1$H in environment B: integral = 3. The signal has a higher chemical shift than that for group A due to the presence of the electronegative O atom. There are no $^1$H on the neighbouring atoms, so no splitting due to coupling is observed.

The signal at ~2.5 ppm is due to the 2 $^{1}H$ in environment C: integral = 2. The signal has a higher chemical shift than that for group A due to the presence of the electronegative O atom. The signal is split into a 1:3:3:1 quartet due to coupling to the 3 $^{1}H$ on the neighbouring $CH_3$ group (A).

3. $H_B$ have the highest shift since they are closest to the electronegative O atoms. There are two $H_B$ atoms so the signal has an integral of 2. The $H_B$ atoms are coupling to 3 × $H_C$ atoms giving rise to a $(n + 1) = (3 + 1) = 4$ line multiplet (a *quartet*).

$H_C$ have the lowest shift since they are further from the electronegative O atoms. There are three $H_B$ atoms so the signal has an integral of 3. The $H_C$ atoms are coupling to 2 × $H_B$ atoms giving rise to a $(n + 1) = (2 + 1) = 3$ line multiplet (a *triplet*).




## Model 6: Mass Spectrometry

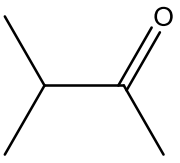
1.

| *m / z* | Fragment |
|---|---|
| 99 | M+ peak: containing one $^{13}C$ (1% chance). |
| 98 | Molecular ion – $C_6H_{10}O$ |
| 83 | $C_5H_7O$ (loss of $-CH_3$ - 15 mass units) |
| 55 | $C_4H_7$ (loss of $-CH_3CO$ - 43 mass units) |
| 43 | $C_3H_7$ (loss –of $CH_3COC$ – 45 mass units) |
| 39 | $C_3H$ |
| 29 | CHO or $C_2H_4$ |

2. Acetonitrile: $CH_3C{\equiv}N$.

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

1. 3-methylbutan-2-one:



2. 2-bromoethyl acetate: