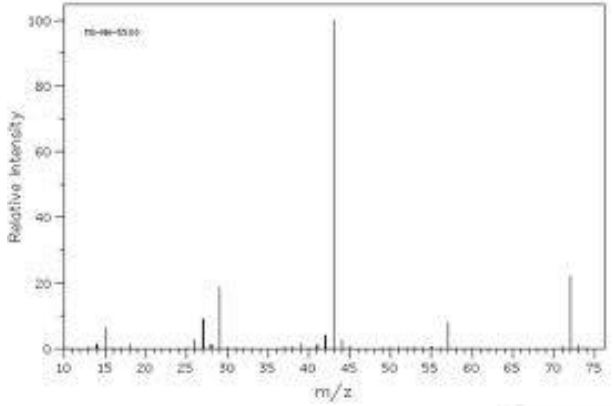
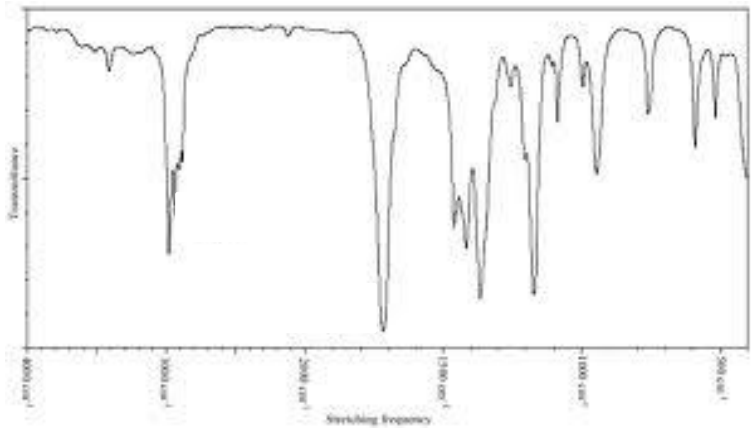
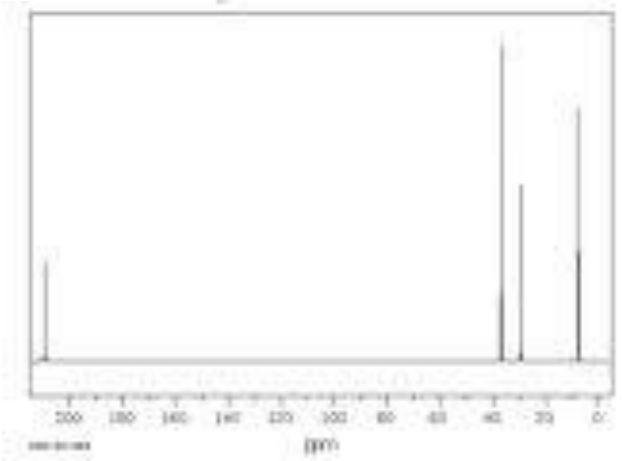
CHEM 3.2 (AS91388)
3 credits

Demonstrate understanding of spectroscopic data in chemistry

- Spectroscopic data is limited to mass, infrared (IR) and ^{13}C nuclear magnetic resonance (NMR) spectroscopy.
- Organic molecules are limited to alkanes, alkenes, alcohols, haloalkanes, amines, aldehydes, ketones, carboxylic acids, amides, acid chlorides and esters.





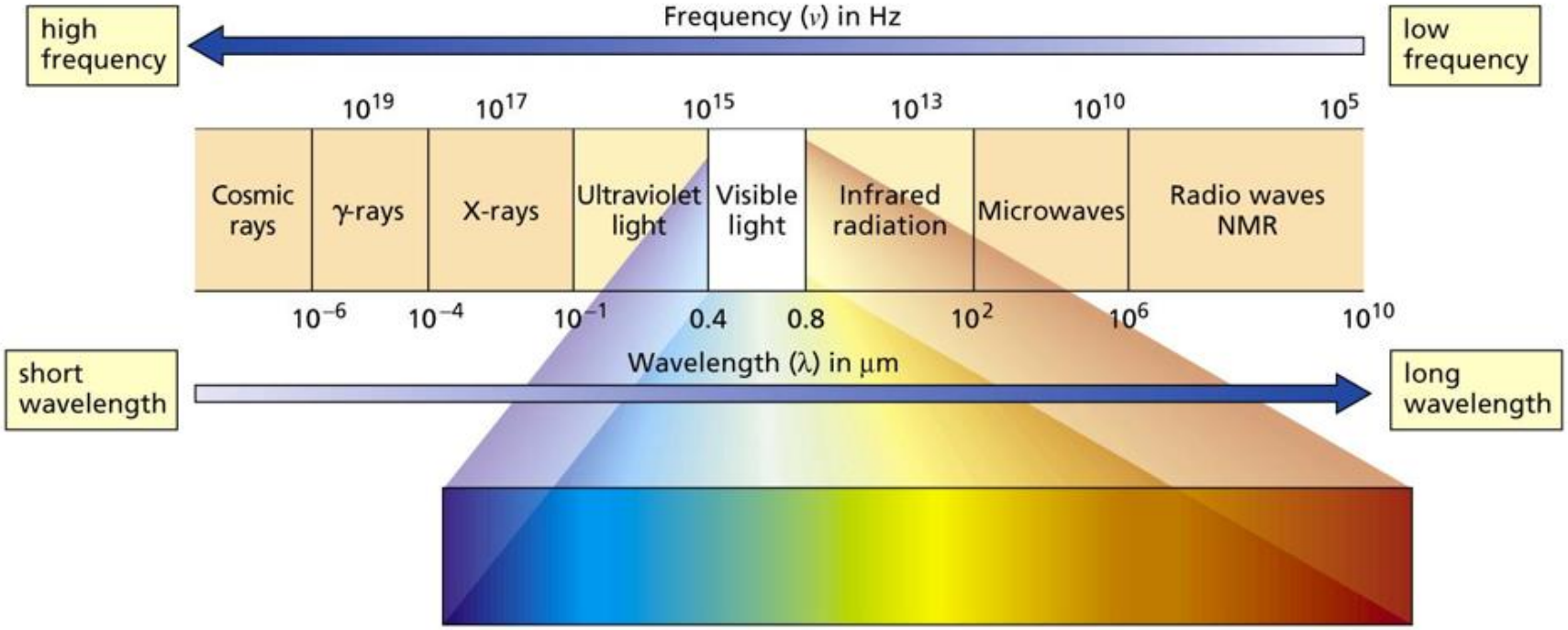


- For A you need to be able to identify parts of molecules from given ^{13}C, IR and mass spectra

- For M you need to be able to determine the structure of a molecule and explain your choice

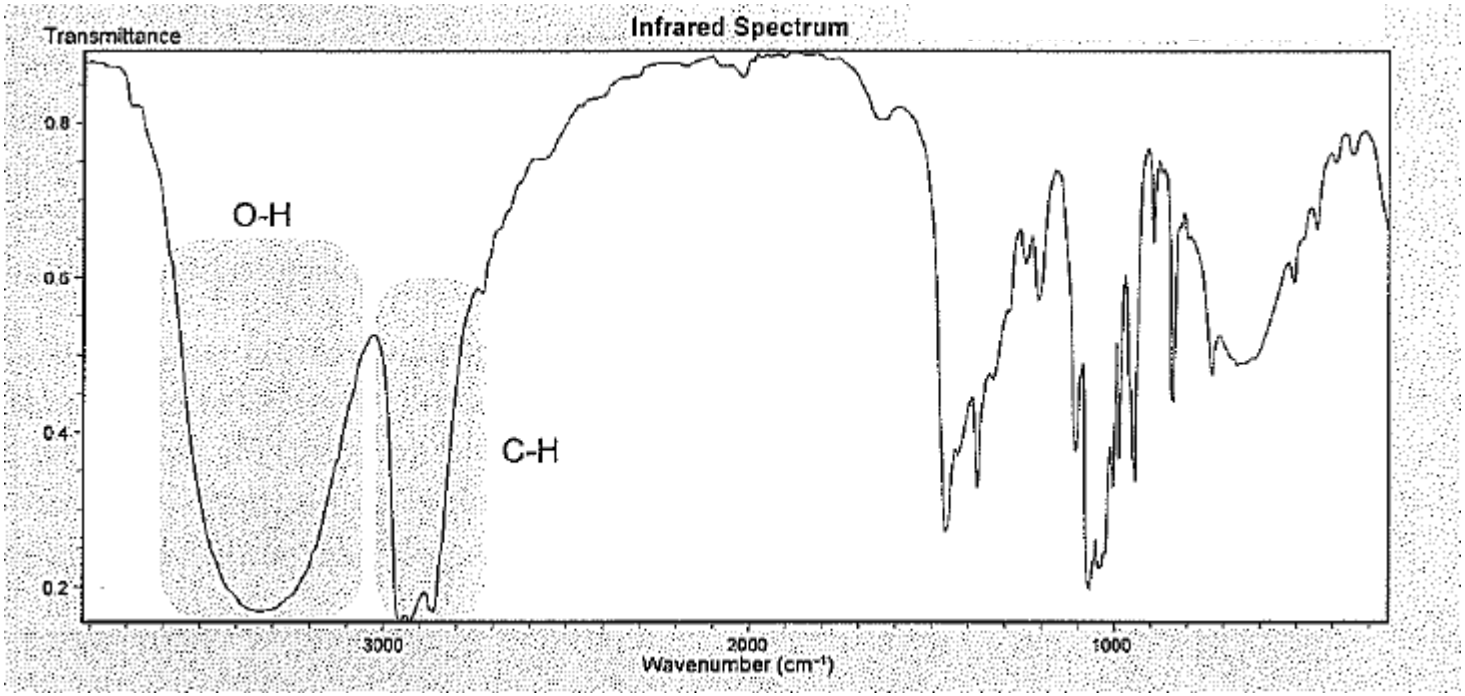
- For E you need to be able to determine the structure of a molecule and justify your choice

What is spectroscopy?



IR spectroscopy

Measures the vibration of the bonds in a molecule. Different bonds vibrate at different frequencies.
An infrared spectrum shows the wavelengths (measured in wavenumbers) where different compounds have absorbed light.
Each absorption corresponds to a different chemical bond



IR Spectroscopy

Wavenumbers (cm^{-1}) are used as a measure of the wavelength or frequency of the absorption.

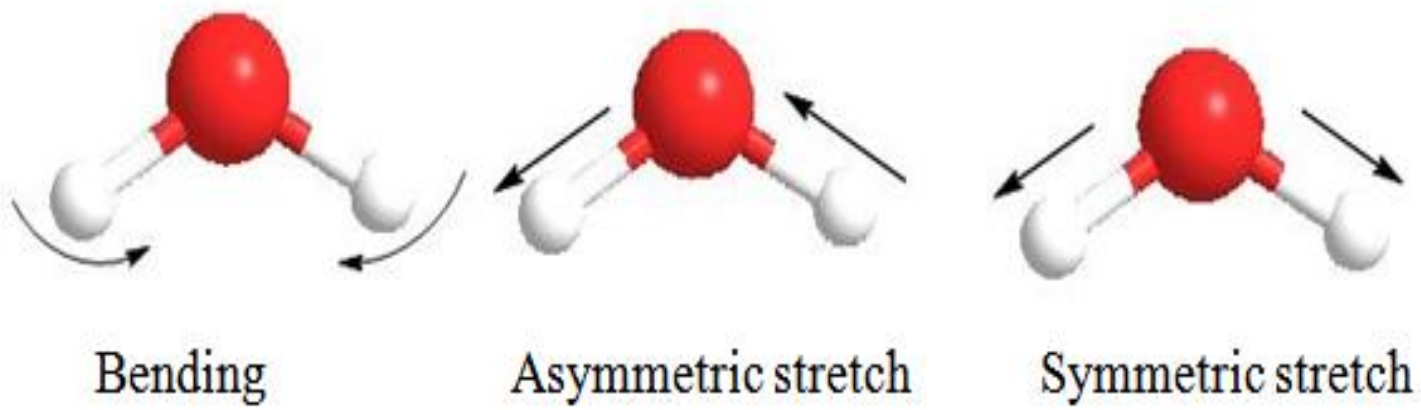
$$\text{Wavenumber} = \frac{1}{\text{wavelength (cm)}}$$

High frequencies, **large** wavenumbers, and **short** wavelengths are associated with **high** energy

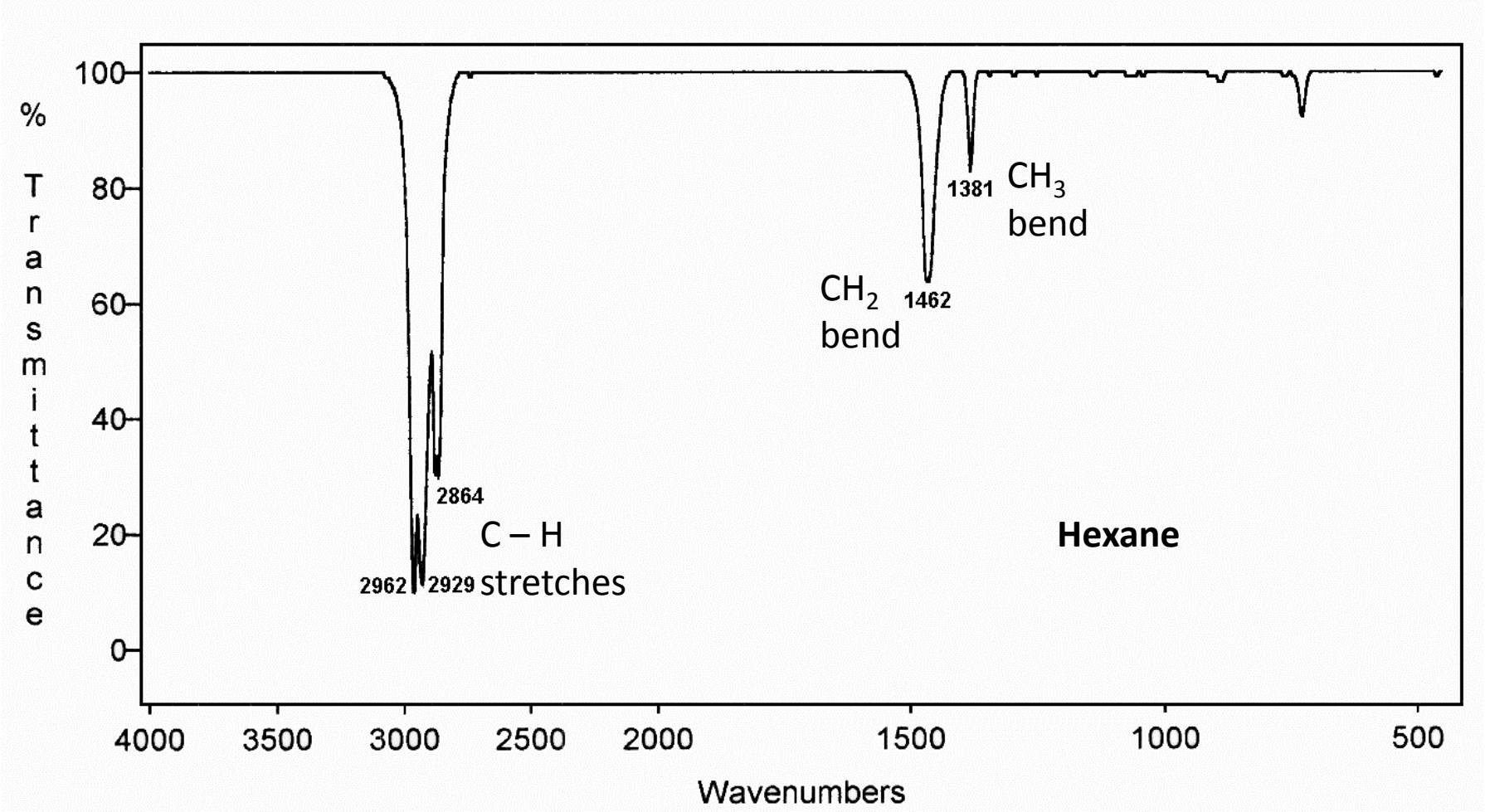
IR Spectroscopy

The energy of vibration depends on the following factors:

1. **The mode of vibration – it is easier to bend than stretch (C-H bend vs C-H stretch)**
2. **The type of bond (single, double or triple) – it takes less energy to stretch a single bond than a double bond (C-O vs C=O)**
3. **The mass of the atoms linked by covalent bonds – heavier atom lower energy (C-Br vs C-Cl)**

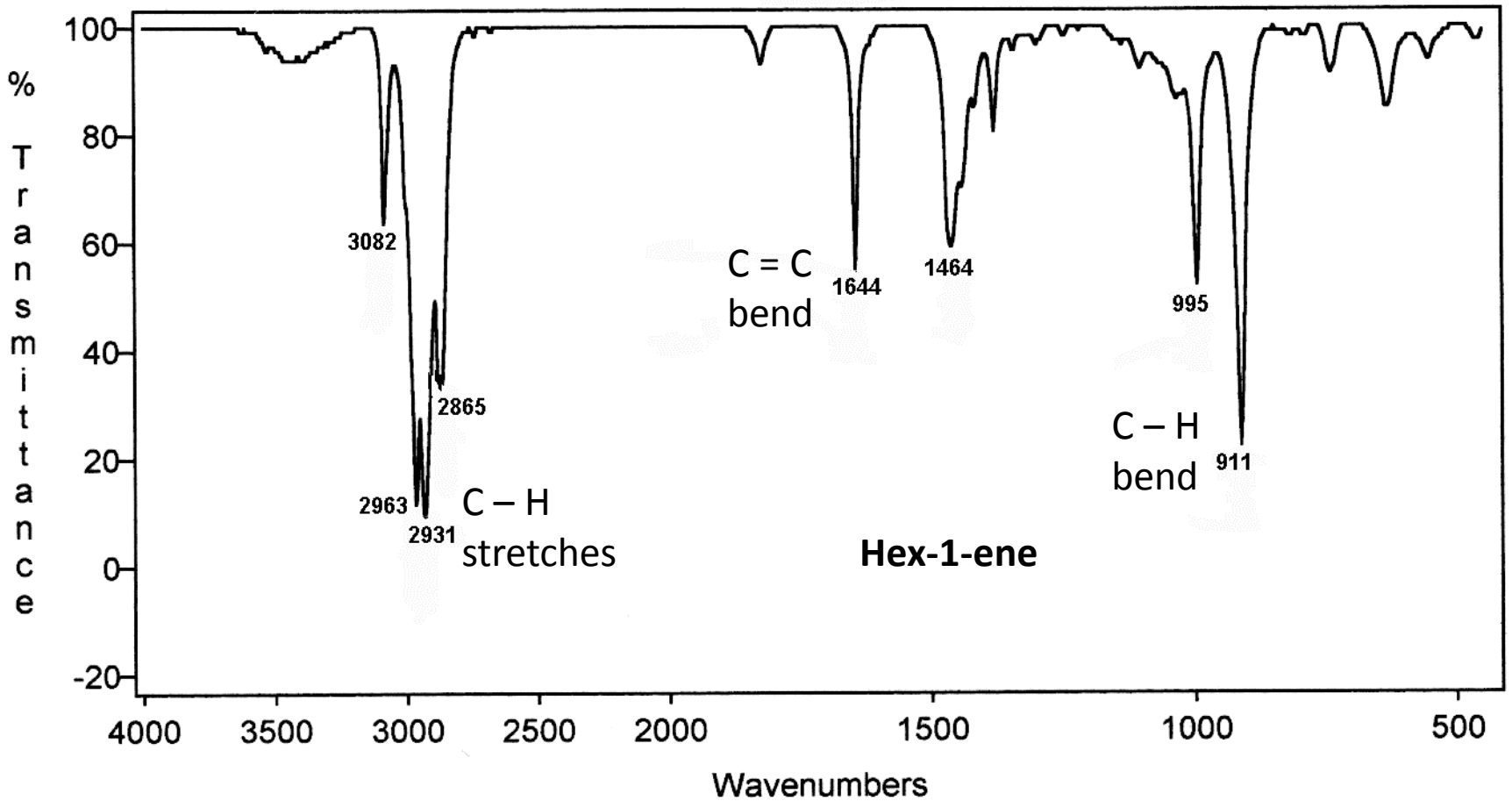


IR Spectroscopy



Nearly all organic compounds have these stretching and bending frequencies as they all have C – H bonds!!

IR Spectroscopy



IR Spectroscopy

We only look at the region of the IR above ~1500 cm^{-1}. The absorptions we are concerned with occur from 1500 cm^{-1} to 4000 cm^{-1}.

Bond	Types of compound	Range (cm^{-1})	Type
C-H	All functional groups	3100-2800	strong
	Aldehyde	2690-2840 (2 bands)	strong
O-H	Alcohol	3700-3300	strong, broad
	Carboxylic acid	3600-2500	strong, very broad
N-H	Amine, amide	3500-3100 (2 bands)	strong
C-O	Alcohols, carboxylic acids, esters	1250-1050	medium
C-N	Amine	1250-1000	medium
C=O	Aldehydes, ketones, carboxylic acids, esters	1850-1600	strong, sharp
C=C	Alkenes	1500-1600	variable
C-Cl	Chloroalkane	600-800	strong
C-Br	Bromoalkane	500-600	strong

Do now:

The following peaks are key to identifying functional groups in IR.

C=O O-H N-H

For the following functional groups write down which of the above peaks you would expect to see

Ester **C=O and C-O**	Amine **N-H**	Amide **N-H and C=O**
Carboxylic acid **C=O and O-H**	Aldehyde **C=O**	Ketone **C=O**
Alcohol **O-H**		

IR Spectroscopy

There are four main peaks to look for when analysing IR.

- All IR spectra have a C-H band at 2800 – 300 cm^{-1}. All organic molecules have C-H bonds.
- Carbonyl (C=O) bands occur at 1600 – 1800 cm^{-1}. They are always sharp. Aldehydes, ketones, carboxylic acids, esters and acid chlorides all have a band in this range.
- Hydroxy (O-H) bands occur at 2500 – 3700 cm^{-1}. Alcohols and carboxylic acids have a broad band in this range. Carboxylic acids bands are so broad they overlap the C-H band.
- Amino (N-H) bands occur at 3100 – 3500 cm^{-1}. Amines and amides have broad bands in this range. Each N-H bond has a different band (ie primary amines and amides have 2 N-H bands)

Telling the difference between compounds

For the following compounds:

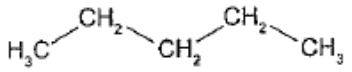
- List the peaks you would expect to see in IR
- Explain, making reference to the peaks you would see, how you would be able to use IR to tell the difference between the two compounds

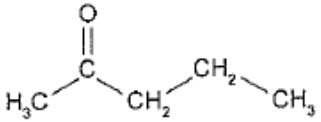
- Propan-2-ol and propanone

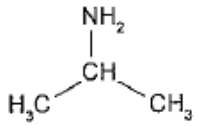
- Ethanal and ethyl propanoate

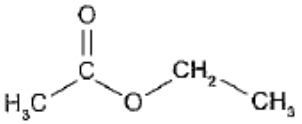
- Propanamide and propanamine

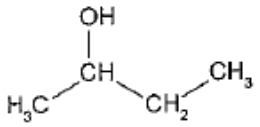
1. Consider the following structures:

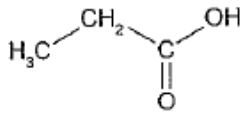
A 

B 

C 

D 

E 

F 

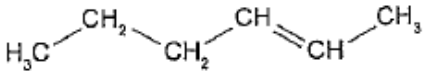
a. Which structure(s) would you expect to have a broad absorption around 3000-3500 cm^{-1}? C, E, F

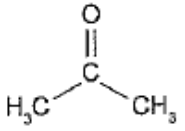
b. What functional group(s) would be responsible for the absorption? NH_2, OH

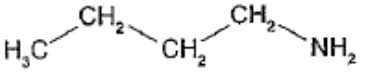
c. Which structure(s) would you expect to have an intense absorption around 1600-1800 cm^{-1}? B, D, F

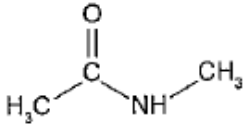
d. What functional group(s) is responsible for this absorption? C=O

2. Consider the following structures and IR spectrum:

A 

B 

C 

D 

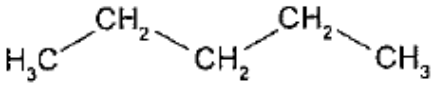
Select the structure that belongs to the spectrum and explain your choice.

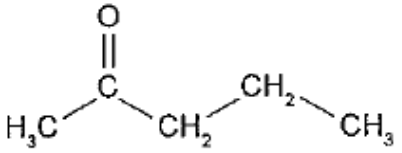
A as it does not have an OH, NH or C=O and therefore will not have a broad absorption at around 3000-3500 cm^{-1} or an absorption around 1600-1800 cm^{-1}. B and D will have an absorption around 1600-1800 cm^{-1} and C and D will have a broad absorption at around 3000-3500 cm^{-1} and therefore are all not a match for the spectrum.

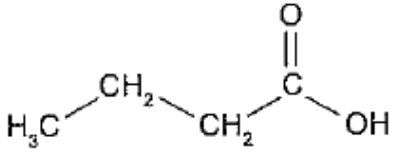
3. Consider the spectrum below and name two families of compounds that could give this spectrum and explain why.

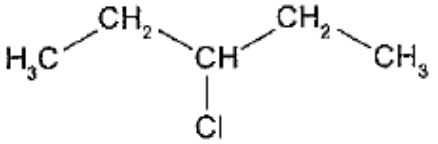
The spectrum has a carbonyl absorption (1700 cm^{-1}) but no N-H/O-H absorption therefore it could be an aldehyde, ketone, ester, acyl chloride or tertiary amide.

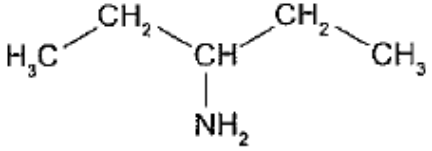
4. Which two of the following could not be easily distinguished with IR spectroscopy? Explain your answer.

A 

B 

C 

D 

E 

A and D. B would have a carbonyl absorption (1600-1800 cm^{-1}); C would have both a carbonyl absorption (1600-1800 cm^{-1}) and an O-H/N-H absorption (3000-3500 cm^{-1}); E would have just an O-H/N-H absorption (3000-3500 cm^{-1}); A and D would not have any distinct absorptions.

Match the following seven compounds to the following seven IR spectra.

hex-2-ene

pentane

methylpropan-1-ol

2-methylpentan-3-one

butanal

butanoic acid

propyl ethanoate

Do now:

Assign spectra 1, 2, 3, 5 and 7 to the following compounds

pentane

methylpropan-1-ol

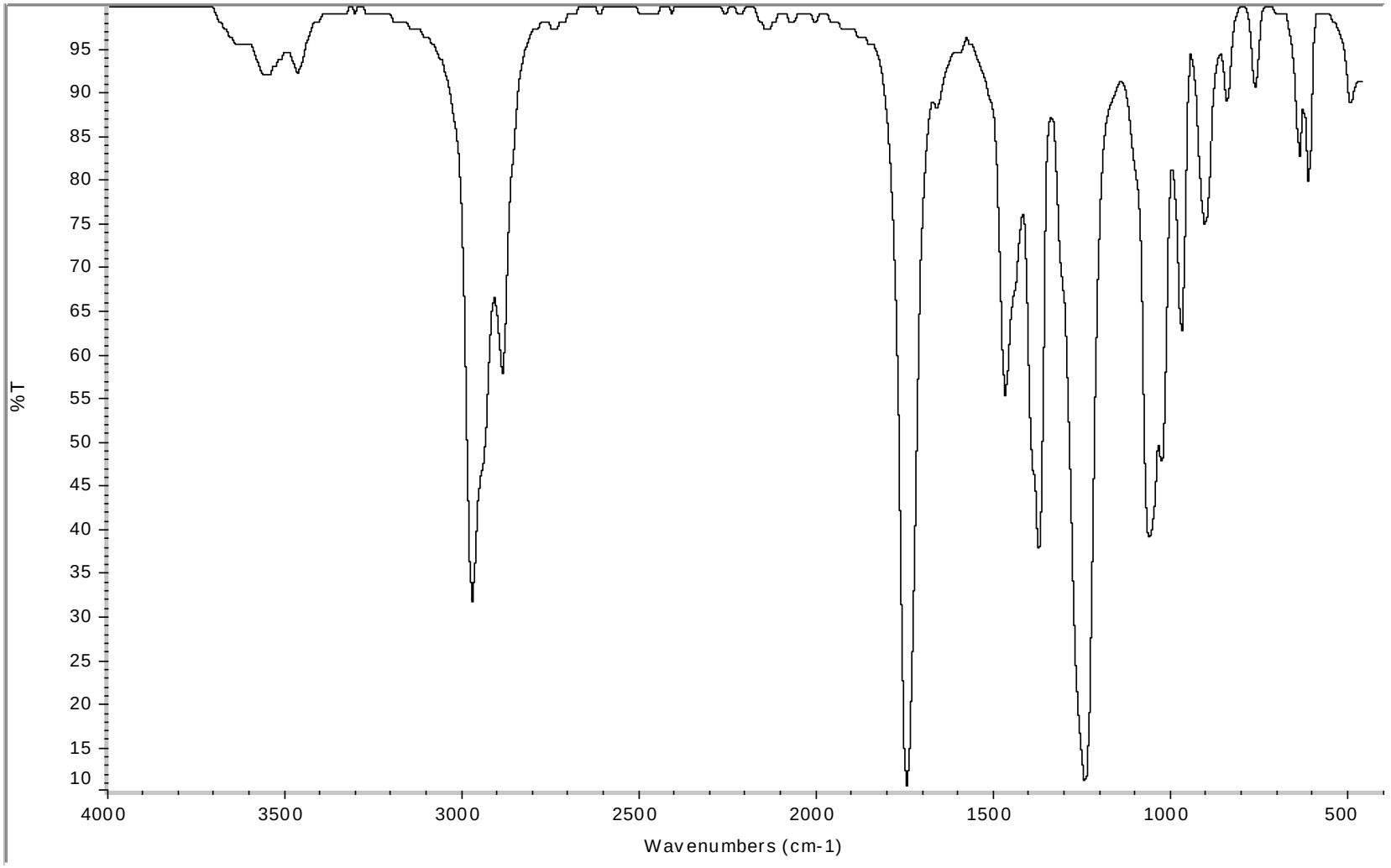
2-methylpentan-3-one

butanoic acid

propyl ethanoate

Spectra 6 is an aldehyde, how can you tell this from the IR?

1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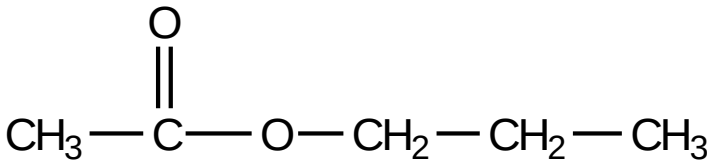
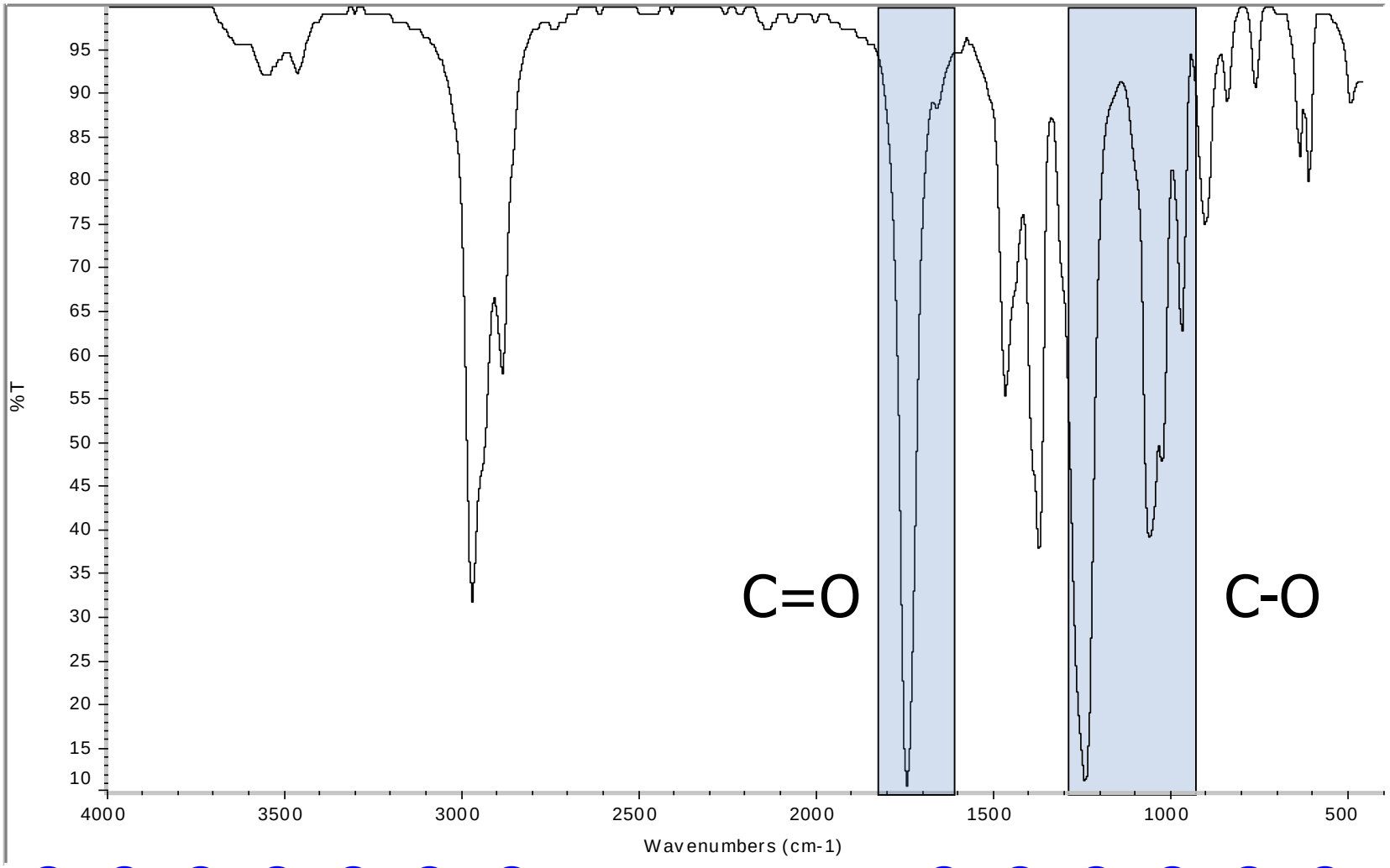
Wavenumbers (cm-1)

❶ propyl ethanoate





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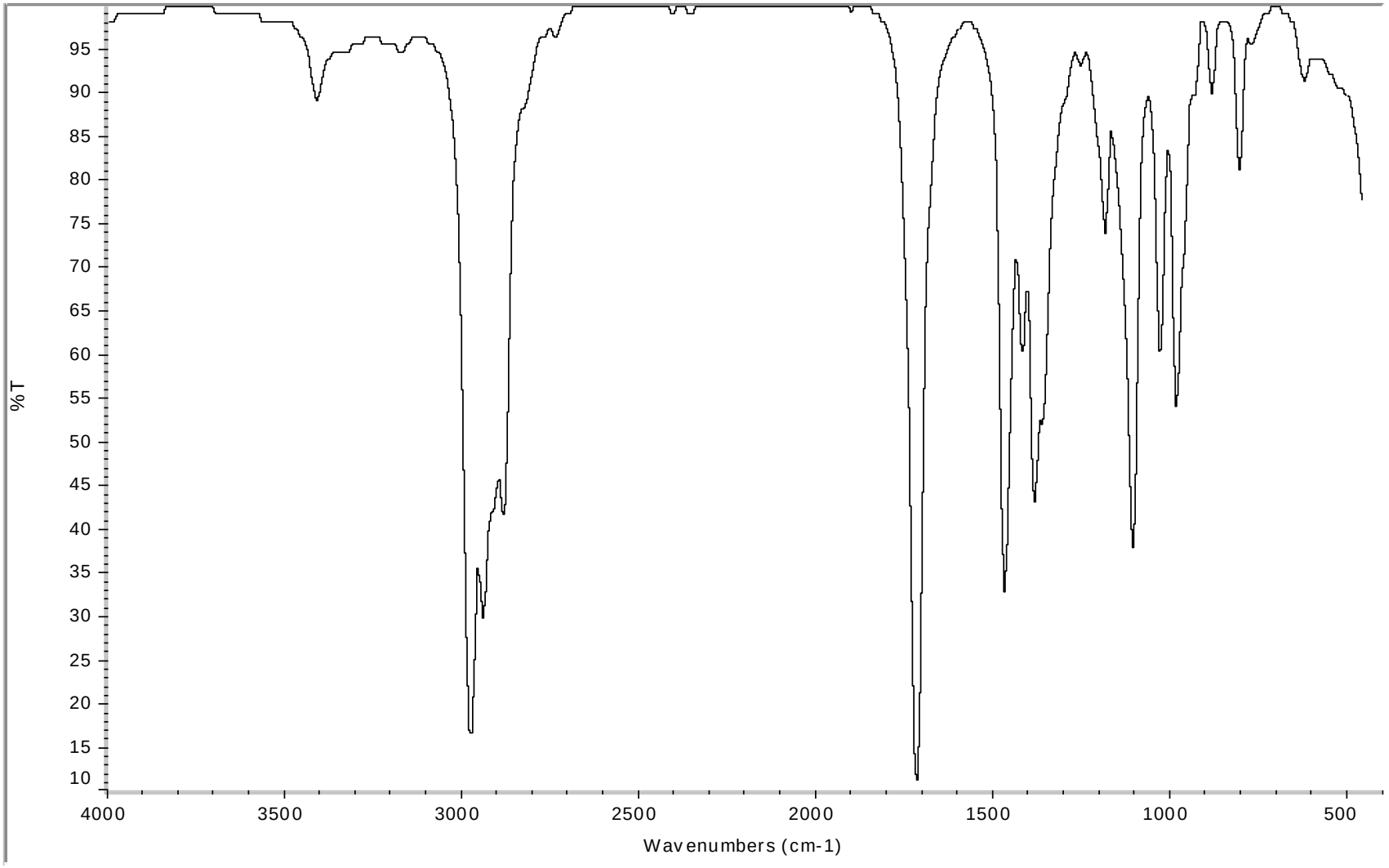
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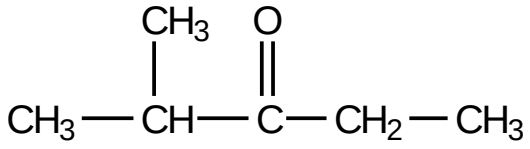
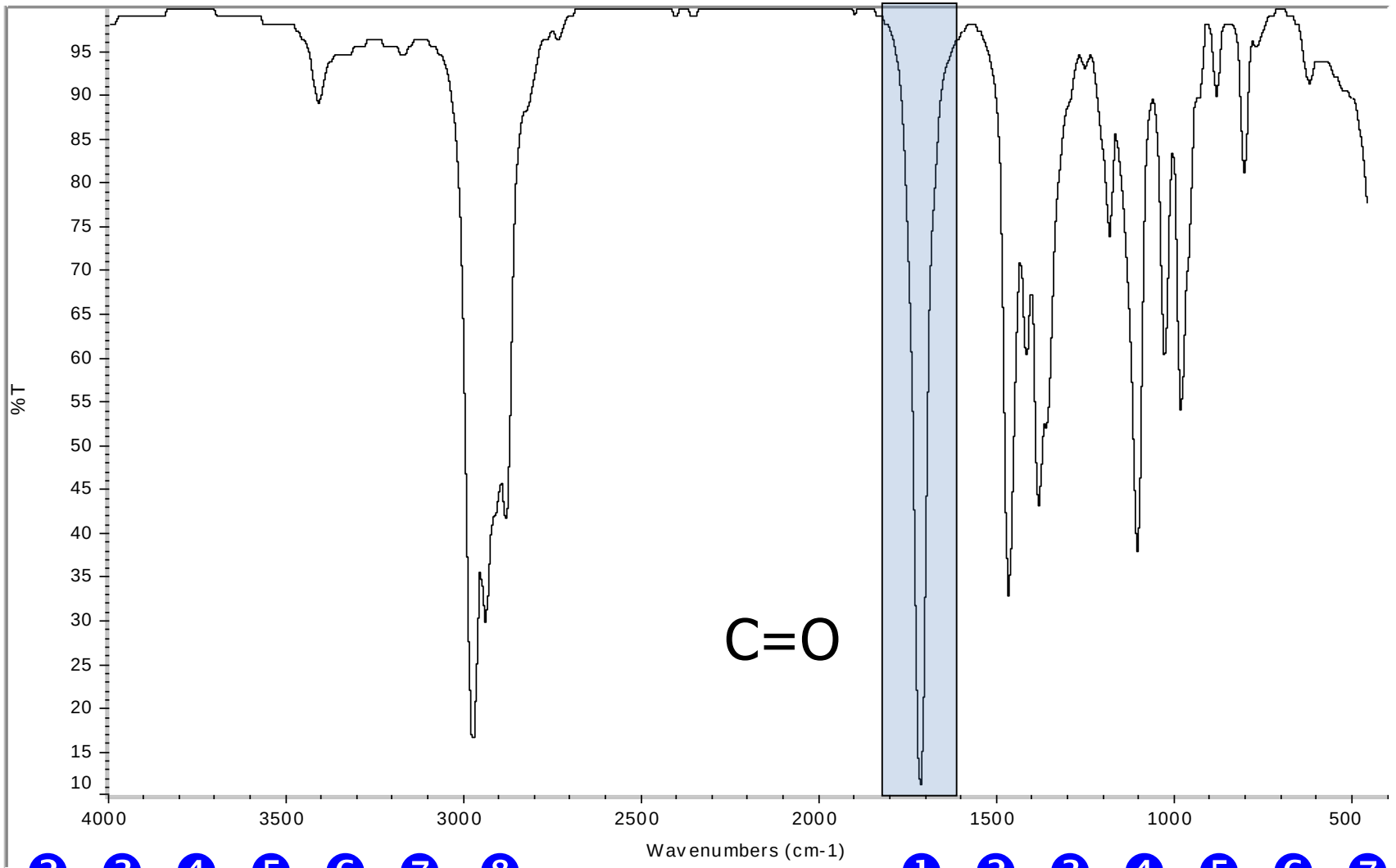
Wavenumbers (cm-1)

❷ 2-methylpentan-3-one





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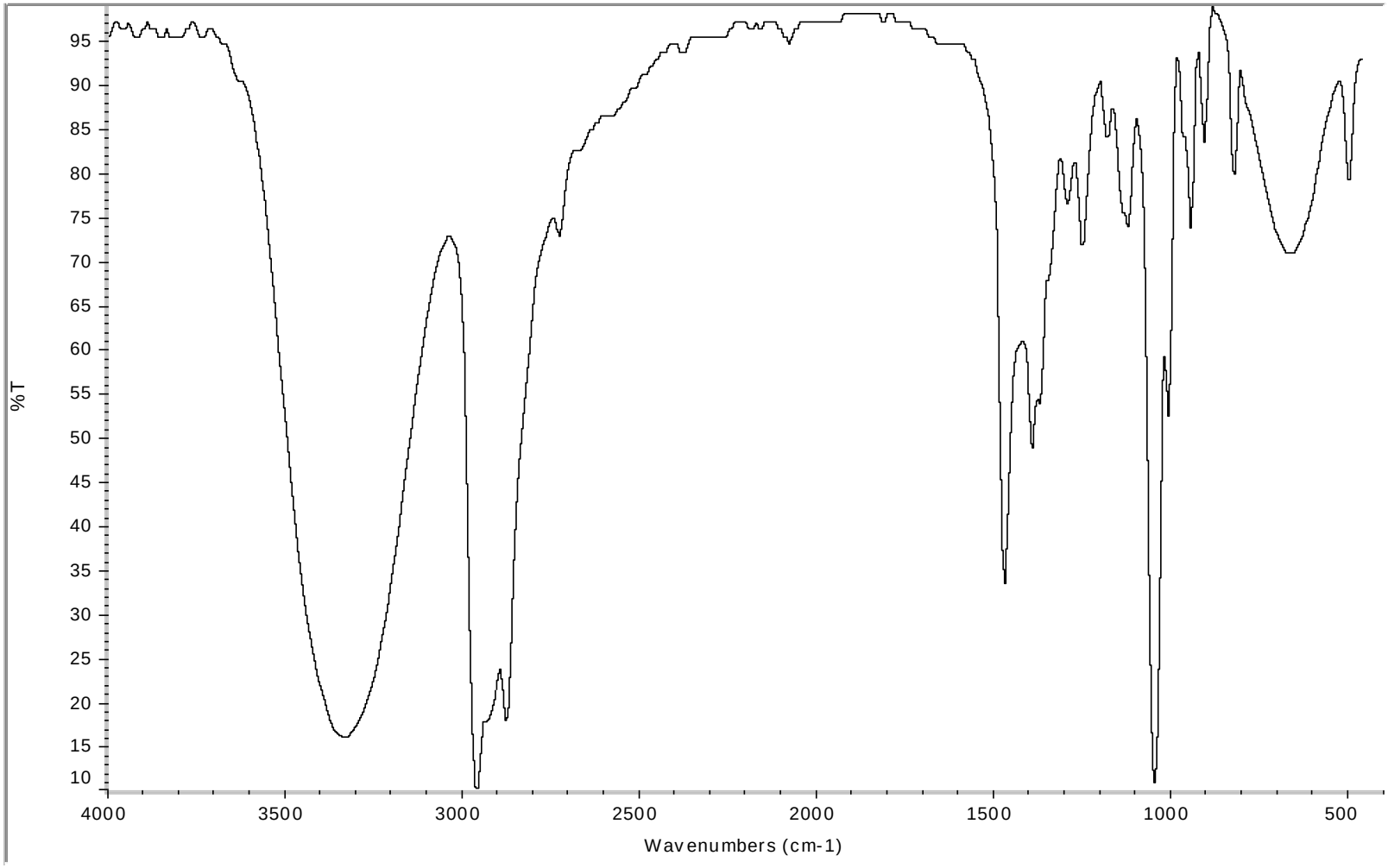
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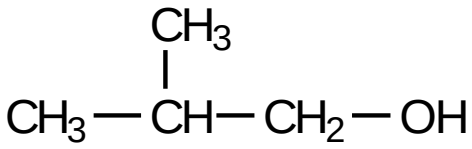
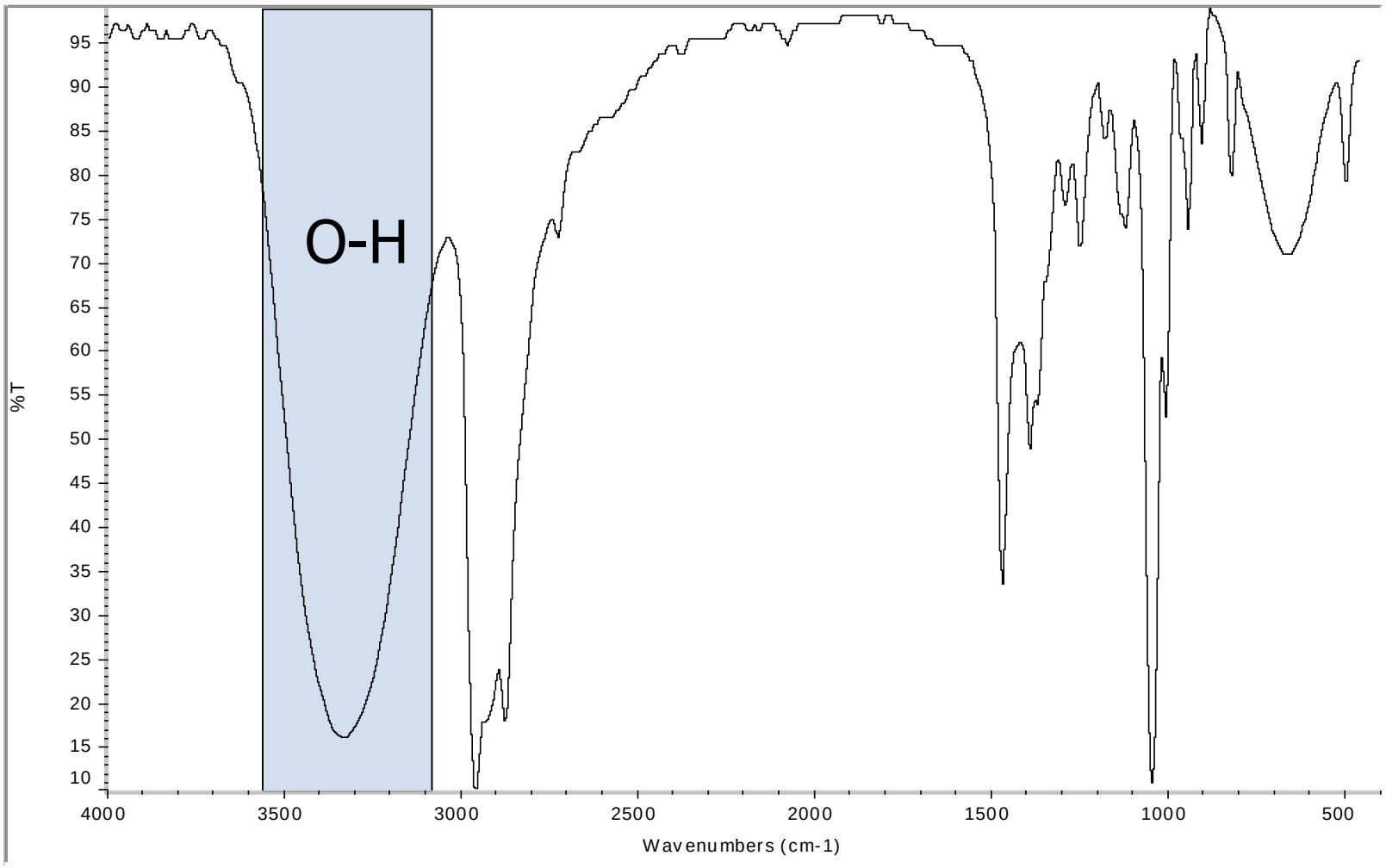
Wavenumbers (cm-1)

❸ methylpropan-1-ol





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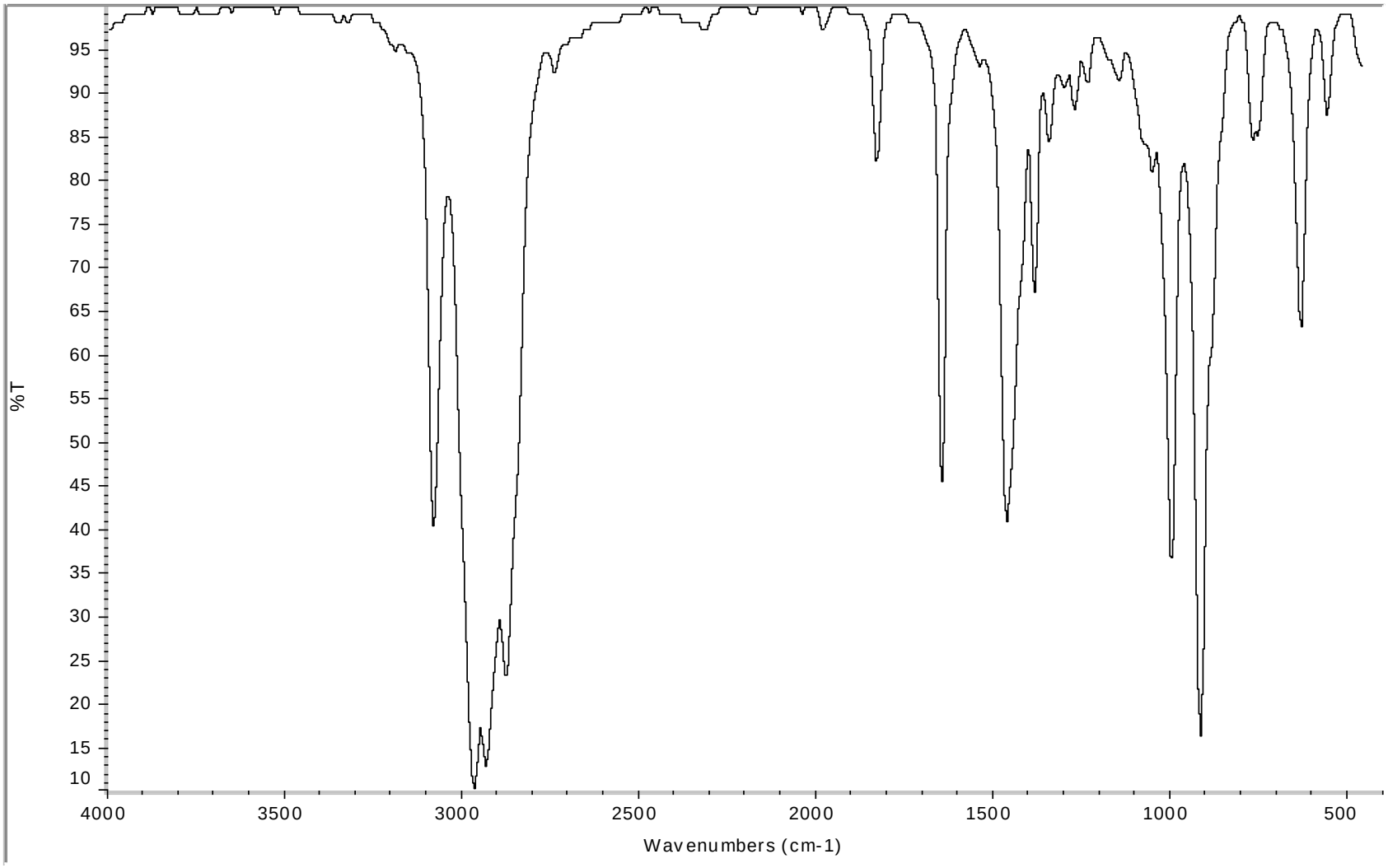
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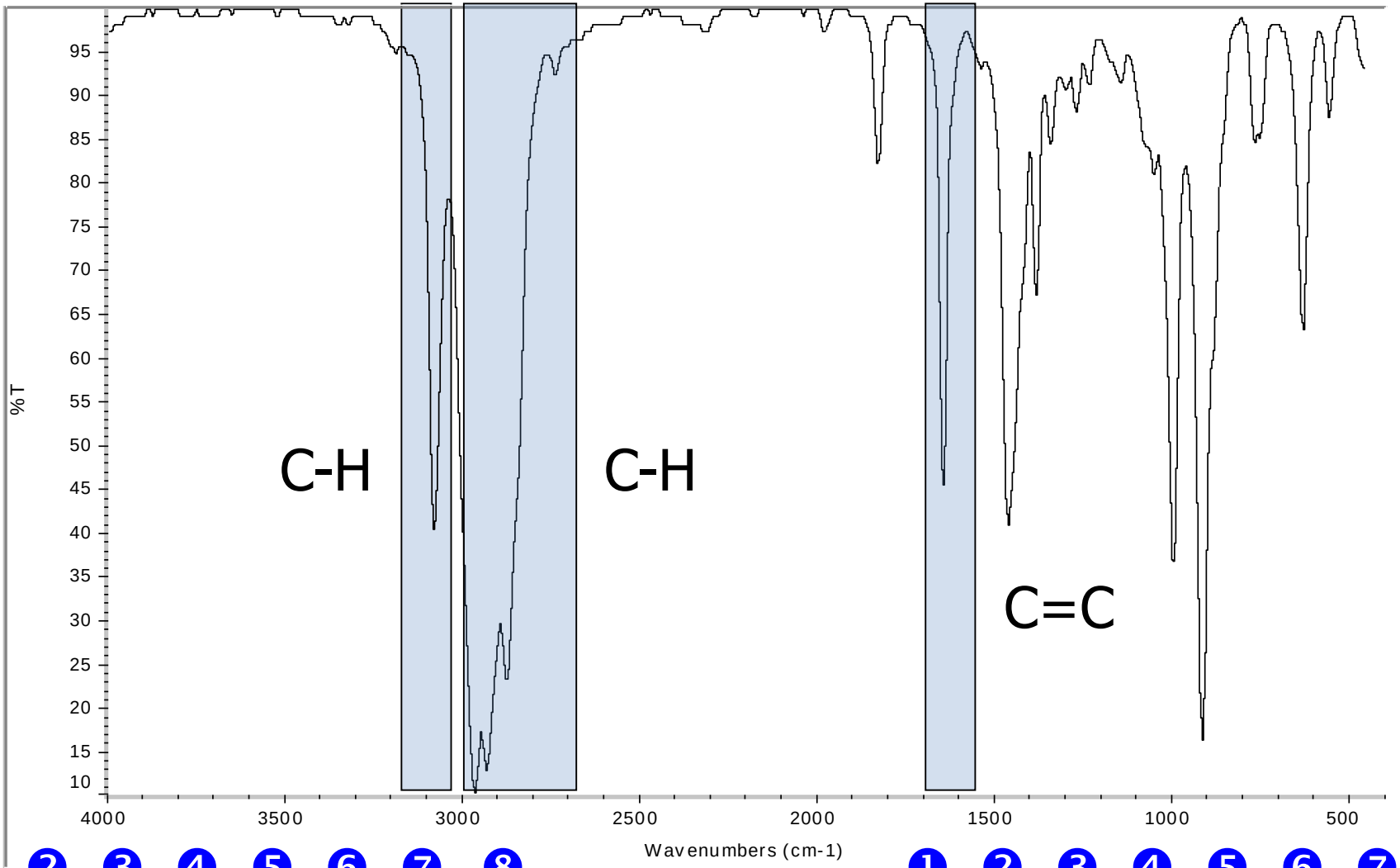
Wavenumbers (cm-1)

4 hex-2-ene

$CH_3—CH=CH—CH_2—CH_2—CH_3$



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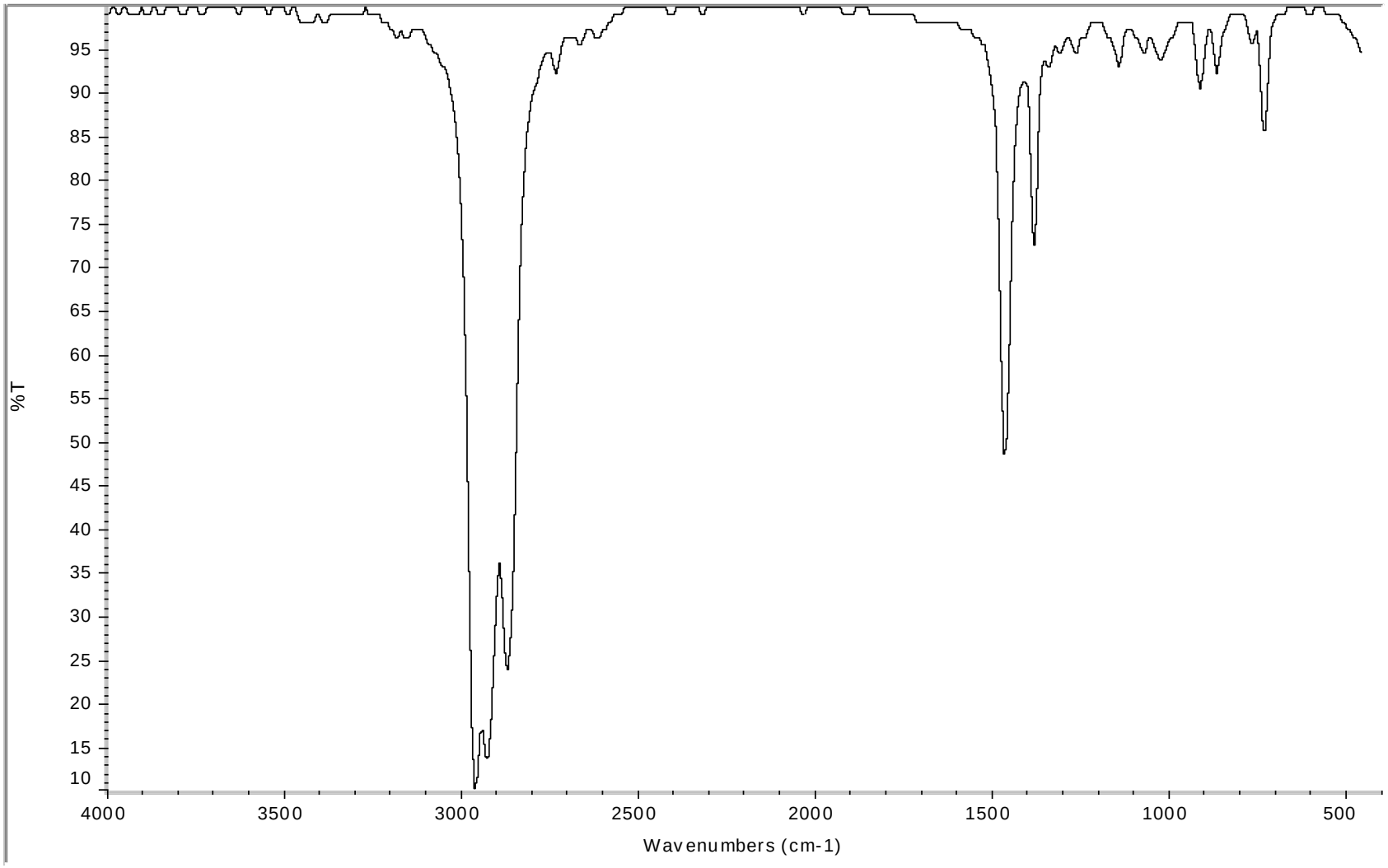
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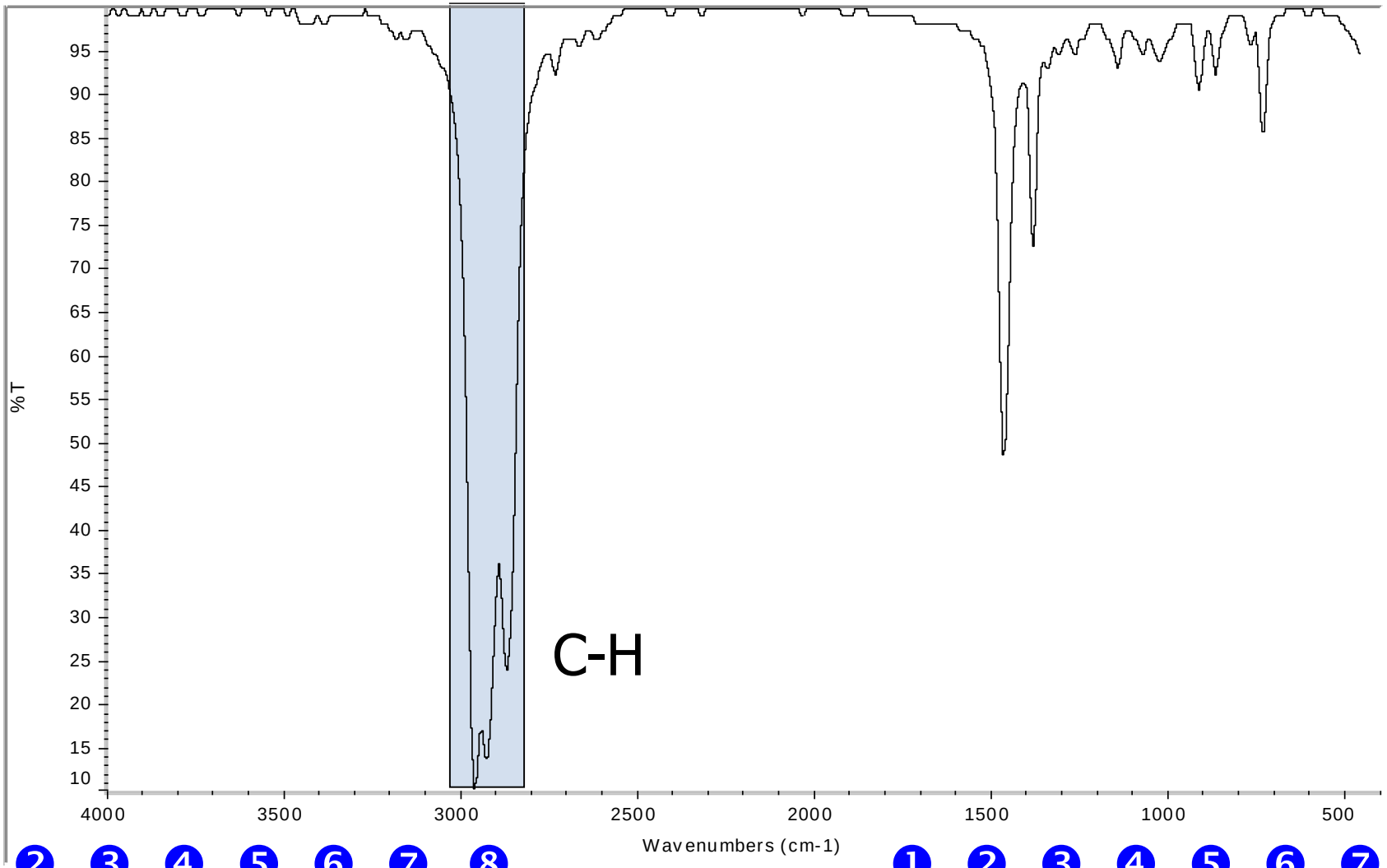
Wavenumbers (cm-1)

❺ pentane

$CH_3—CH_2—CH_2—CH_2—CH_3$



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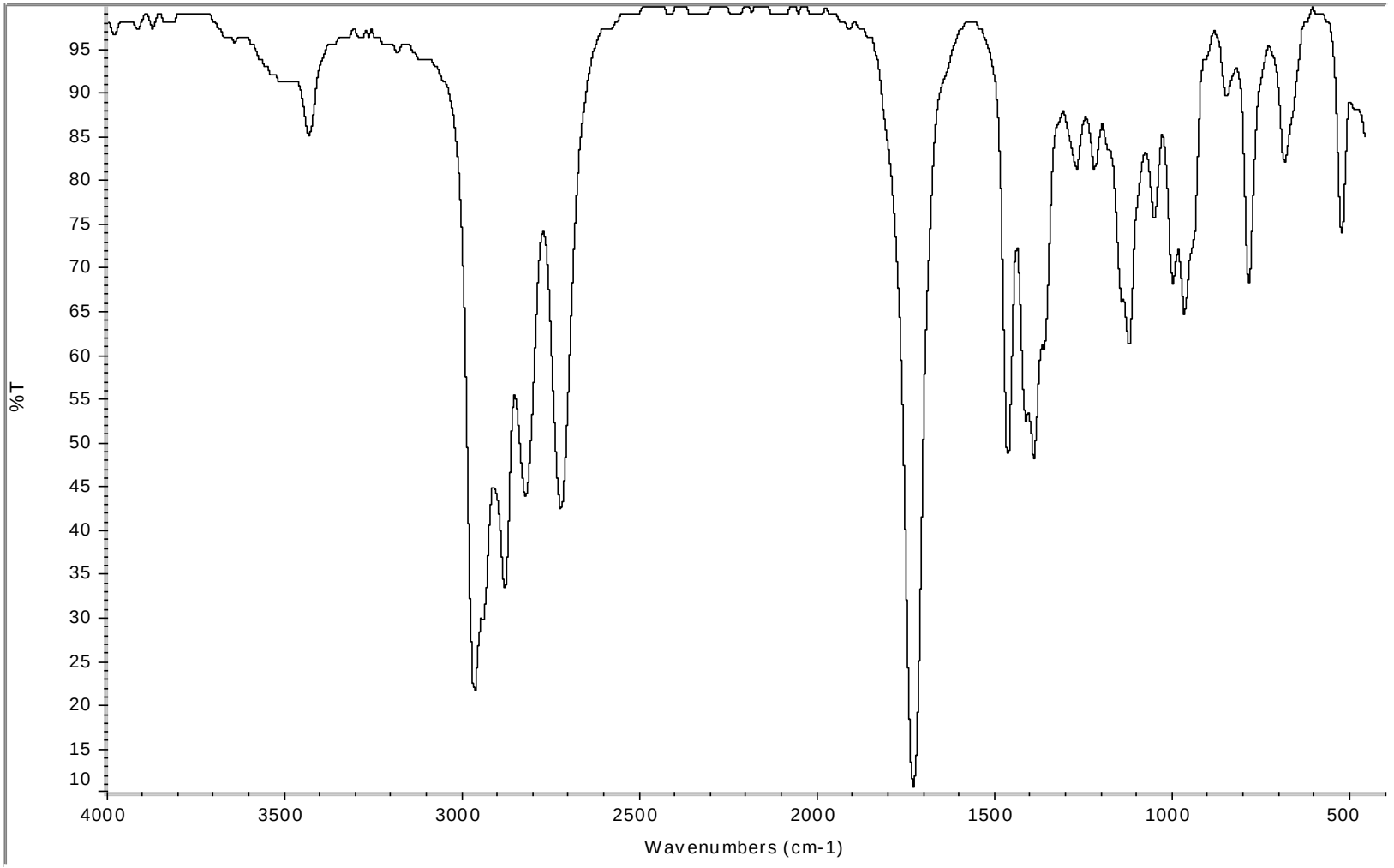
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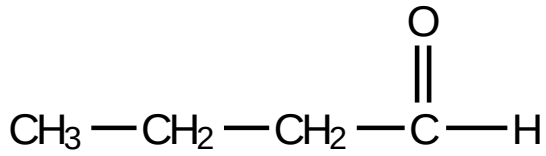
Wavenumbers (cm-1)

❻ butanal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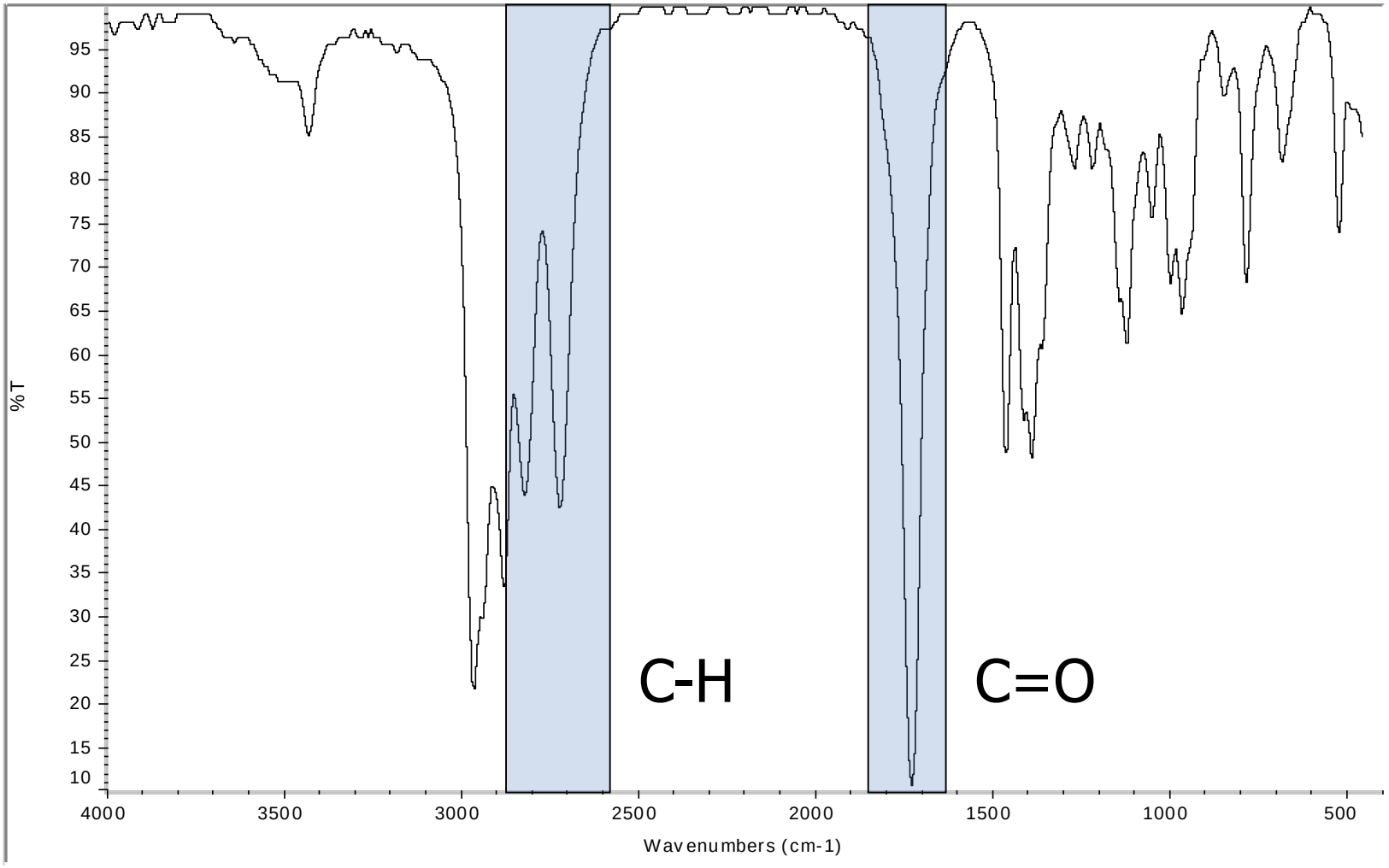
CH3 — CH2 — CH2 — C — H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Wavenumbers (cm-1)
C-H
C=O

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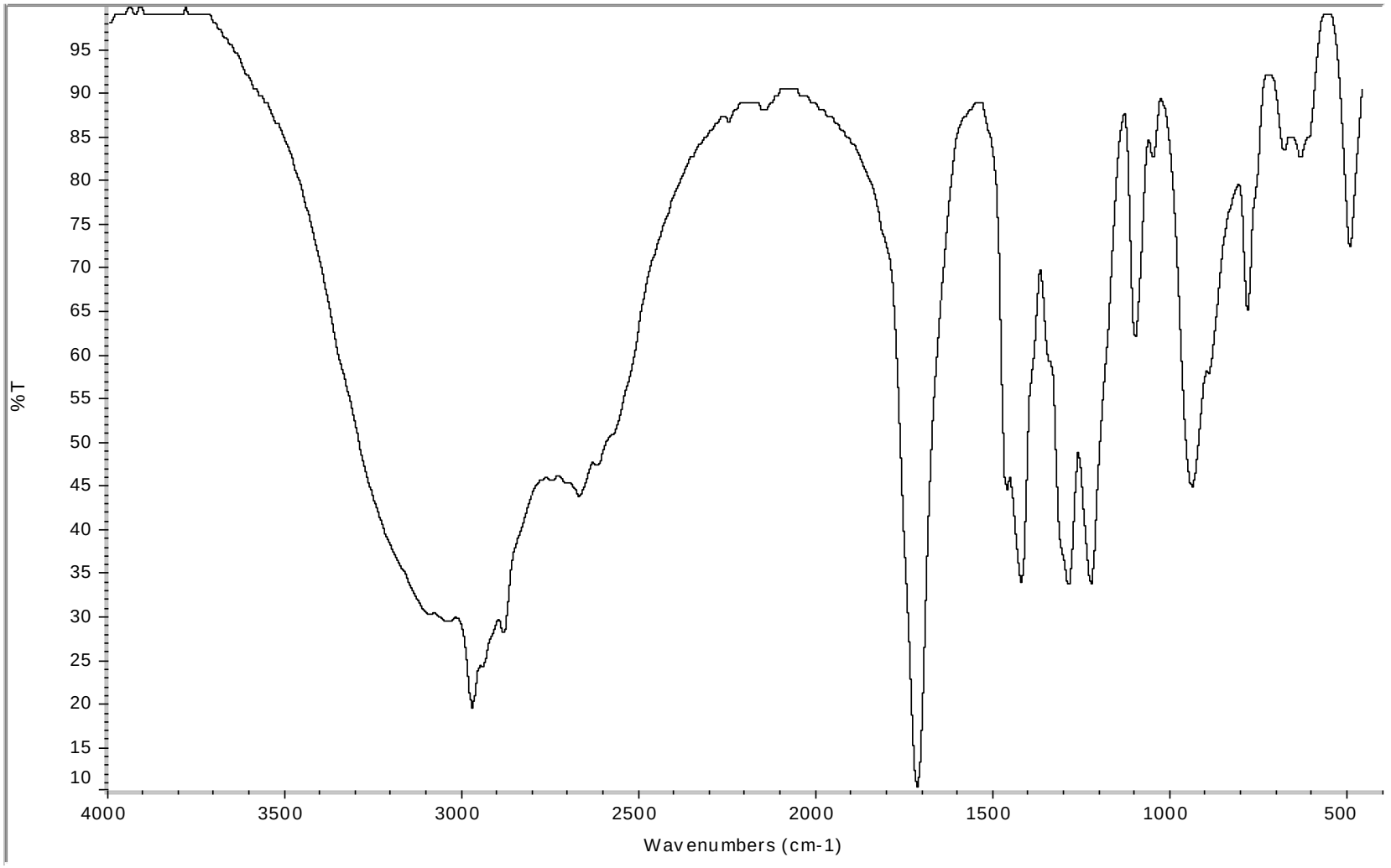
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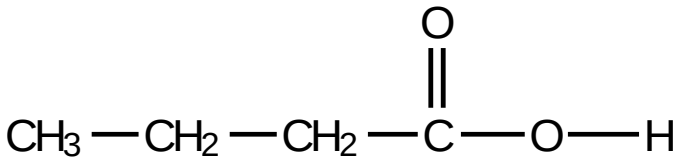
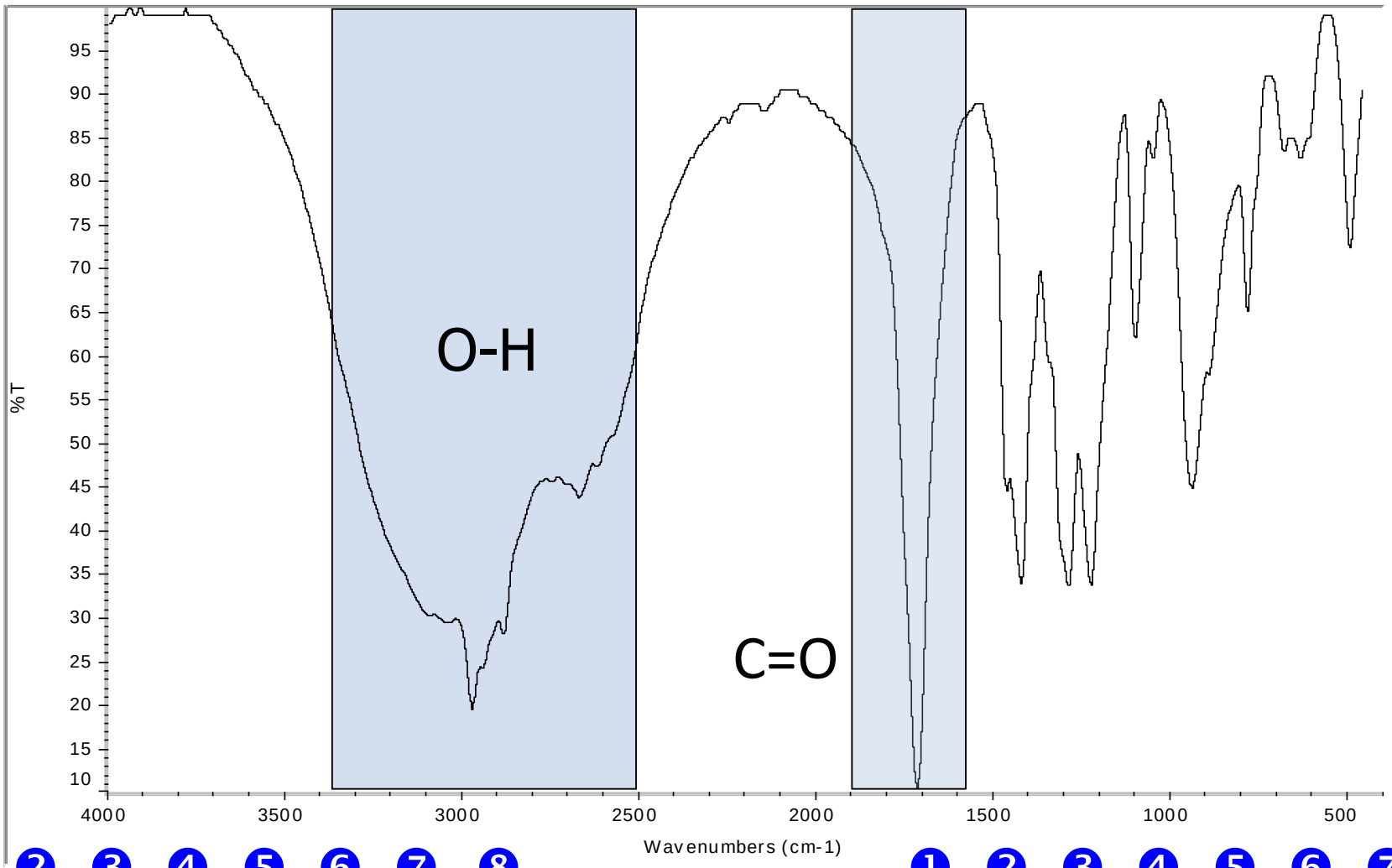
Wavenumbers (cm-1)

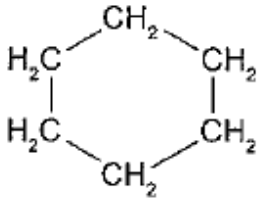
7 butanoic acid

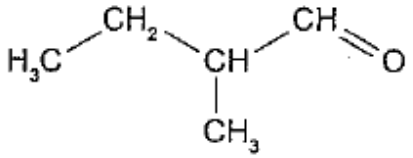


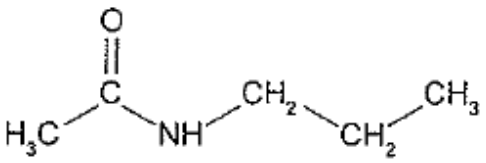


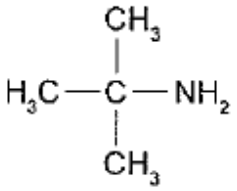
1 2 3 4 5 6 7 8 1 2 3 4 5 6 7 8

5. Spectra 1-3 below, belong to three of the following compounds. Work out which compound goes with which spectrum and justify your answer.

A 

B 

C 

D 

Spectrum 1 is compound D as it has an N-H/O-H absorption (3000-3500 cm^{-1}) but no carbonyl absorption.

Spectrum 2 is compound C as it has both a carbonyl absorption (1600-1800 cm^{-1}) and an O-H/N-H absorption (3000-3500 cm^{-1}).

Spectrum 3 is compound B as it has a carbonyl absorption (1600-1800 cm^{-1}) but not an N-H/O-H absorption.

6. IR spectroscopy can readily distinguish tertiary amides from primary and secondary amides. Discuss why this is true and what you would find in an IR spectrum for a primary or secondary amide compared to a tertiary amide.

All amides have a carbonyl group and will have an intense absorption around 1600-1800 cm^{-1}. Primary and secondary amides both have N-H bonds but tertiary amides do not. Consequently, primary and secondary amides will have a broad absorption around 3000-3500 cm^{-1} whereas a tertiary amide will not.

7. Group the following compounds into four groups based on which will have similar IR spectra. Give a brief reason for each grouping.

A, C, H and J do not have any N-H, O-H or C=O and therefore will have similar looking IR spectra.

B and D have an O-H or N-H but no C=O and therefore will have similar looking IR spectra.

E, G, K and L all have C=O but no O-H or N-H and therefore will have similar looking IR spectra.

F and I have both C=O and an O-H or N-H and therefore will have similar looking IR spectra.