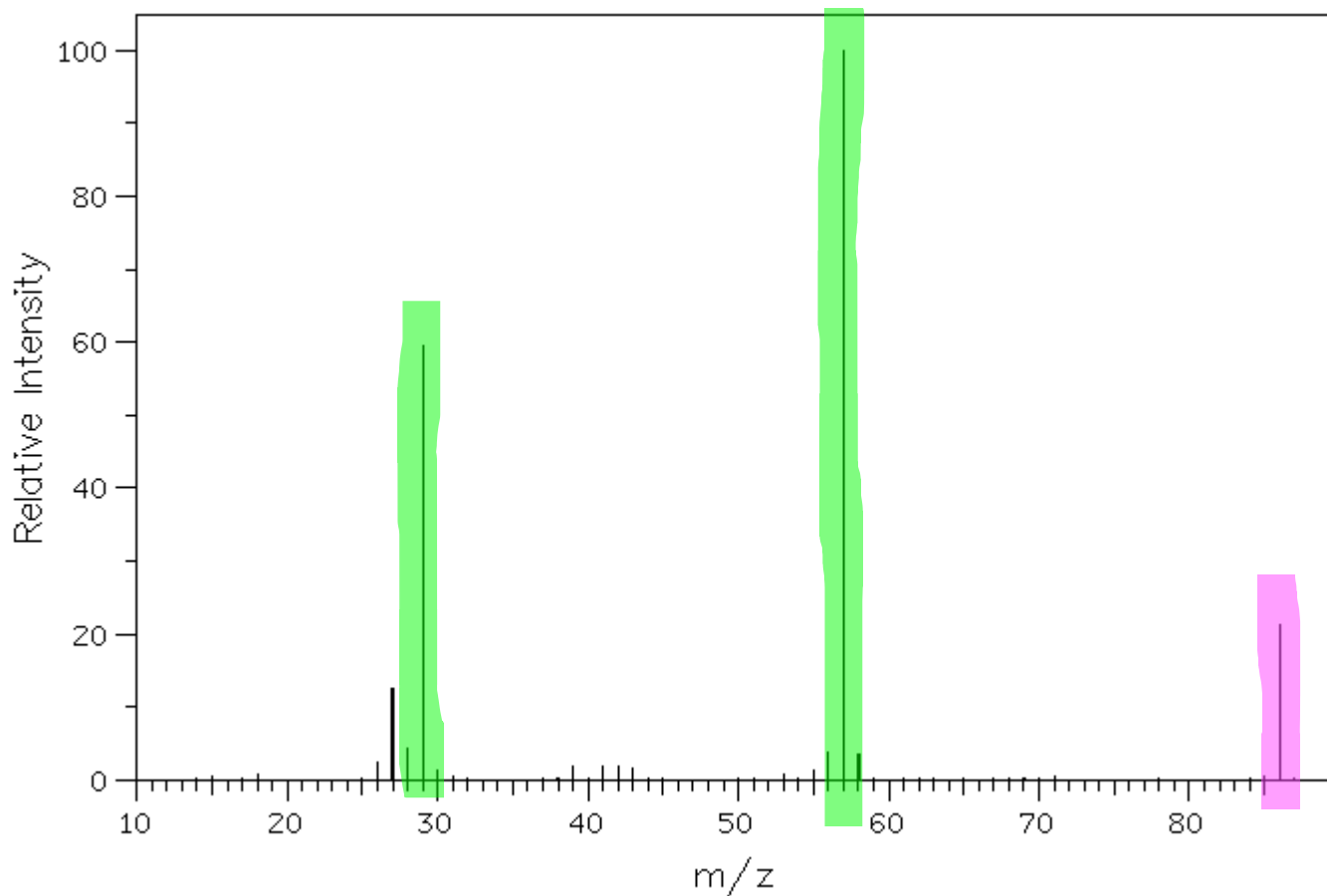
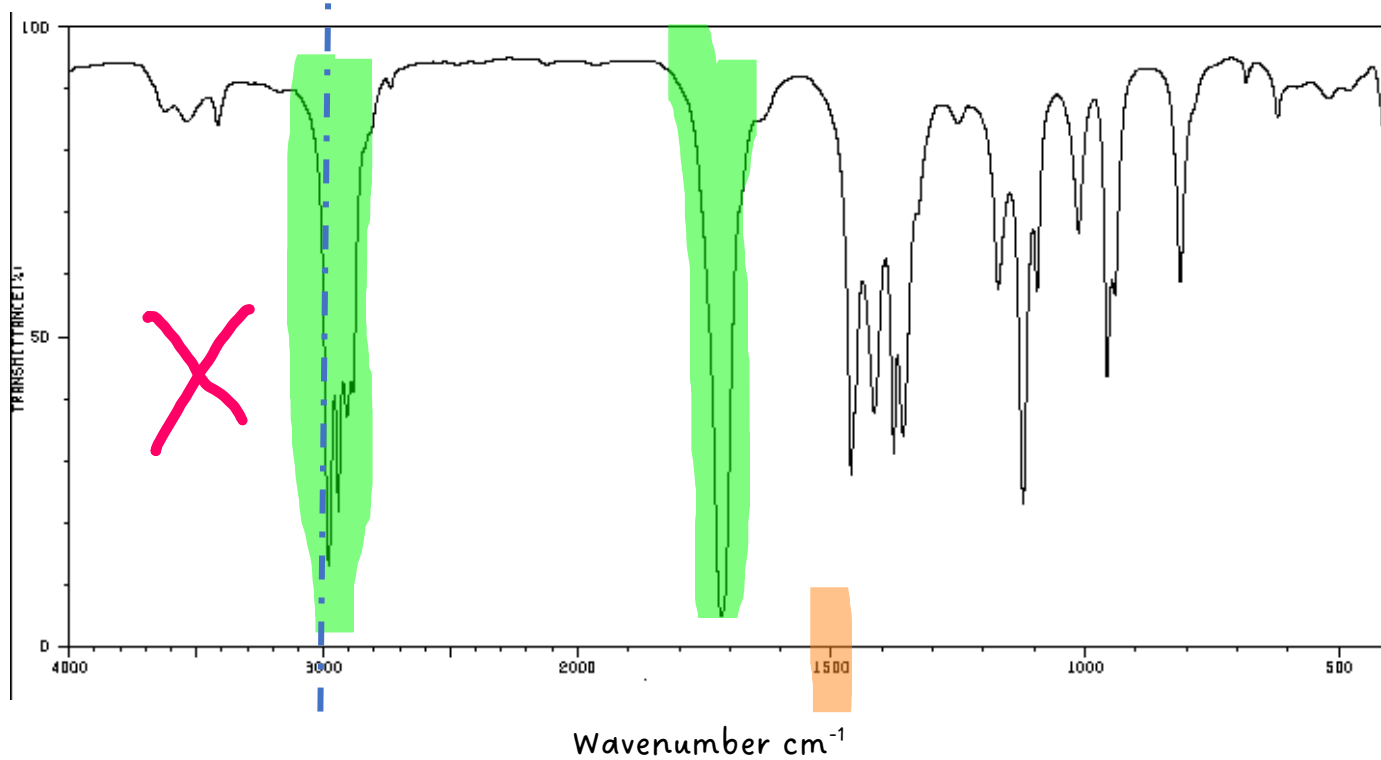


Sample Task

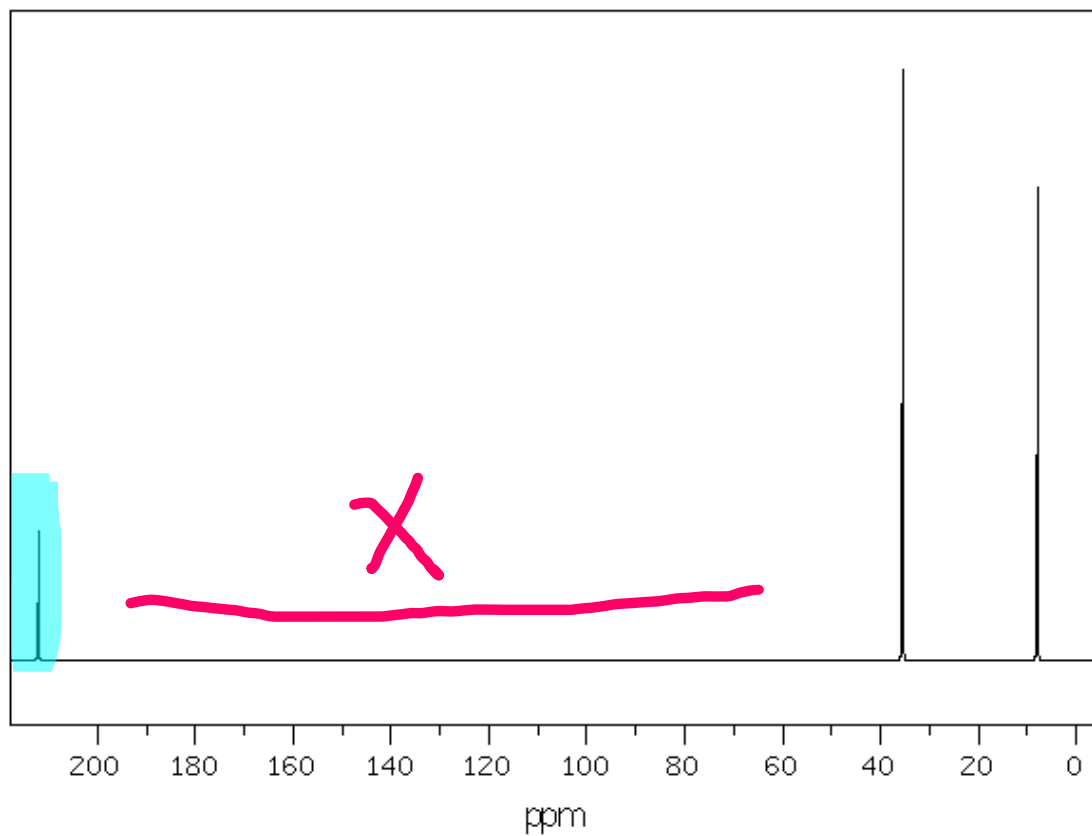
Mass Spec



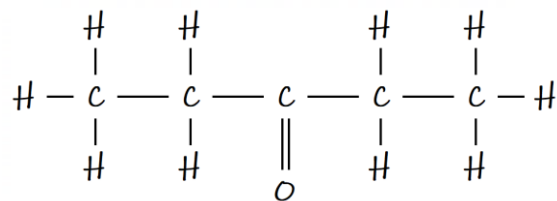
IR



^{13}C NMR



The molecule is:



Using the mass spec, the M^+ ion is at 86 m/z which gives a molar mass of 86 g mol^{-1} . The lack of 2 peaks (M^+ and $M+2$) in a 3:1 or 1:1 ratio excludes Cl and Br respectively, thereby eliminating haloalkanes and acyl halides. Further evidence for the absence of Cl and Br are the lack of strong peaks in the IR between 500-600 cm^{-1} (C-Br) and 600-800 cm^{-1} (C-Cl) associated with haloalkanes. Haloalkanes can therefore also be eliminated. The fact that the M^+ peak has an even value suggests zero (or an even number) of N atoms. The absence of weak-medium peaks between 3300 and 3500 cm^{-1} due to N-H bond stretching vibrations in the IR spectrum further suggests that there are no N atoms, excluding both amides and amines.

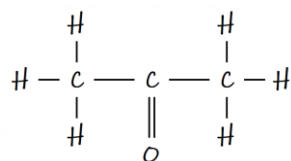
Looking at the IR spectra, a strong peak exists between 2550-3000 cm^{-1} , associated with C-H bond stretching vibrations, common in all organic molecules.

It is possible to use the absence of significant peaks ($>1500 \text{ cm}^{-1}$) to exclude O-H bond of an alcohol (which would be seen between 3200-3550 cm^{-1}) and carboxylic acid (2500-300 cm^{-1}), both present as strong, broad peaks if in the molecule.

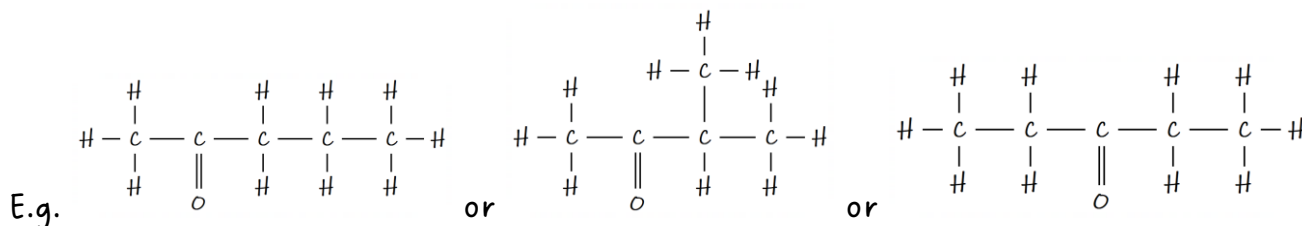
The strong peak at around 1700 cm^{-1} is typical of C=O bond stretching vibrations. Other molecules that contain C=O have already been excluded such as amides (molecule does not contain N), acid chlorides (molecule does not contain Cl), and carboxylic acids (molecule does not contain O-H). The peak appears to be in the region 1720-1740 cm^{-1} which could suggest an aldehyde or ketone functional group. Looking at the CNMR spectrum there is a downfield peak at 212 ppm which is in the range associated with a ketone (chemical shift 205-220 ppm); it is too high to be an aldehyde (190-200 ppm). Additional evidence used to exclude an aldehyde is the lack of two medium peaks in the IR spectrum between 2690-2840 cm^{-1} due to C-H bond stretching vibrations that are associated with aldehydes. A peak at 212 ppm is far too high to be associated with C=O of a carboxylic acid, acid chloride or amide - all already previously excluded) or ester. The molecule can't be an ester as the C=O peak seen in the IR is too low (ester C=O peak between 1735-1750 cm^{-1}), and although there are IR peaks between 1000-1300 cm^{-1} that could be considered as evidence for a C-O bond, the CNMR evidence certainly suggests a ketone.

The molecule is a ketone. The three peaks on the CNMR show that there are 3 different C environments and therefore there must be a minimum of 3 carbon atoms.

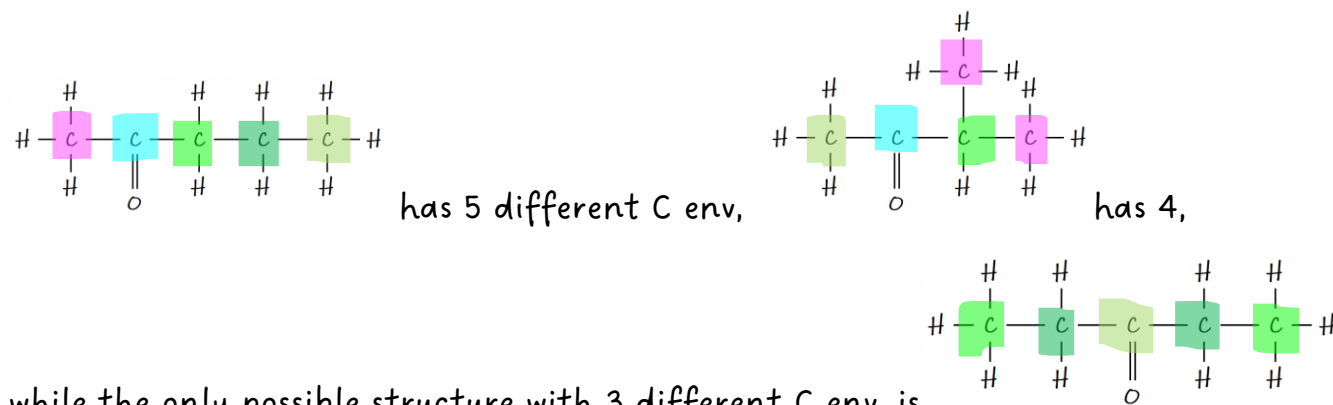
CH_3COCH_3 meets the 3 C environments requirement but is too small a molecule with a molar mass of just 58 g mol^{-1} . $(12 \times 3) + 16 + (1 \times 6)$



To achieve a molar mass of 86 g mol^{-1} and be a ketone the molecule must have 5 C atoms. $(12 \times 5) + 16 + (1 \times 10)$



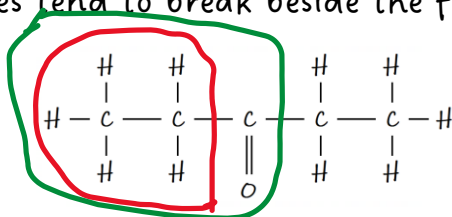
It is possible to narrow these down to the correct structure using the number of different C environments.



while the only possible structure with 3 different C env. is

In the CNMR the most downfield peak/signal due to $\text{C}=\text{O}$ is at 212 ppm, the $-\text{CH}_2-$ peak at 35 ppm (falls within approx. 15-50 ppm range) and the $-\text{CH}_3$ at 8 ppm (falls within approx. 8-35 ppm range).

Finally looking at the Mass spec, it is possible to find fragments to back up the proposed structure: Molecules tend to break beside the functional group.



Peak @ 57 m/z $\text{CH}_3\text{CH}_2\text{CO}^+$ This is the base peak, and the most abundant fragment since it can occur by fragmentation from either end as $\text{C}=\text{O}$ is C atom #3.

Peak at 29 m/z CH_3CH_2^+

Peak at 28 m/z CO^+ (a common fragment in molecules with a carbonyl / $\text{C}=\text{O}$ group).

NOTE:

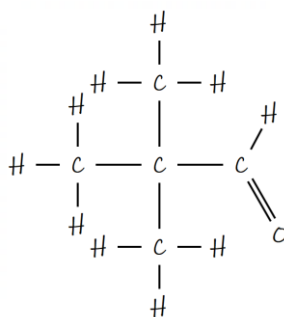
There is no set order to tackle the spectra. Many people will start with the IR (to identify the functional groups) and then CNMR to back up presence of / explain exclusion of specific functional groups as well as work out the number of different C environments.

For Excellence it is all about integrating ideas from the 3 spectra. It is best to do a 'quick flyover' of all 3 spectra to work out what you can see (and what you can't see) before writing the report.

The more ideas you can 'group' will lead to better integration of the information from the 3 spectra. This also avoids a lot of unnecessary repetition.

E.g. In the Mass Spec, the lack of peaks at $M+$ and $M+2$, in a 3:1 ratio due to Cl isotopes, coupled with no strong peak in the IR between 1785 - 1815 ppm, eliminates the acid chloride functional group.

Student didn't consider / exclude $C=C$ ($3020-3100\text{ cm}^{-1}$) in IR and CNMR (115-140 ppm).



Student could have suggested excluding CCC(=O)C as this has the correct molar mass, and possesses 3 different C environments BUT it is probably not worthwhile including as it has the wrong functional group (in this case the unknown is not an aldehyde but is a ketone).

Student could have ruled out ester (as well as c.acid. acid chloride and amide) from the CNMR earlier in report.