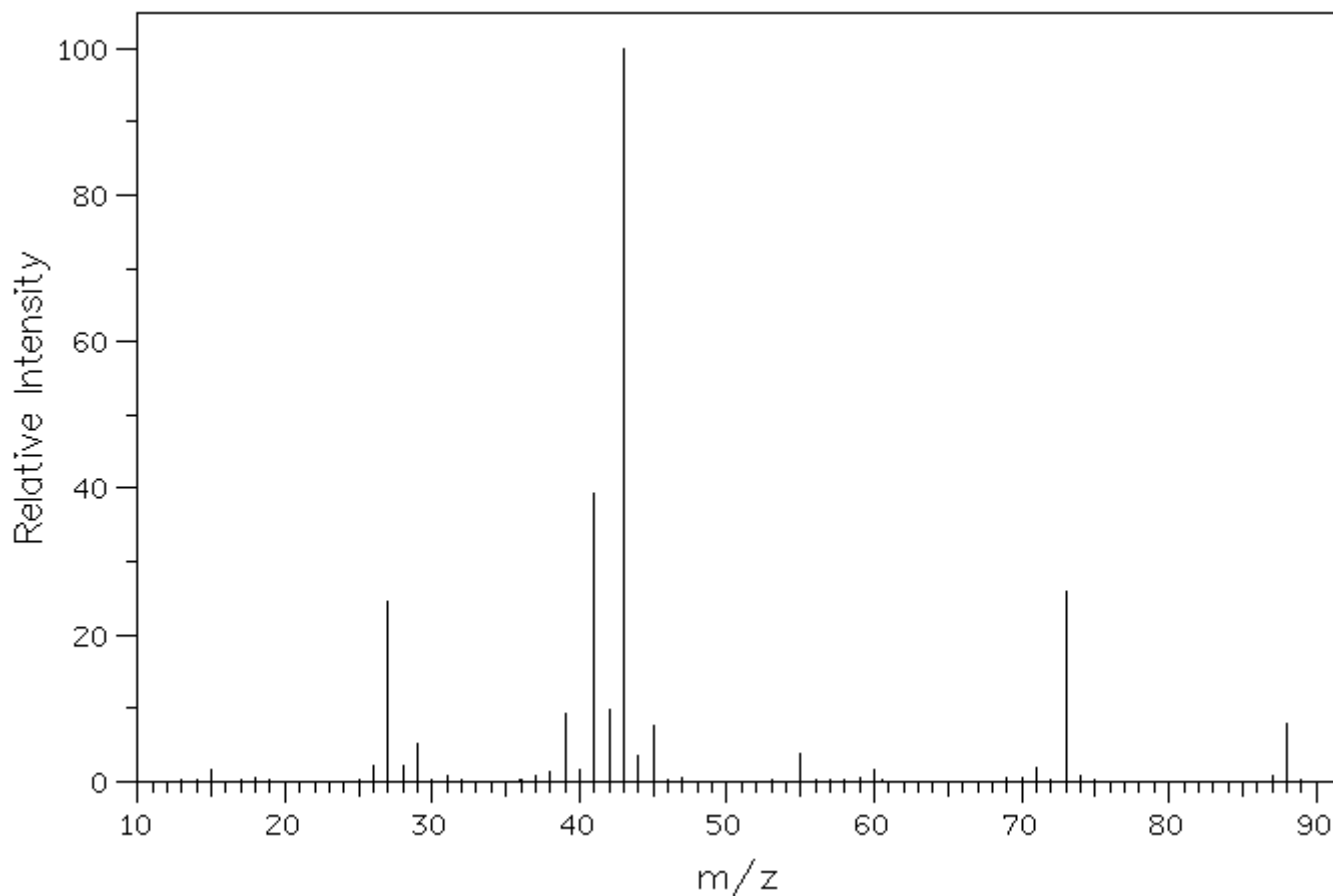
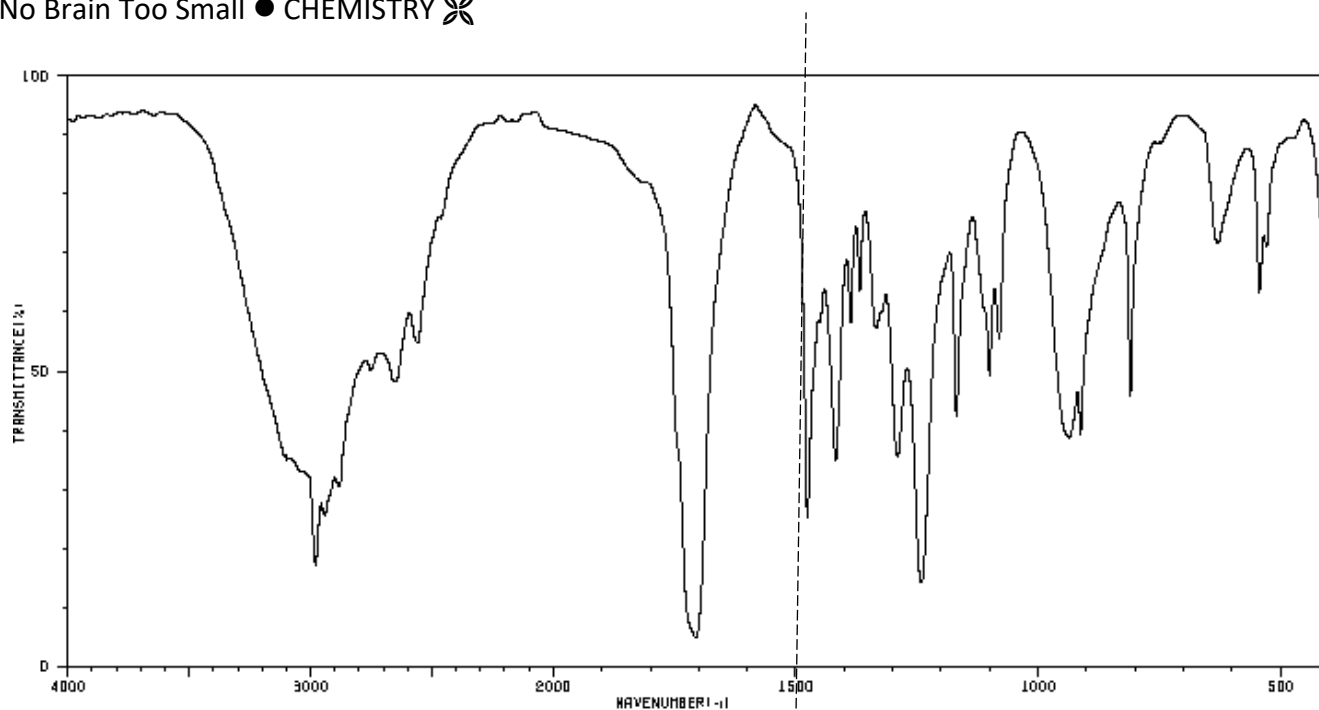


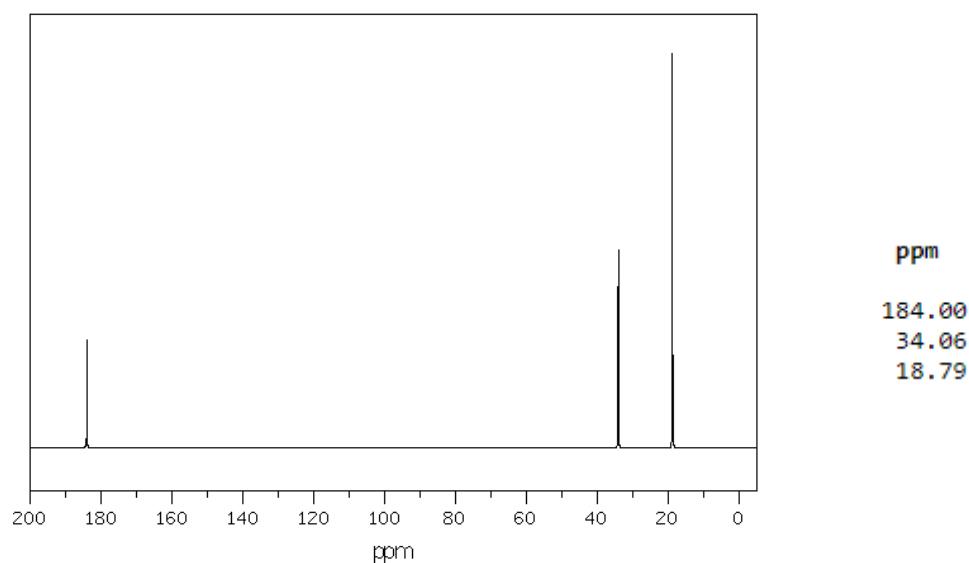
Tackle the questions in number order **1-14** – yes you will jump around the spectra and revisit them!



- M⁺ ion at _____ therefore molar mass is _____ g mol⁻¹.
- N rule? What probably is / isn't there?
- Any Cl or Br? How do you know?
- Use your answers to 4. and 7. to 9. to draw a molecule that has a molar mass matching 1.
- Draw an isomer of your answer in 10. and explain why it could NOT be this isomer.
- Try and assign at least 3 more "fragments" to the mass spec from your proposed structure.

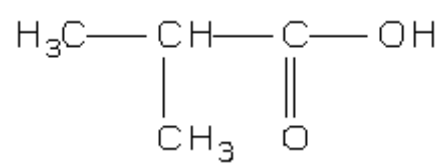


4. Assign **3** peaks above 1500 cm^{-1} . (Hint: there is some overlap but find the one that always has to be there).
5. What “easily recognised” peak is NOT there above 1500 cm^{-1} ? (It’ll match with your answer 2).
6. What is the most likely functional group in this molecule?
12. Once you have a structure can you find any more peaks to match a bond (s) in the IR?

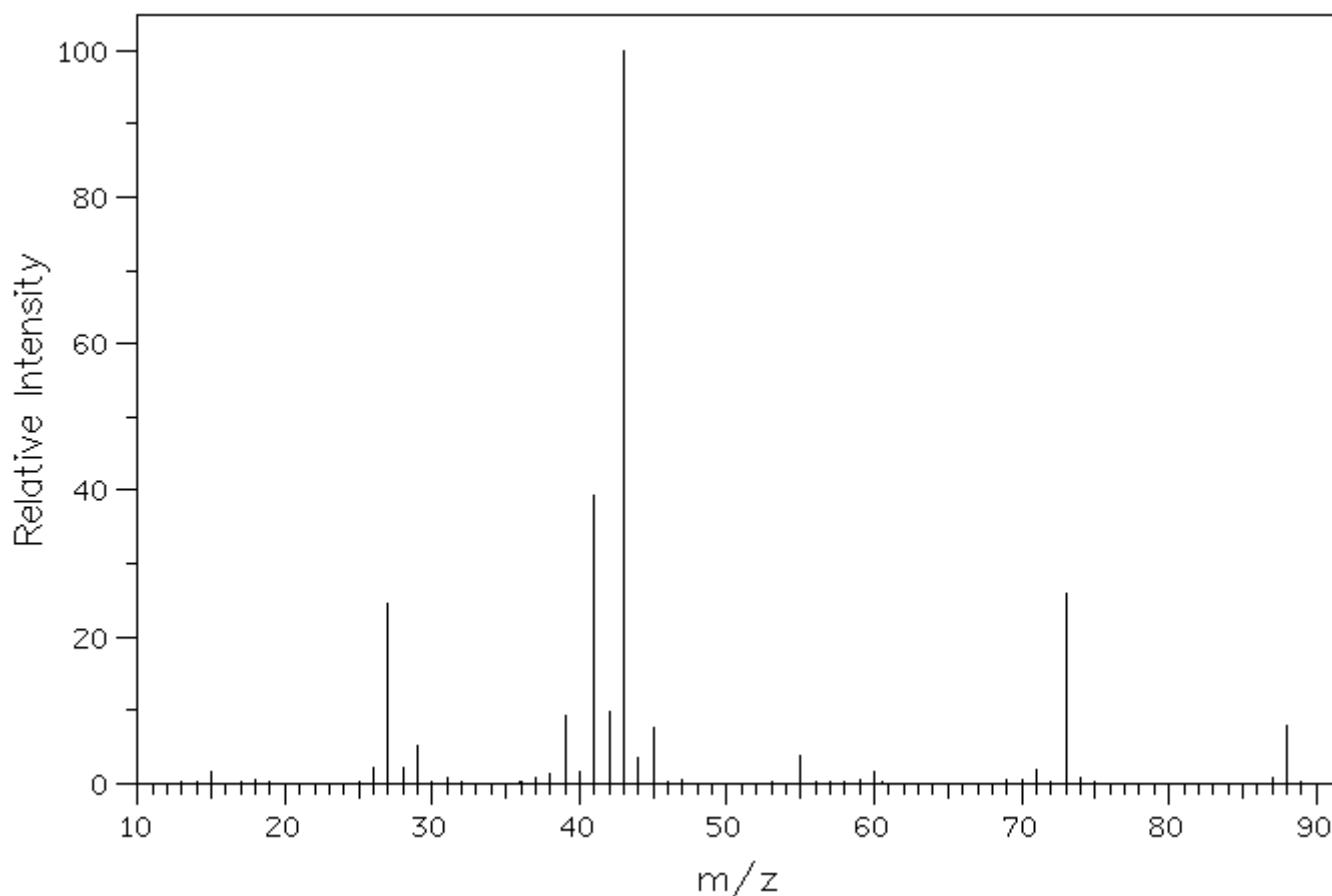


7. At least _____ C atoms
8. How many different C environments?
9. Peak at 184 ppm suggests C atom in a _____ bond
13. Try and assign peaks 34 ppm and 19 ppm to your molecule.

Answer

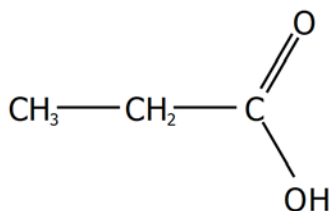


Answers Tackle the questions in number order 1-14



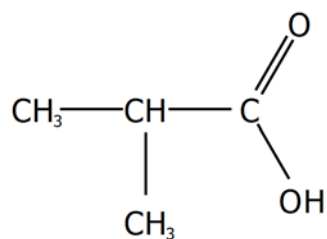
1. M^+ ion at **88 m/z** therefore molar mass is **88 g mol⁻¹**.
 2. N rule? What probably is / isn't there? **Even number so no / even number of nitrogen atoms.**
 3. Any Cl or Br? How do you know? **Neither. No 3:1 ratio or 1:1 ratio of peaks for M^+ therefore no Cl or Br isotopes; eliminates haloalkanes and acyl halides.**
10. Use your answers to 4. and 7. to 9. to draw a molecule that has a molar mass matching 1.

We need a COOH group and 3 carbon environments and molar mass of 88 g mol⁻¹.

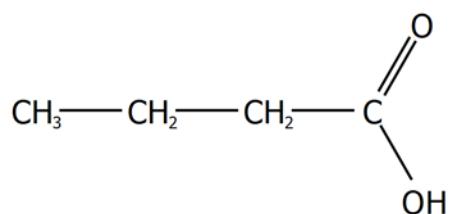


This has the correct functional group and carbon environments but molar mass of 74 g mol⁻¹. Adding one more C atom (and 2 H atoms) would give a molar mass of 88 g mol⁻¹.

To get the right number of C environments the molecule must be branched. This has the correct molar mass and three carbon environments.

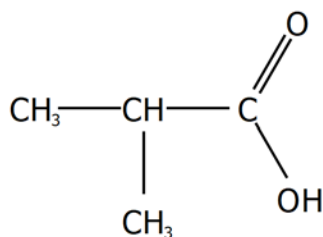


11. Draw an isomer of your answer in 10. and explain why it could NOT be this isomer.

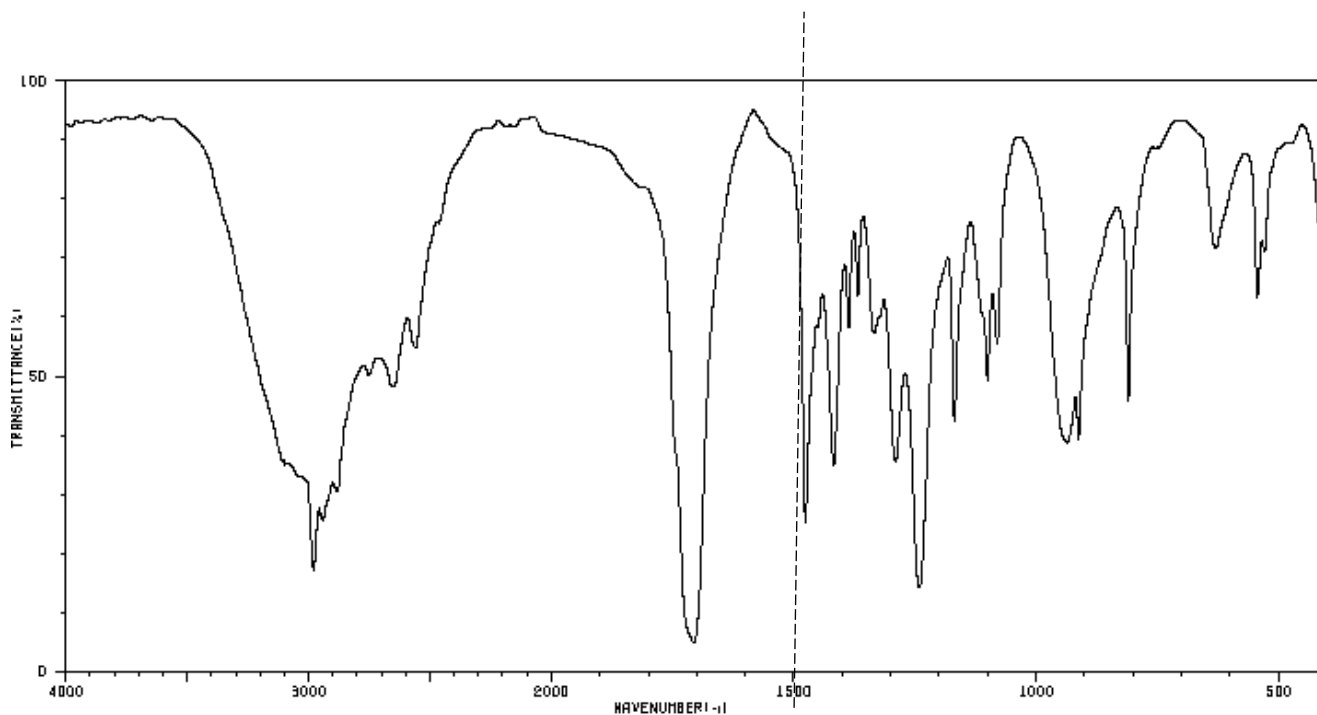


This has the right molar mass but has 4 carbon environments and so cannot be the molecule.

14. Try and assign at least 3 more “fragments” to the mass spec from your proposed structure.



COOH⁺ @ 45 m/z CH₃CHCOOH⁺ @ 73 m/z (CH₃)₂CH @ 43 m/z CO⁺ @ 28 m/z (small)



4. Assign **3** peaks above 1500 cm^{-1} . (Hint: there is some overlap but find the one that always has to be there).

Strong peaks (2-3 peaks) between $2850\text{-}3000\text{ cm}^{-1}$ due to C-H bond stretching vibrations.

Strong and very broad peak (overlaps the C-H peak) between $2500\text{-}3330\text{ cm}^{-1}$ due to O-H bond stretching due to O-H bond of a carboxylic acid.

Strong peak around 1700 cm^{-1} that suggests C=O bond stretching vibration. Molecule might be a carboxylic acid and the peak is a strong peak at $1705\text{-}1720\text{ cm}^{-1}$ which matches a peak expected for a C=O bonding vibration associated with a carboxylic acid.

5. What "easily recognised" peak is NOT there above 1500 cm^{-1} ? (It'll match with your answer 2).
There are no (two) weak to medium peaks at $3300\text{-}3500\text{ cm}^{-1}$ associated with N-H bond stretching vibrations, which is more evidence to eliminate amines and amides. (The peak due to C=O bond stretching vibration associated with the amide is also in the wrong place as this peak is between $1630\text{-}1695\text{ cm}^{-1}$ which is clearly not seen on this IR spectrum).

6. What is the most likely functional group in this molecule?

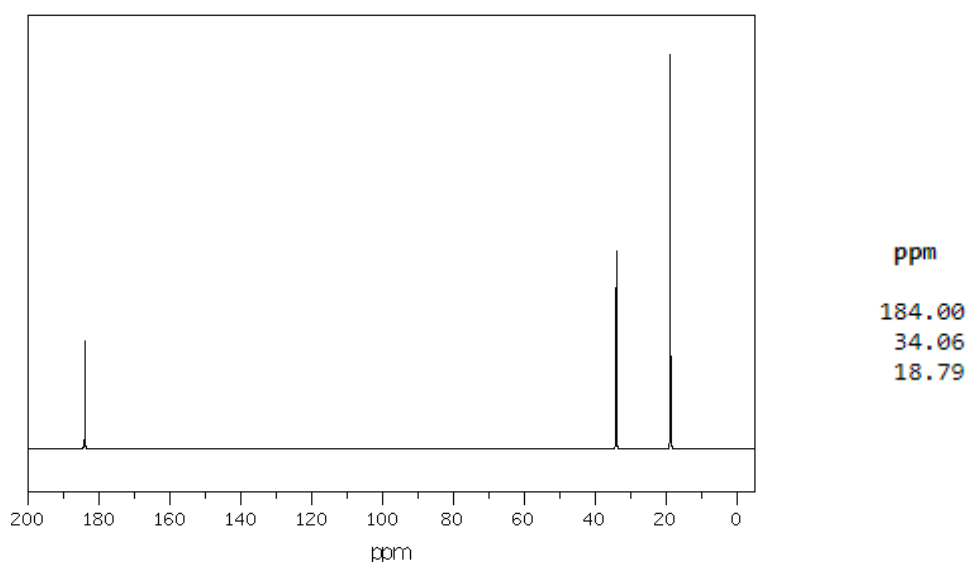
With a C=O and an O-H peak in the region associated with O-H of a carboxylic acid, the likely functional group in this molecule is a carboxylic acid!

12. Once you have a structure can you find any more peaks to match a bond (s) in the IR?

A strong peak between $1000\text{-}1300\text{ cm}^{-1}$ due to O-C bond stretching vibrations associated with carboxylic acids and derivatives.

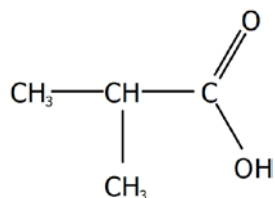
A medium peak between $910\text{-}950\text{ cm}^{-1}$ due to O-H bond bending vibrations associated with carboxylic acids.

A medium peak between $1450\text{-}1470\text{ cm}^{-1}$ due to C-H bond bending vibrations associated with alkanes (most of the molecule is alkane).



7. At least **3** C atoms
8. How many different C environments? **Three**
9. Peak at 184 ppm suggests C atom in a C=O bond. **The Chemical shift for a C=O for carboxylic acids, acid chlorides, amides and esters is between 160-185 ppm which matches this. Acid chlorides have been ruled out (no Cl) as have amides (no N). The molecule is not an ester as it contains an O-H group.**

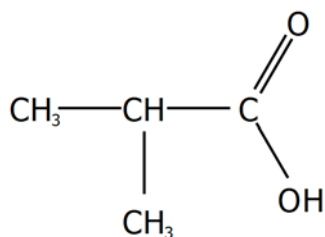
13. Try and assign peaks 34 ppm and 19 ppm to your molecule.



C=O @ 184 ppm, most downfield (160-185 ppm) R₃CH @ 34.06 ppm (25-60 ppm) R-CH₃ @ 18.79 ppm (8-35 ppm)

Report

The molecule is:



In the mass spec the M^+ ion is at 88 m/z therefore molar mass is 88 $g\ mol^{-1}$.

Applying the Nitrogen rule the m/z for the M^+ ion is an even number so there are no nitrogen atoms or an even number of nitrogen atoms in the molecule. There is an absence of 3:1 ratio or 1:1 ratio of peaks for M^+ therefore no Cl or Br isotopes; eliminates haloalkanes and acyl halides.

Looking at the IR spectrum, there are strong peaks (2-3 peaks) between 2850-3000 cm^{-1} due to C-H bond stretching vibrations.

There is a strong and very broad peak (overlaps the C-H peak) between 2500-3330 cm^{-1} due to O-H bond stretching due to O-H bond of a carboxylic acid.

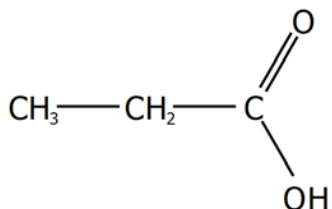
There is a strong peak around 1700 cm^{-1} that suggests C=O bond stretching vibration. This suggests that the molecule might be a carboxylic acid and the peak is a strong peak at 1705-1720 cm^{-1} which matches a peak expected for a C=O bond stretching vibration associated with a C=O bond of a carboxylic acid.

There are no (two) weak to medium peaks at 3300-3500 cm^{-1} associated with N-H bond stretching vibrations, which is more evidence to eliminate amines and amides. The peak due to C=O bond stretching vibration associated with the amide is also in the wrong place as this peak is between 1630-1695 cm^{-1} which is clearly not seen on this IR spectrum.

The C-NMR spectrum has 3 peaks which means the molecule must have at least 3 C atoms, as it shows there are three different carbon environments. The peak at 184 ppm suggests a C atom in a C=O bond. The chemical shift for a C=O for carboxylic acids, acid chlorides, amides and esters is between 160-185 ppm which matches

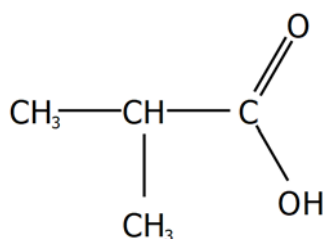
this. Acid chlorides have been ruled out (no Cl) as have amides (no N). The molecule is not an ester as it contains an O-H group.

The molecule has a carboxylic acid group and 3 carbon environments and molar mass of 88 g mol^{-1} . This has the correct functional group and number of carbon environments but molar mass of 74 g mol^{-1} is too low.

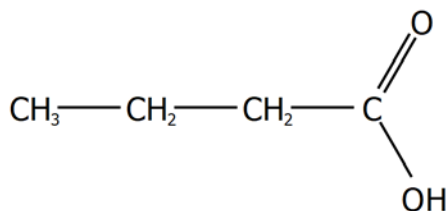


Adding one more C atom (and 2 H atoms) would give a molar mass of 88 g mol^{-1} .

To get the right number of C environments the molecule must be branched. The molecule below has the correct molar mass and the correct number of carbon environments (three).



The molecule cannot be the straight chain isomer (below) because although this has the right molar mass, it has 4 carbon environments and so cannot be the molecule.

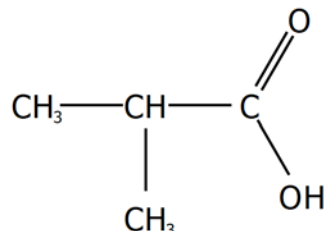


To back up that the molecule is indeed a carboxylic acid, further IR evidence includes

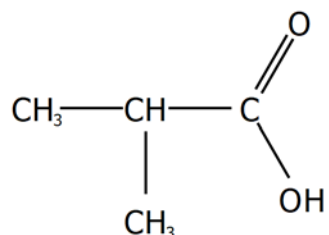
- A strong peak between $1000\text{--}1300 \text{ cm}^{-1}$ due to O-C bond stretching vibrations associated with carboxylic acids and derivatives.
- A medium peak between $910\text{--}950 \text{ cm}^{-1}$ due to O-H bond bending vibrations associated with carboxylic acids.

- A medium peak between $1450-1470\text{ cm}^{-1}$ due to C-H bond bending vibrations associated with alkanes (most of the molecule is alkane).

In the C-NMR the peaks at approximately 34 ppm are due to $R_3\text{C-H}$ (25-60 ppm) and $R-\text{C-H}_3$ @ at approximately 19 ppm (8-35 ppm), in addition to the C=O @ 184 ppm, which is most downfield (160-185 ppm).



Finally, a number of peaks can be found in the mass spectrum that match feasible fragments that could occur from the proposed molecule. Many peaks are due to rearrangements and cannot be assigned.



- COOH^+ @ 45 m/z
- $\text{CH}_3\text{CHCOOH}^+$ @ 73 m/z
- $(\text{CH}_3)_2\text{CH}$ @ 43 m/z (base peak)
- CO^+ @ 28 m/z (small)