Unit 11

Instrumentation (SL)

Mass, Infrared and NMR Spectroscopy

Spectroscopic Identification of Organic Compounds

Qualitative analysis: *presence* but not quantity (i.e. PEDs)

Quantitative analysis: *quantity* of substance (i.e. DUI)

Structural analysis: arrangement of atoms (i.e. natural products)

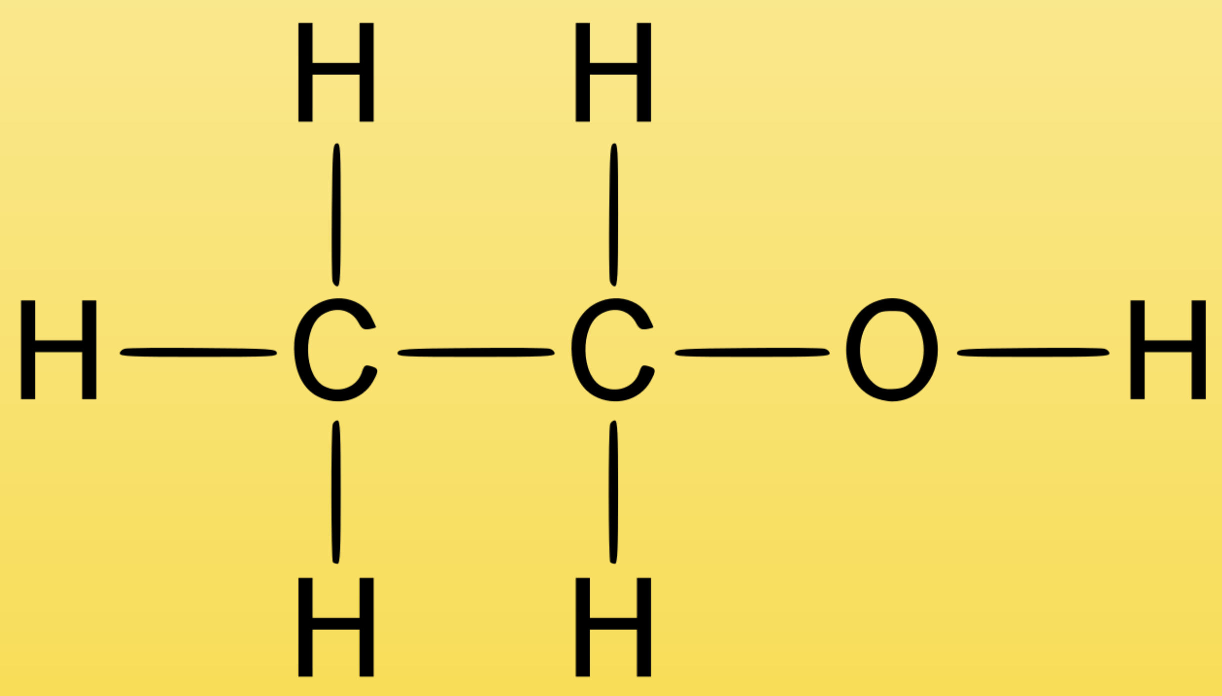
Infrared (IR) spectroscopy: bond identification

Mass spectroscopy: atomic/molecular mass

Nuclear magnetic resonance (NMR) spectroscopy: vital structural information

Mass Spectroscopy

- find the mass of individual atoms and relative abundance of different isotopes.
- find relative molecular mass of compounds
- clues about structure (fragmentation patterns)

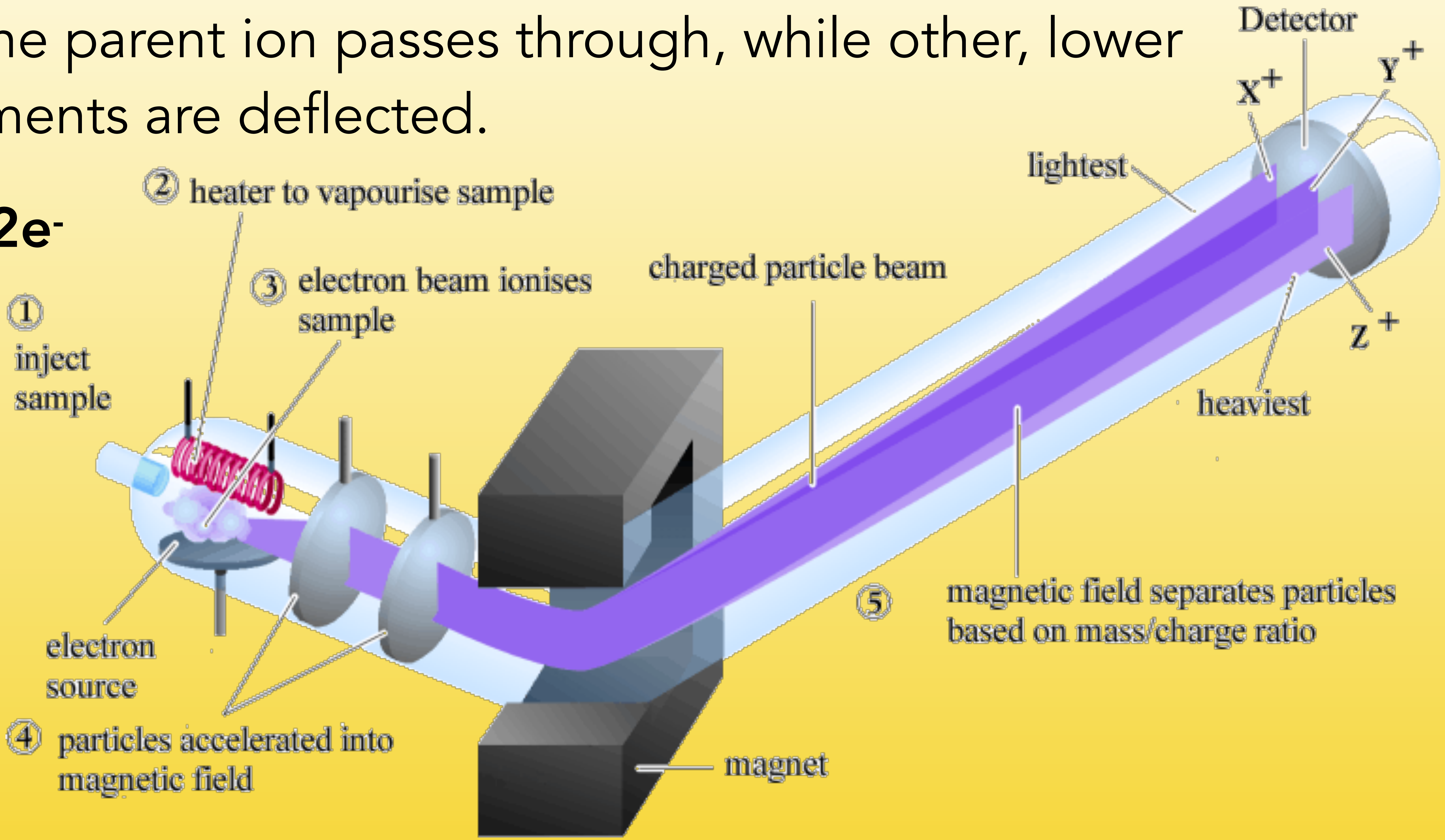


Ethanol

Mass Spectroscopy

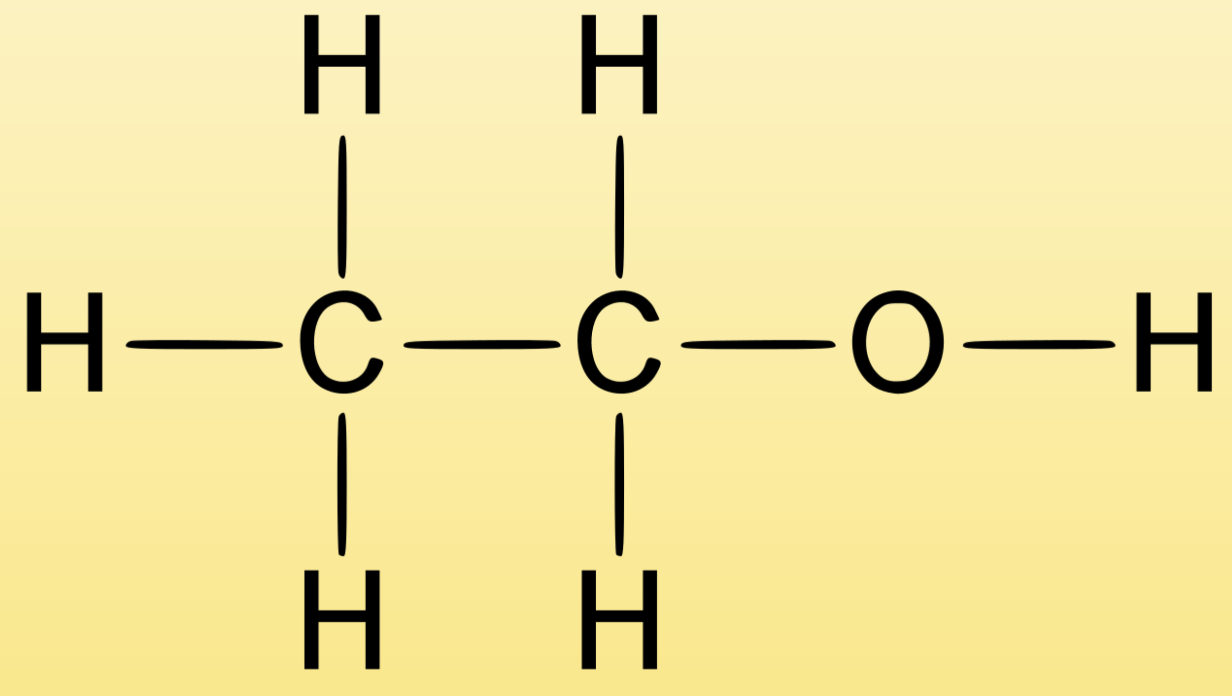
- electron from electron gun hits gaseous molecule.
- Molecule breaks up. The parent ion passes through, while other, lower molecular weight fragments are deflected.

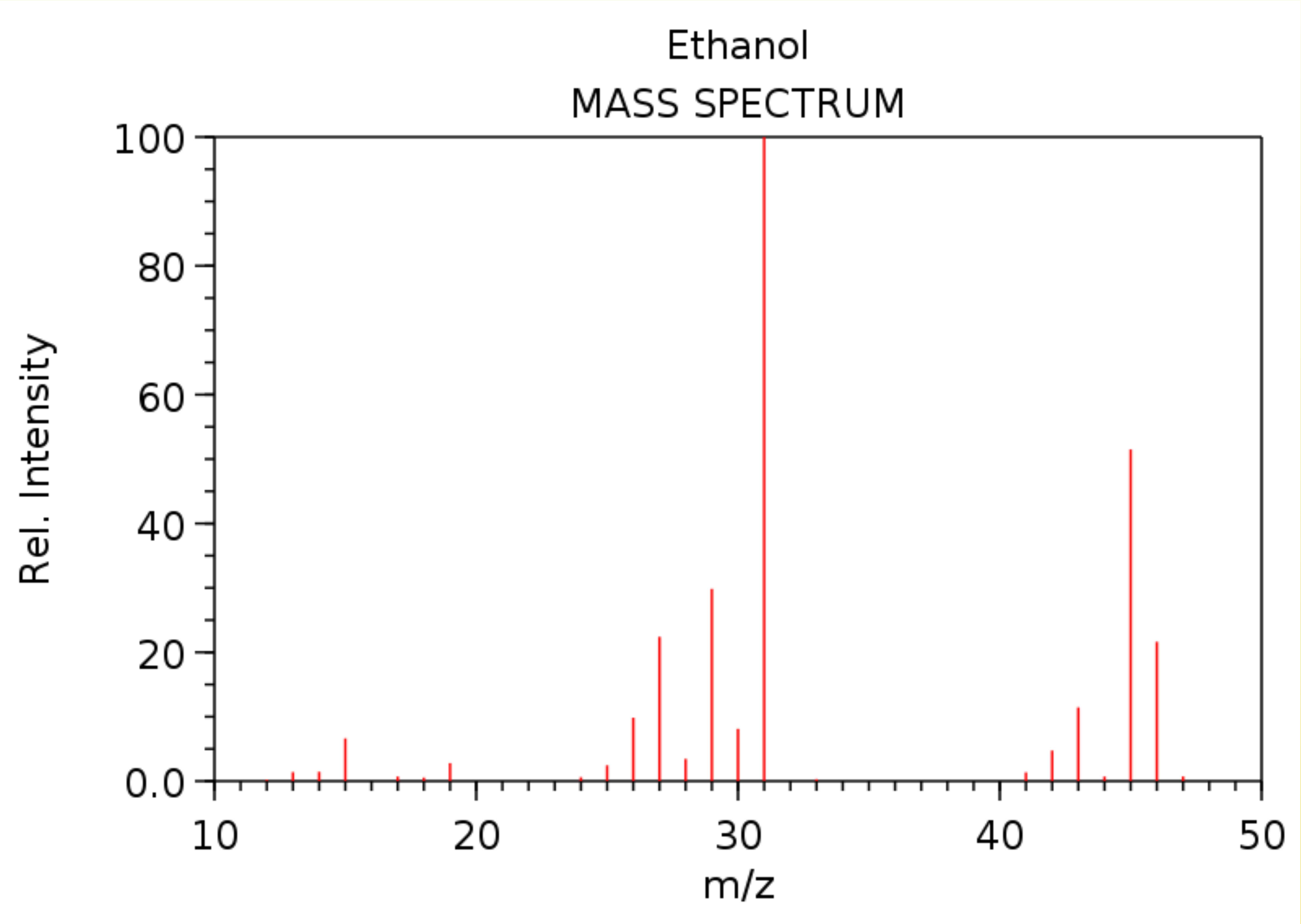
$X(g) + e^- \rightarrow X^+(g) + 2e^-$



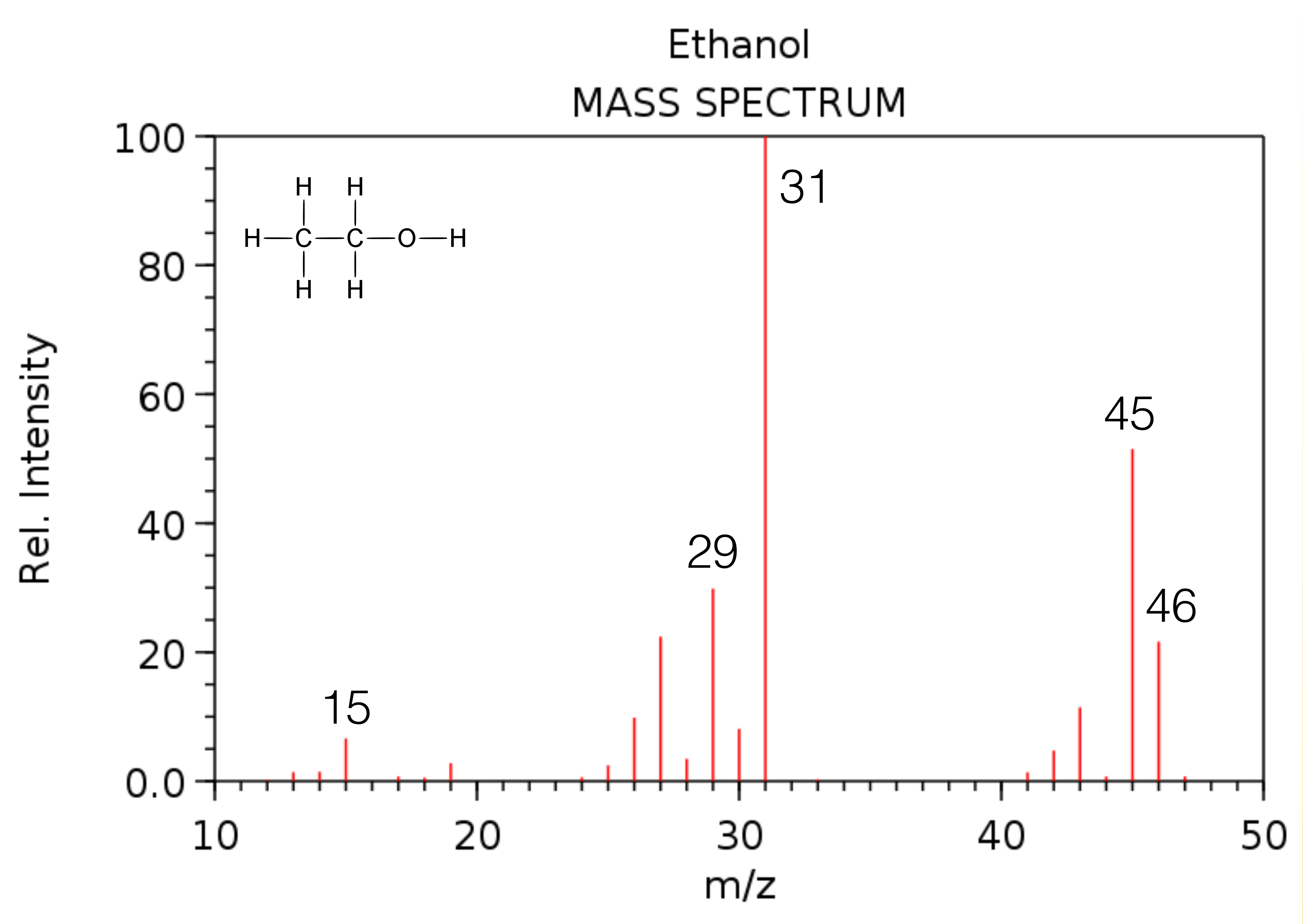
By piecing together the fragments, it's possible to form a picture of the complete structure.

Fragmentation Patterns

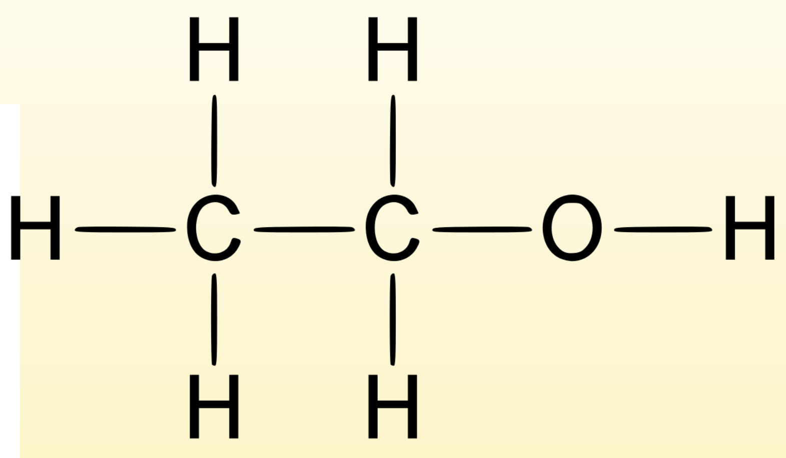


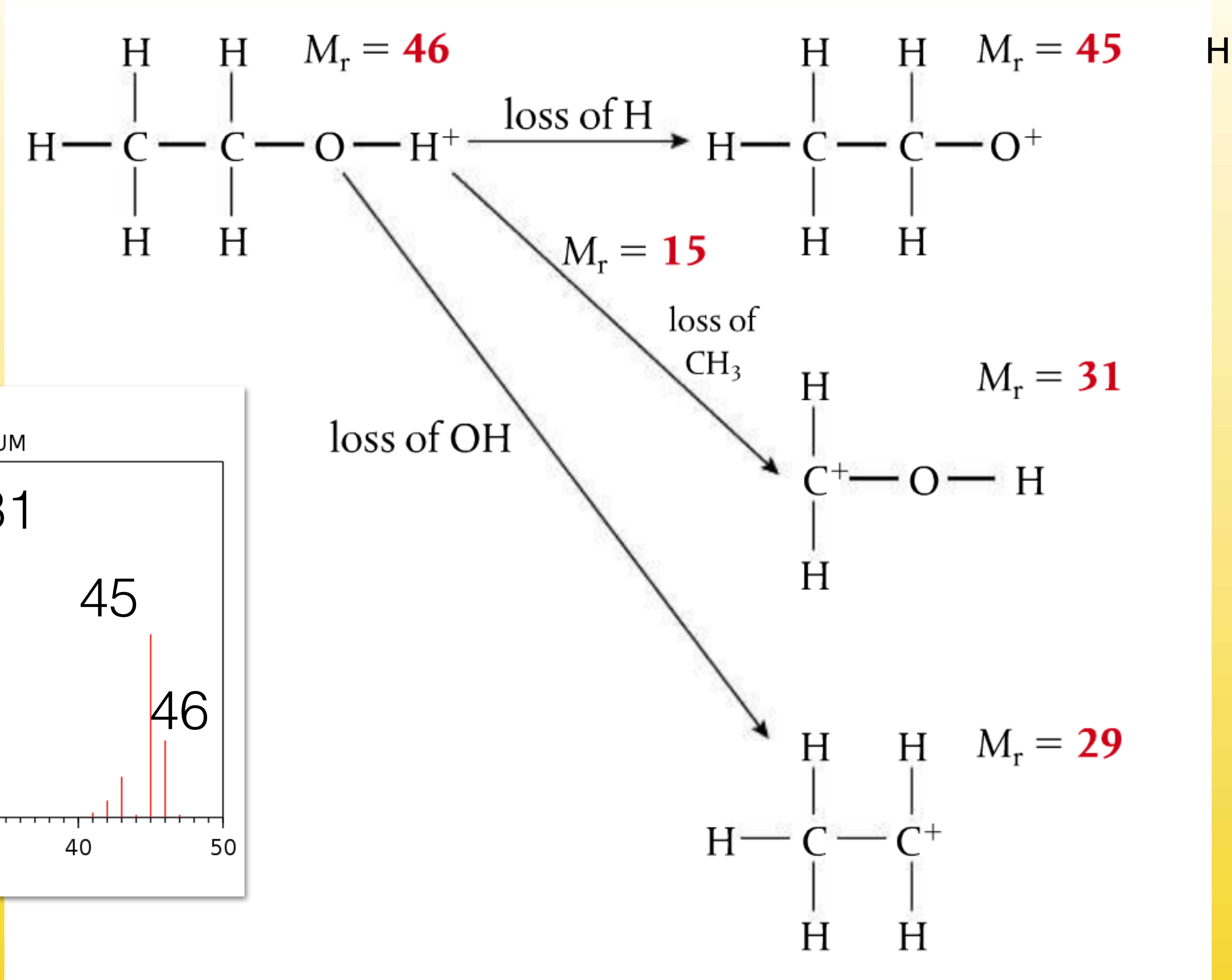


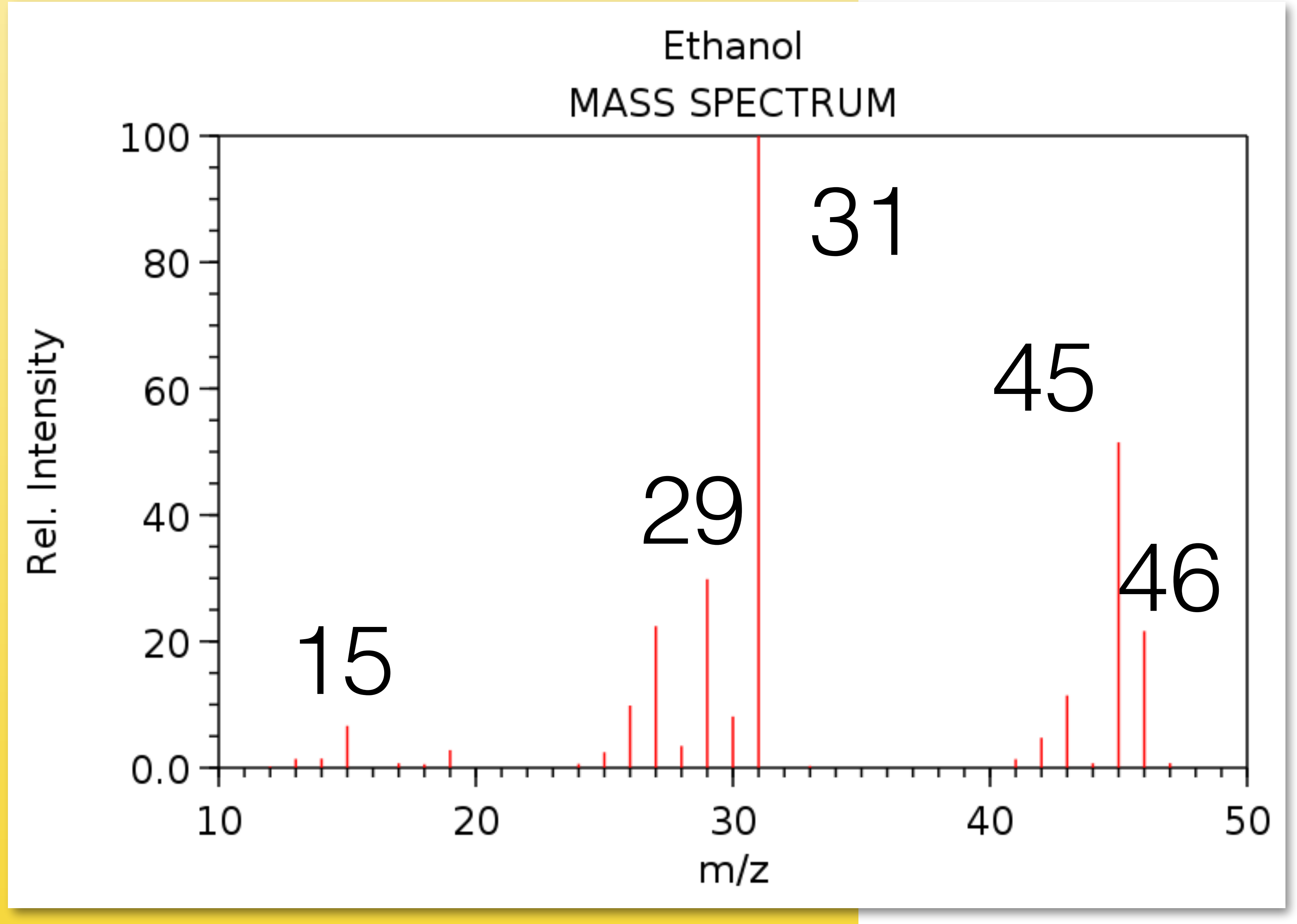
Fragmentation Patterns



Fragmentation Patterns





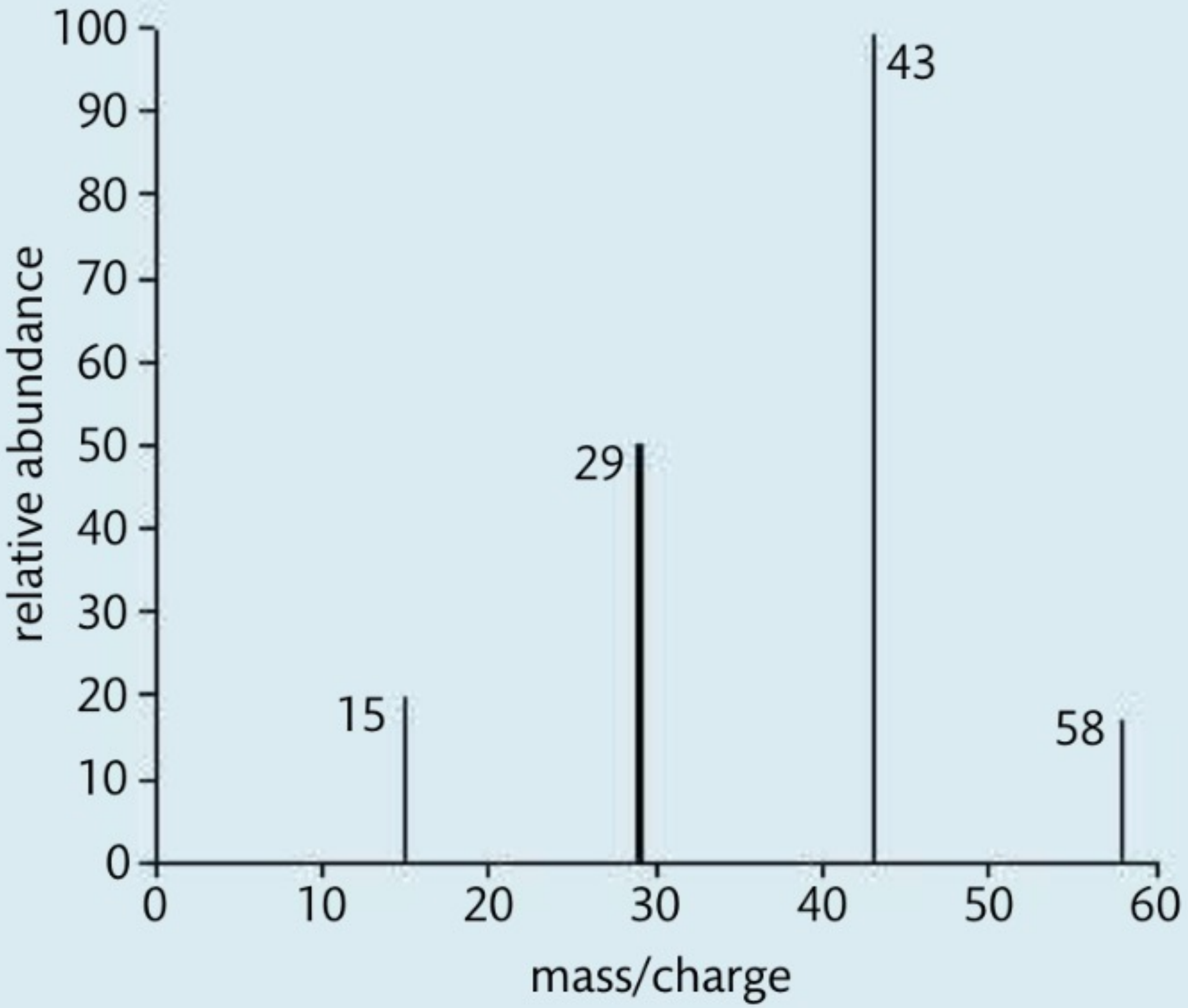


Example: Fragmentation Patterns

The simplified mass spectrum of a compound with empirical formula C_2H_5 is shown below.

(a) Explain which ions give rise to the peaks shown.

(b) Deduce the molecular structure of the compound.



Fragmentation Patterns

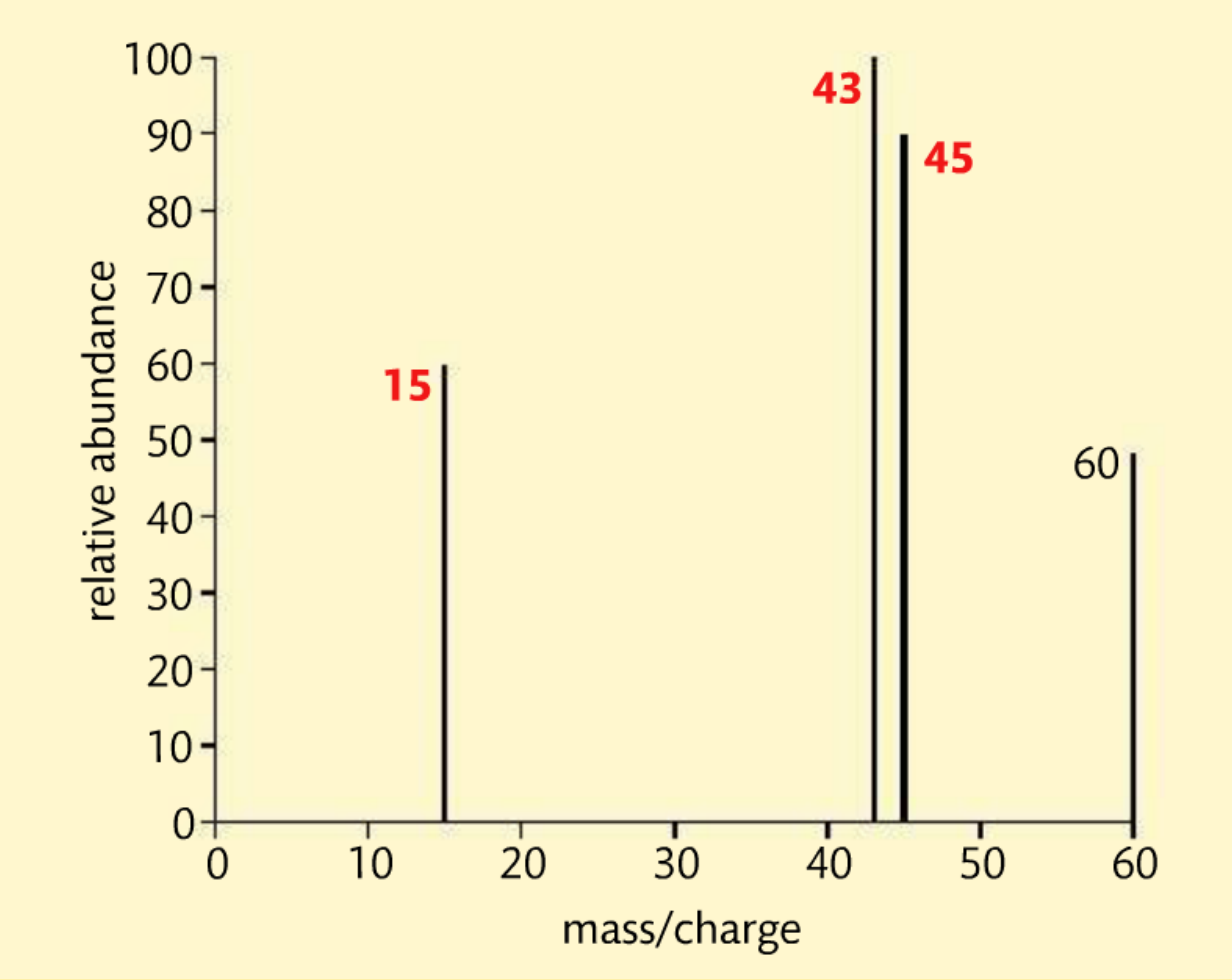
- Use Table 28 in your data booklet to help identify fragments. You're expected to recognize the following, however:

Mass lost	Fragment lost
15	$CH_3\cdot$
17	$OH\cdot$
18	H_2O
28	$CH_2{=}CH_2$, $C{=}O\cdot$
29	$CH_3CH_2\cdot$, $CHO\cdot$
31	$CH_3O\cdot$
45	$COOH\cdot$

- Don't forget to include the POSITIVE CHARGE on the ions detected by the instrument.

Example

- A molecule with an empirical formula CH_2O has the simplified mass spectrum below. Deduce the molecular formula and give a possible structure of the compound.



Degree of Unsaturation/IHD

- IHD (index of hydrogen deficiency) - clue to structure once molecular formula is known. How much H_2 needed to make an alkane.

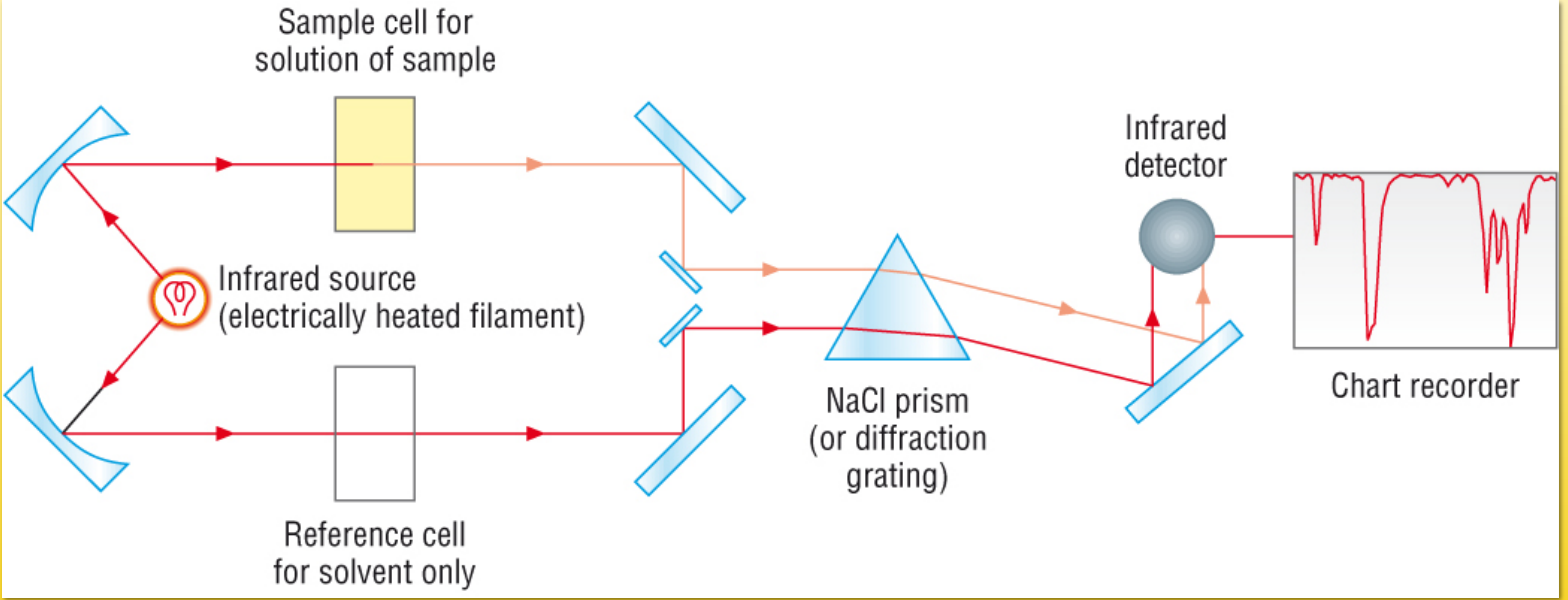
$$DoU = \frac{2C + 2 + N - X - H}{2}$$

- C is the number of carbons
- N is the number of nitrogens
- X is the number of halogens (F, Cl, Br, I)
- H is the number of hydrogens

Molecule	Saturated non-cyclic target	Index of hydrogen deficiency (IHD)
C_2H_4	C_2H_6	1
C_2H_2	C_2H_6	2
cyclobutane and but-1-ene, C_4H_8	C_4H_{10}	1
C_2H_5OH	C_2H_5OH	0
C_2H_4O	C_2H_6O	1
C_2H_5Cl	C_2H_5Cl	0

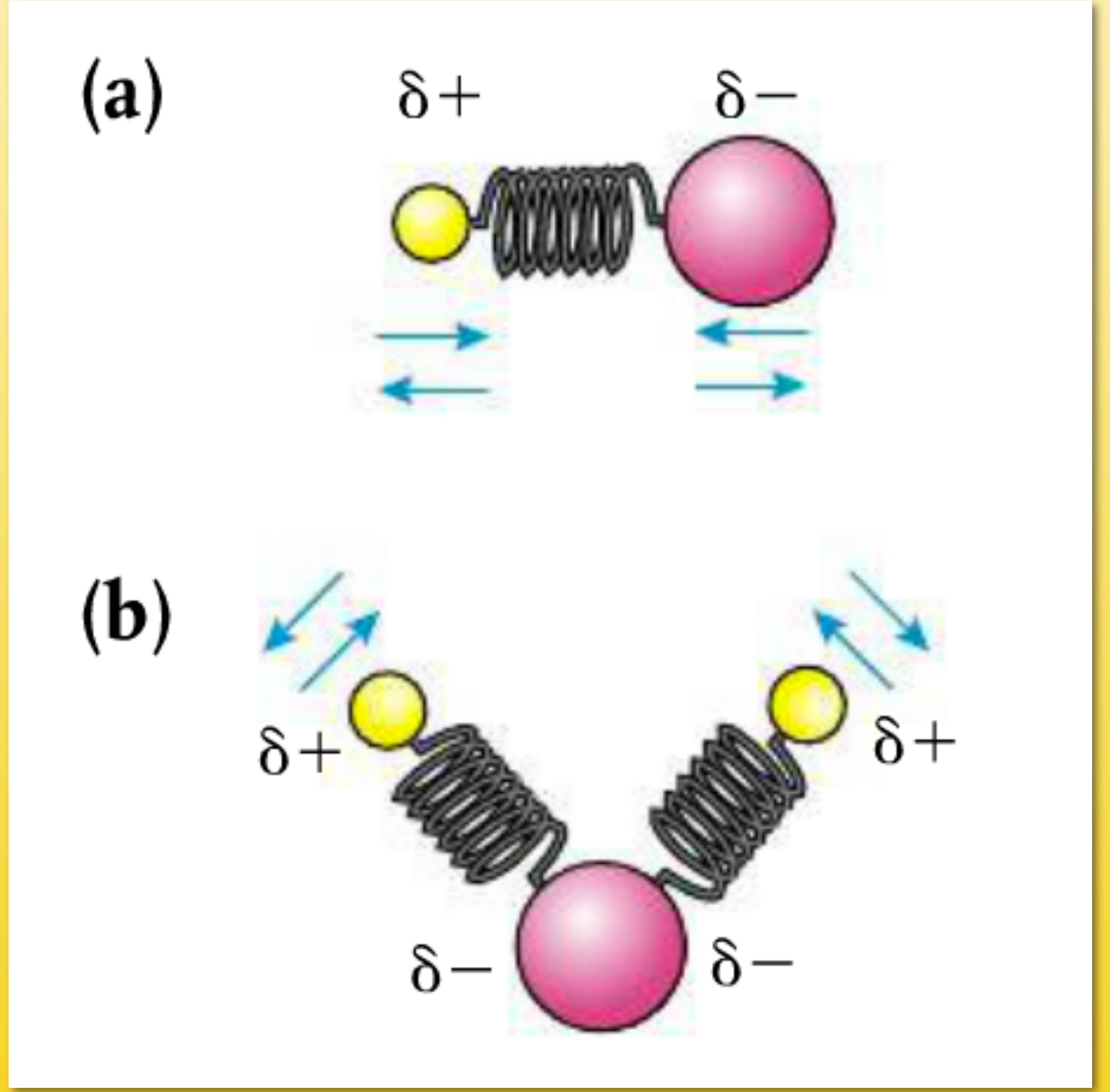
Infrared (IR) Spectroscopy

- IR radiation absorbed by certain bonds causing them to stretch or bend, giving information about bonds in a molecule.
- Frequency of radiation is often measured as number of waves per cm (cm^{-1}), also called the **wavenumber**.



Infrared (IR) Spectroscopy

- bonds are like springs, vibrating according to **bond strength** and **masses of the atoms**.
- Light atoms vibrate at higher frequencies than heavier atoms and multiple bonds vibrate at higher frequencies than single bonds

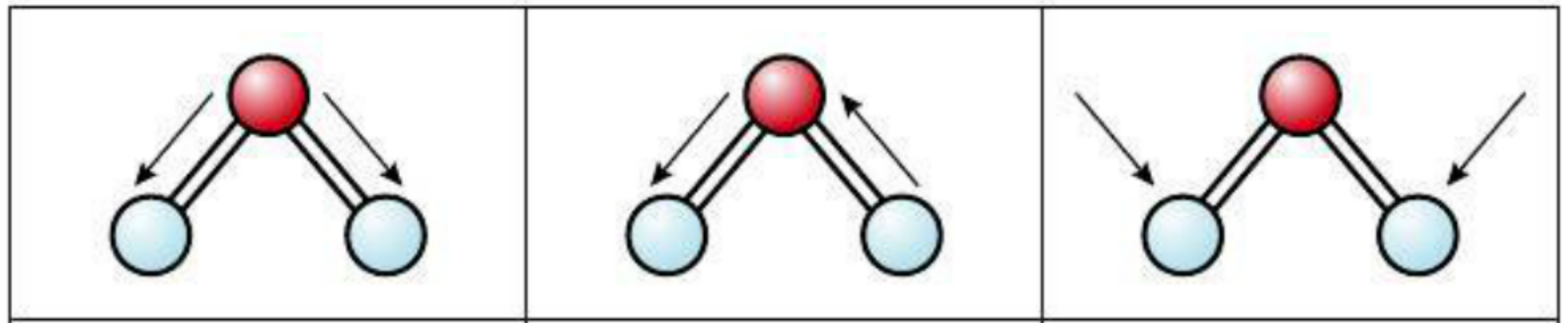


Bond Excitation

- IR energy causes an induced dipole. The more polar the bond, the more it reacts to the IR radiation, the more intense the vibration of the bond (stretch or bend)

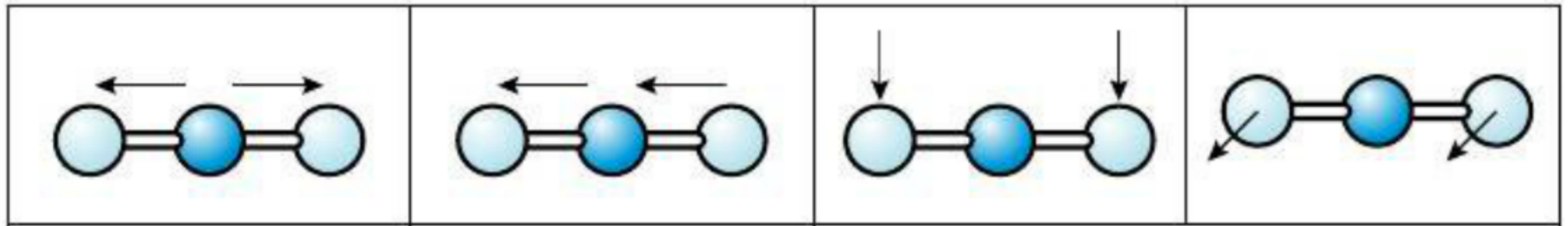
Stretching / bending in polyatomic molecules

- **Water** - stretching & bending as a whole
- 3 frequencies of vibration all of which are detectable



symmetric stretch	asymmetric stretch	symmetric bend
≈ 3650 cm^{-1}	≈ 3760 cm^{-1}	≈ 1600 cm^{-1}

- **Carbon dioxide** - symmetrical linear molecule
- 4 modes of vibration (symmetric stretch undetectable)



symmetric stretch	asymmetric stretch	two symmetric bends ≈ 670 cm^{-1}
inactive As the molecule remains symmetrical, it has no change in dipole.	≈ 2350 cm^{-1} The molecule has a temporary dipole moment when the C=O bond lengths are of unequal length.	The molecule has a temporary dipole moment as it bends away from its linear geometry. The two vibrations are identical, except that one is in the plane of the page and the other is out of the plane of the page.

Matching wavenumbers with bonds

- Different functional groups absorb IR radiation differently and distinctly. Chemists can use that information to identify different bonds. (Table 26 of IB data booklet)

Bond	Wavenumber / cm^{-1}	Intensity
C–O	1050–1410	strong
C=C	1620–1680	medium-weak; multiple bands
C=O	1700–1750	strong
C≡C	2100–2260	variable
O–H, hydrogen bonded in carboxylic acids	2500–3000	strong, very broad
C–H	2850–3090	strong
O–H, hydrogen bonded in alcohols and phenols	3200–3600	strong
N–H	3300–3500	strong

Matching wavenumbers with bonds

- Different functional groups absorb IR radiation differently and distinctly. Chemists can use that information to identify different bonds. (Table 26 of IB data booklet)

Bond	Wavenumber / cm^{-1}	Intensity
C–O	1050–1410	strong
C=C	1620–1680	medium-weak; multiple bands
C=O	1700–1750	strong
C≡C	2100–2260	variable
O–H, hydrogen bonded in carboxylic acids	2500–3000	strong, very broad
C–H	2850–3090	strong
O–H, hydrogen bonded in alcohols and phenols	3200–3600	strong
N–H	3300–3500	strong

Matching wavenumbers with bonds

- Different functional groups absorb IR radiation differently and distinctly. Chemists can use that information to identify different bonds. (Table 26 of IB data booklet)

Bond	Wavenumber / cm^{-1}	Intensity
C–O	1050–1410	strong
C=C	1620–1680	medium-weak; multiple bands
C=O	1700–1750	strong
C≡C	2100–2260	variable
O–H, hydrogen bonded in carboxylic acids	2500–3000	strong, very broad
C–H	2850–3090	strong
O–H, hydrogen bonded in alcohols and phenols	3200–3600	strong
N–H	3300–3500	strong

Matching wavenumbers with bonds

- Different functional groups absorb IR radiation differently and distinctly. Chemists can use that information to identify different bonds. (Table 26 of IB data booklet)

Bond	Wavenumber / cm^{-1}	Intensity
C–O	1050–1410	strong
C=C	1620–1680	medium-weak; multiple bands
C=O	1700–1750	strong
C≡C	2100–2260	variable
O–H, hydrogen bonded in carboxylic acids	2500–3000	strong, very broad
C–H	2850–3090	strong
O–H, hydrogen bonded in alcohols and phenols	3200–3600	strong
N–H	3300–3500	strong

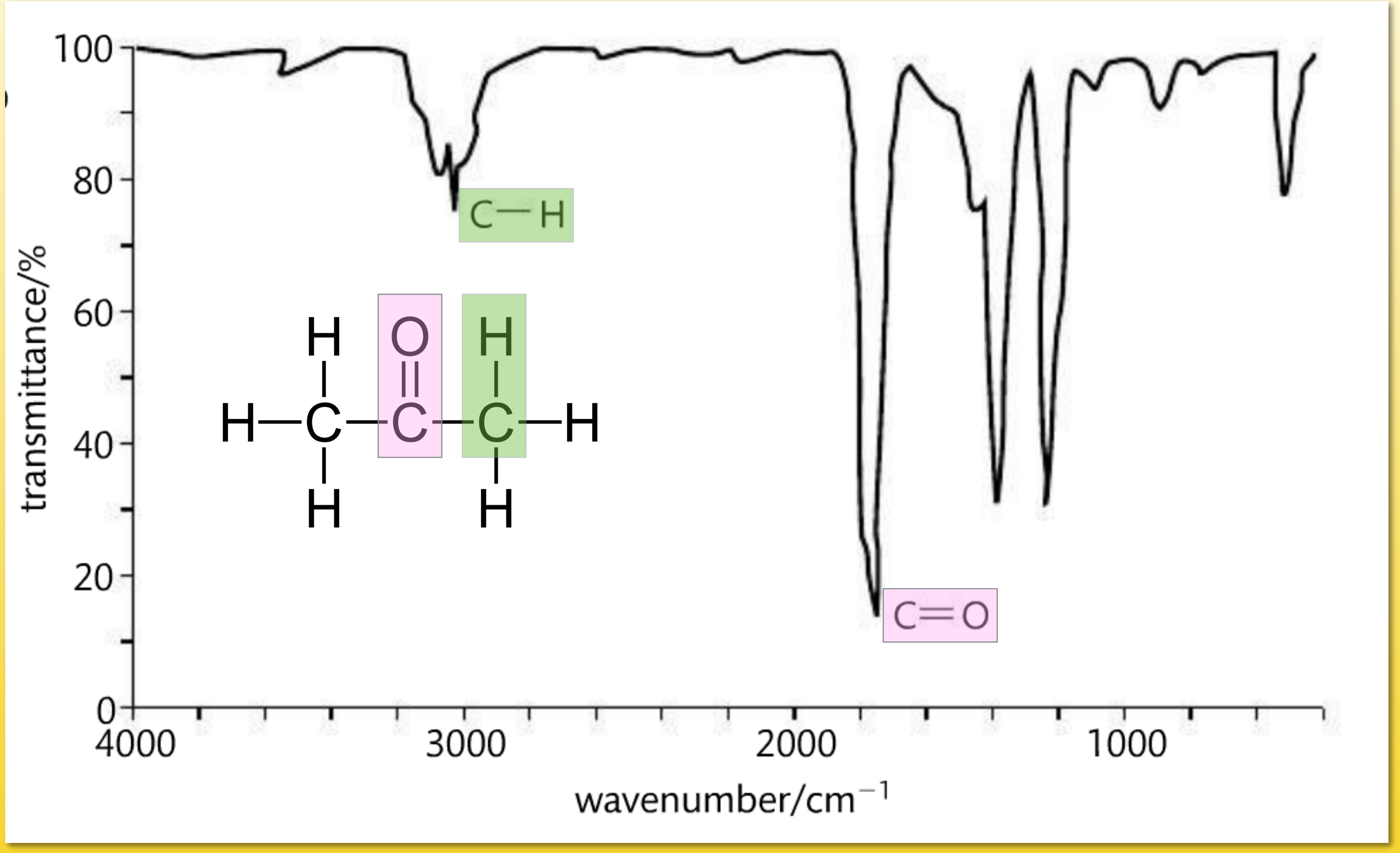
Matching wavenumbers with bonds

- Different functional groups absorb IR radiation differently and distinctly. Chemists can use that information to identify different bonds. (Table 26 of IB data booklet)
- **Hydrogen bonds!!**

Bond	Wavenumber / cm^{-1}	Intensity
C–O	1050–1410	strong
C=C	1620–1680	medium-weak; multiple bands
C=O	1700–1750	strong
C≡C	2100–2260	variable
O–H, hydrogen bonded in carboxylic acids	2500–3000	strong, very broad
C–H	2850–3090	strong
O–H, hydrogen bonded in alcohols and phenols	3200–3600	strong
N–H	3300–3500	strong

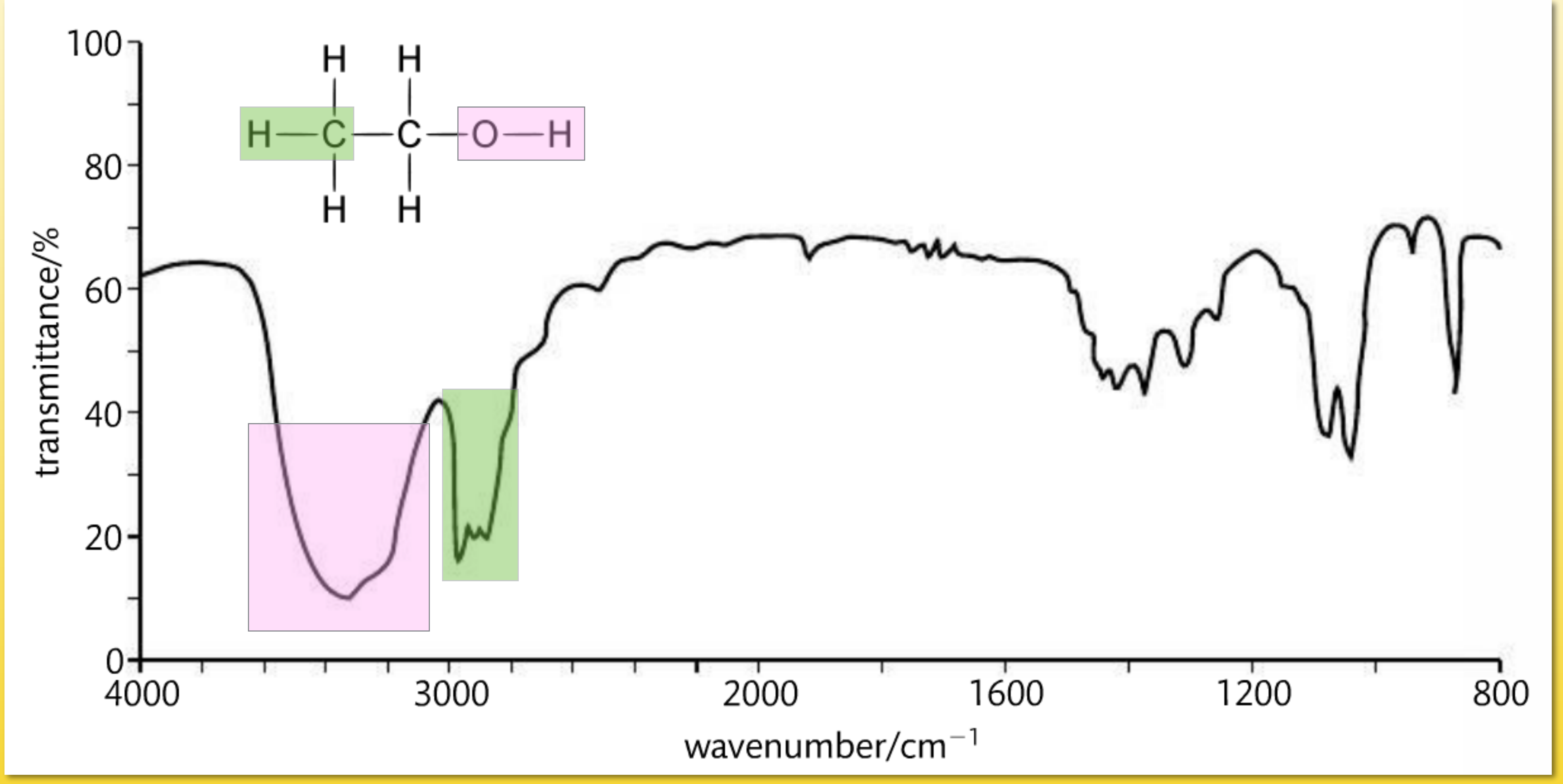
Sample IR Spectra

- Let's compare propanone (acetone) and ethanol

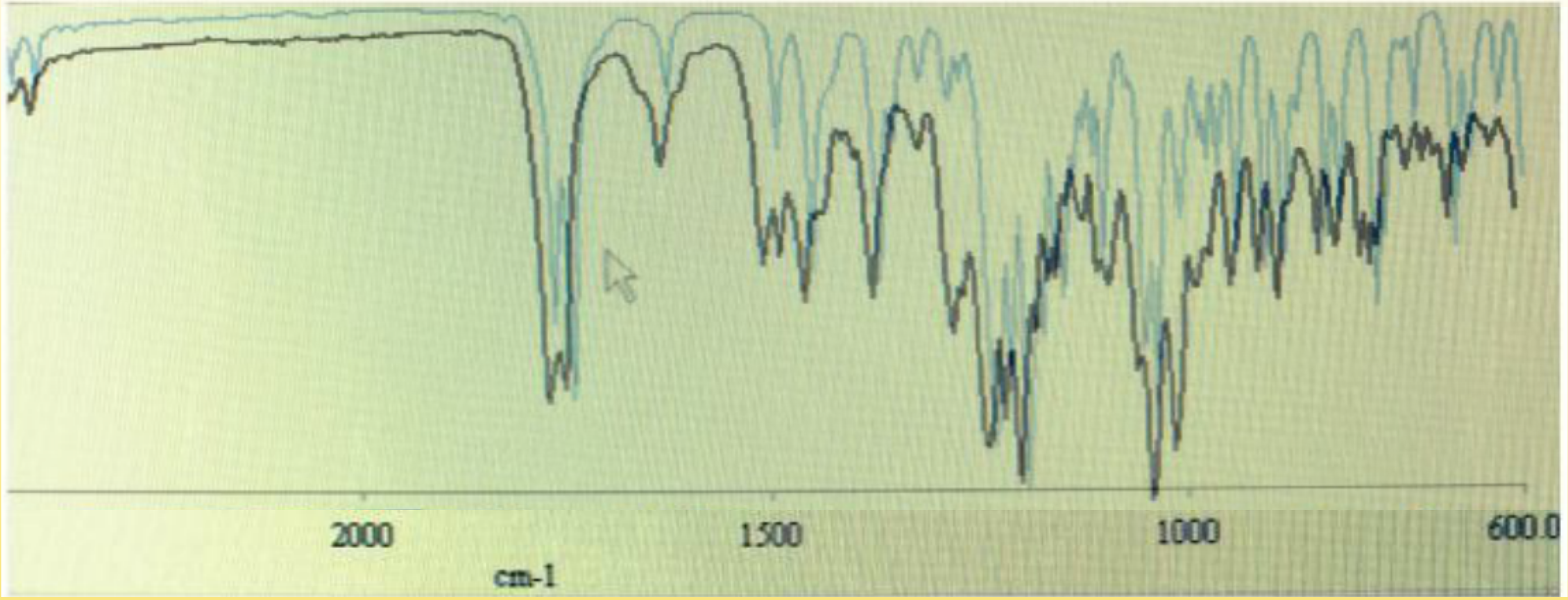


Sample IR Spectra

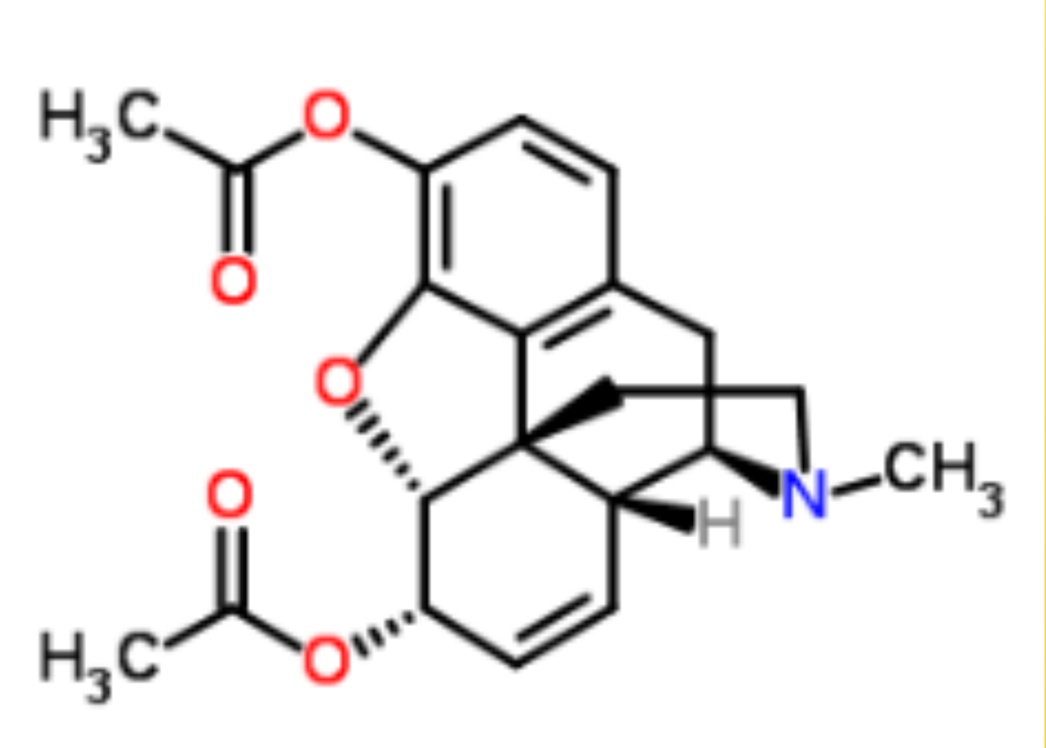
- Let’s compare propanone (acetone) and ethanol



Unknown Comparisons

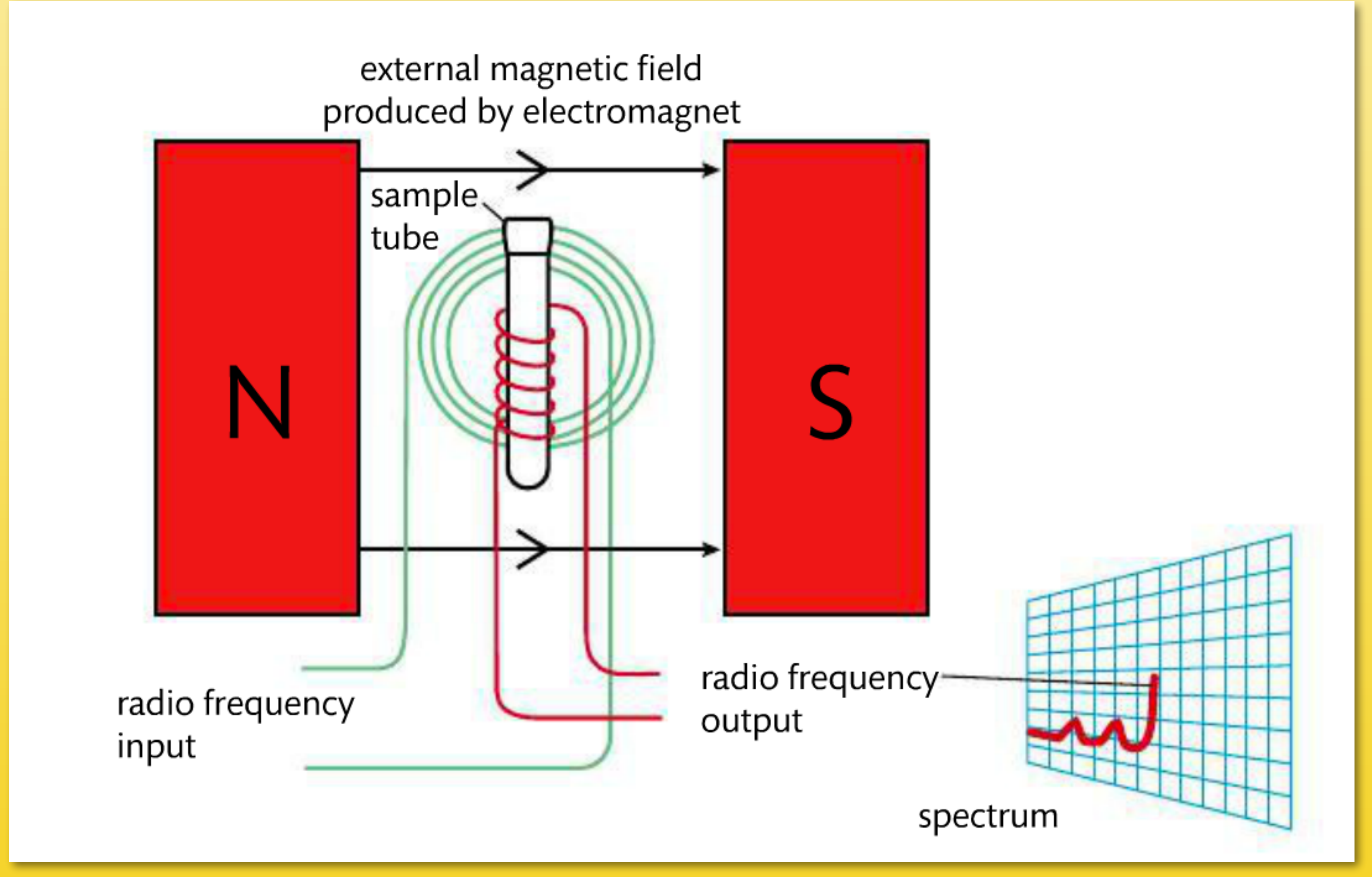


- The blue spectrum is pure heroin while the superimposed black spectrum is an unknown sample … Forensics connection.



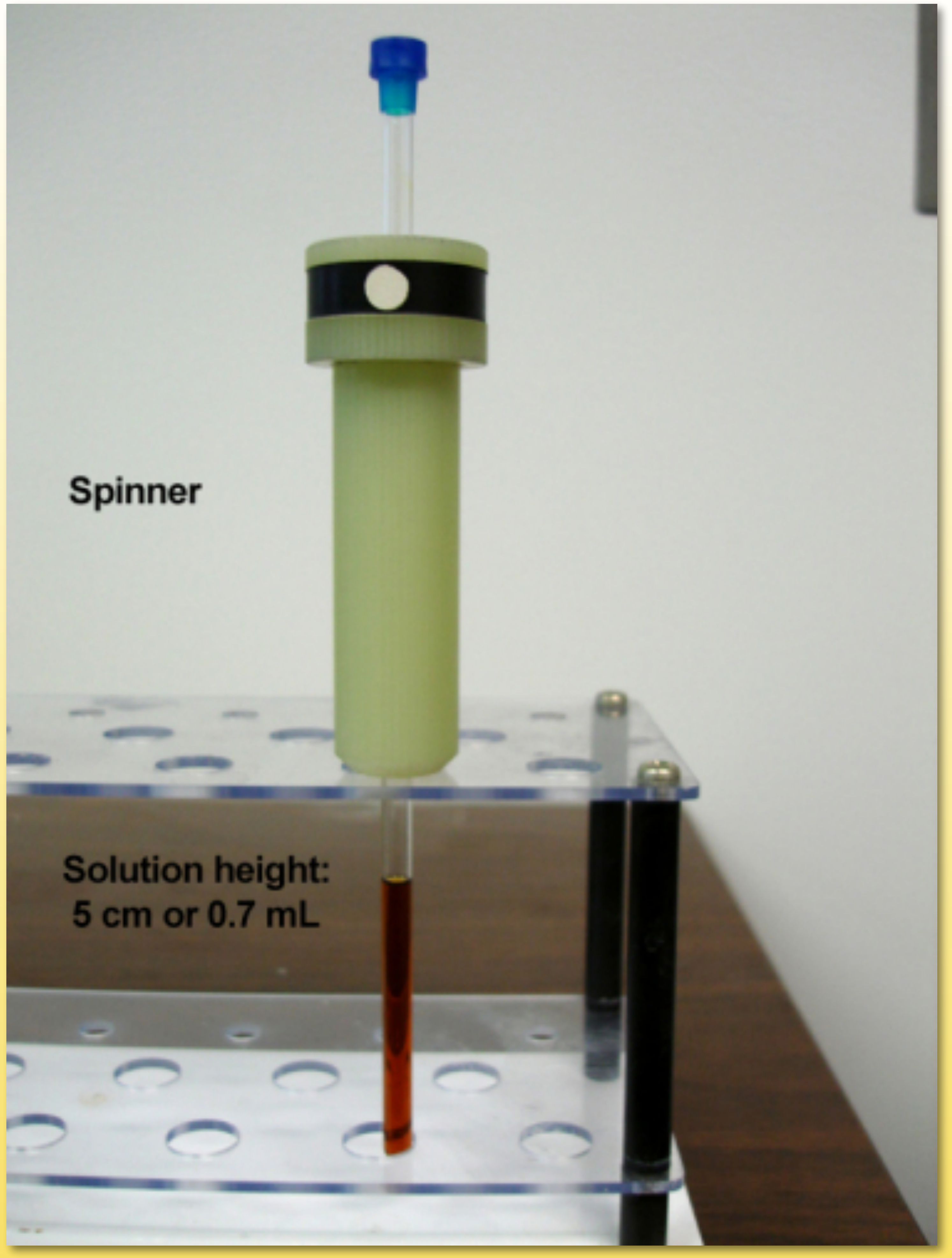
Nuclear Magnetic Resonance (NMR)

- Powerful technique for finding structure and shape of molecules
- Nuclei of atoms with odd #s of protons (^{1}H, ^{13}C, ^{19}F, ^{31}P) behave like tiny bar magnets.
- When placed in a magnetic field some will line up with and others against the field.
- Sample placed in an electromagnet, field strength is varied until nuclei flip (resonance), which can be detected.



NMR

- Non-invasive technique

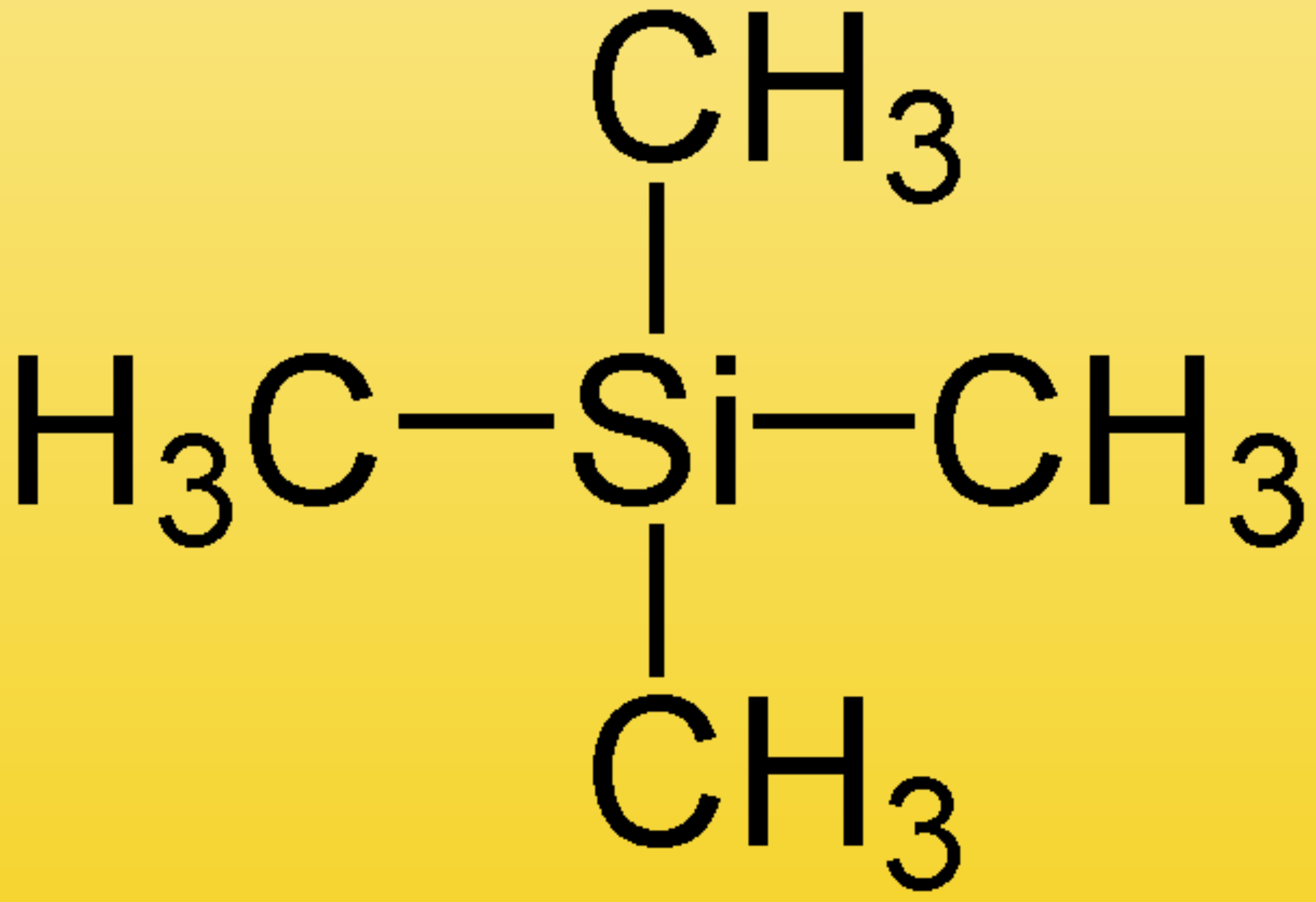


- Can erase debit cards
- Anything ferromagnetic could be attracted to the powerful magnet
- Cooled with LN_2.

NMR

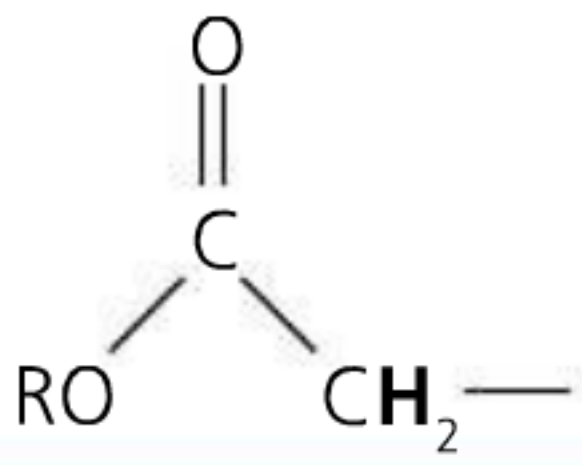
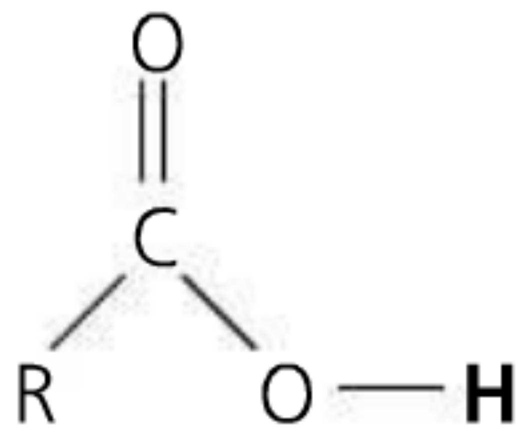
- Electrons shield nucleus (where the protons live) from the magnet.
- Different **chemical environments** for various protons then exist and produce different signals in the spectrum.
- Hydrogen nuclei (present in all organic molecules) give information about their position in the molecule.
- Measured against a standard, tetramethylsilane (TMS).
- Position of signal relative to the standard is the **chemical shift**.

- TMS is therefore assigned a shift of 0 ppm
- All of the protons are in the same chemical environment.
- Chemically inert.



Sample Shifts

- See Table 27 for a comprehensive list.

Type of proton	Chemical shift / ppm
TMS	0
$—CH_3$	0.9–1.0
	2.0–2.5
	9.0–13.0*
R—O—H	1.0–6.0*

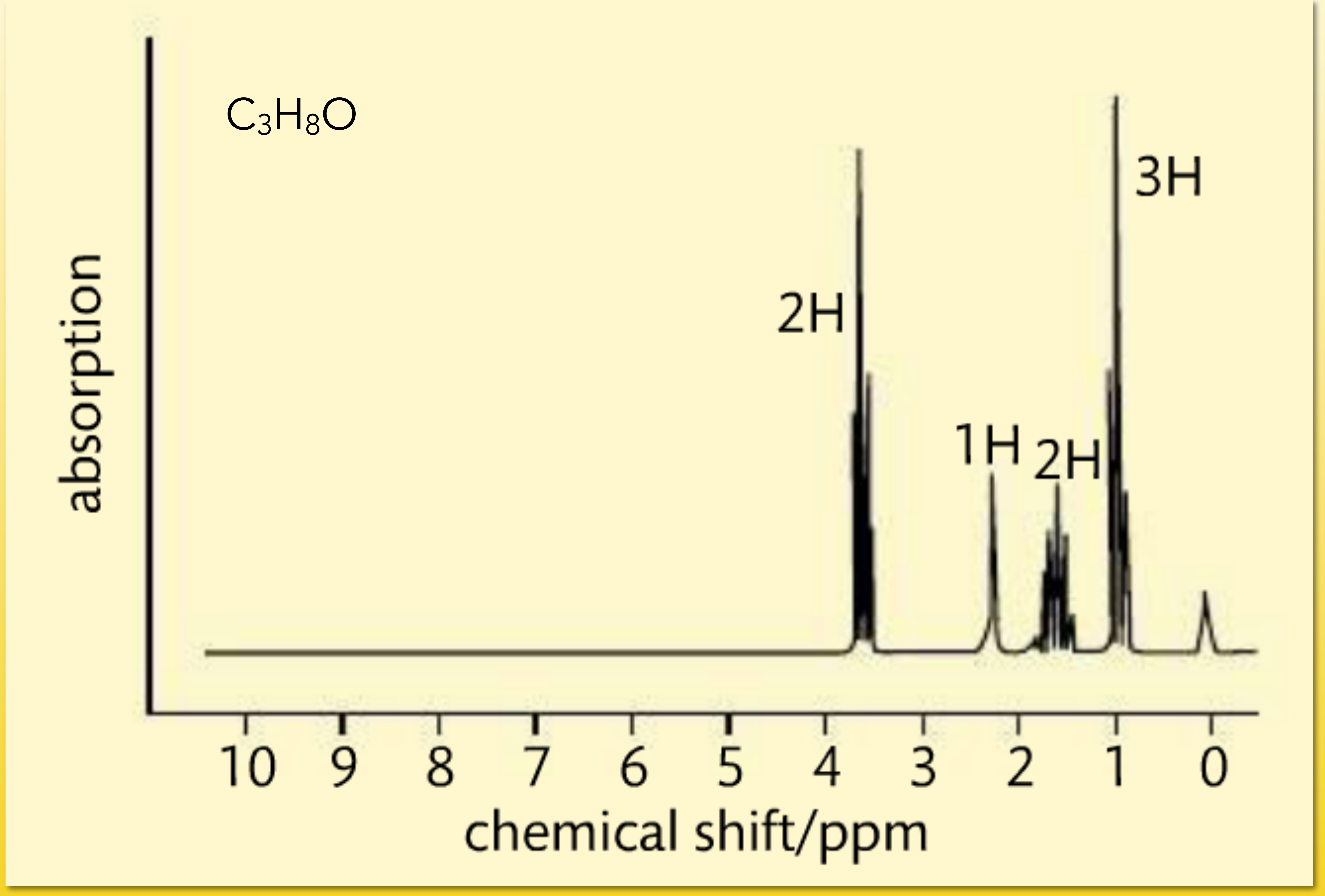
*variance due to hydrogen bonding

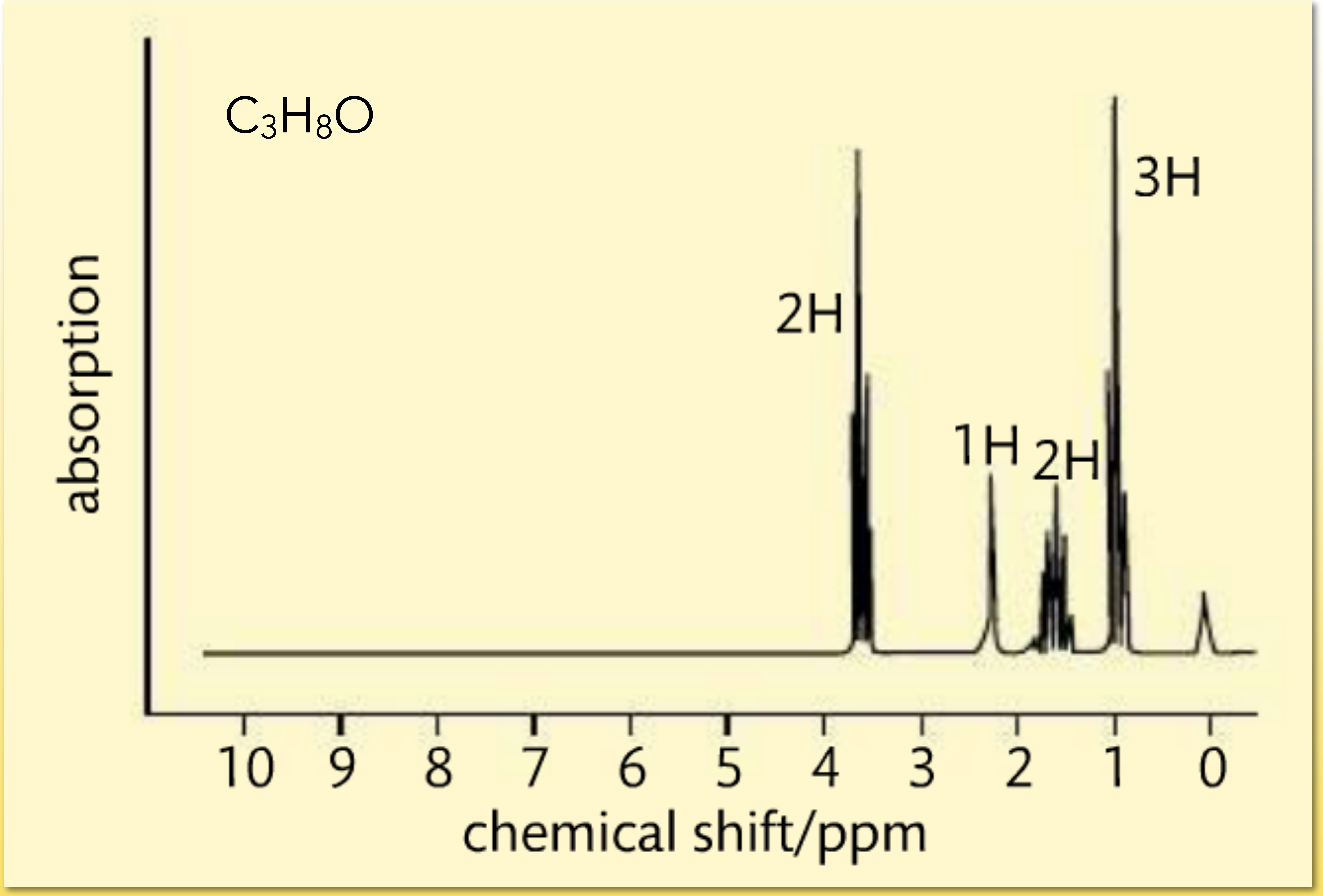
Interpreting ^{1}H NMR spectra

- Sample spectrum of ethanal.
- Integration included to show # of protons attached to carbons.

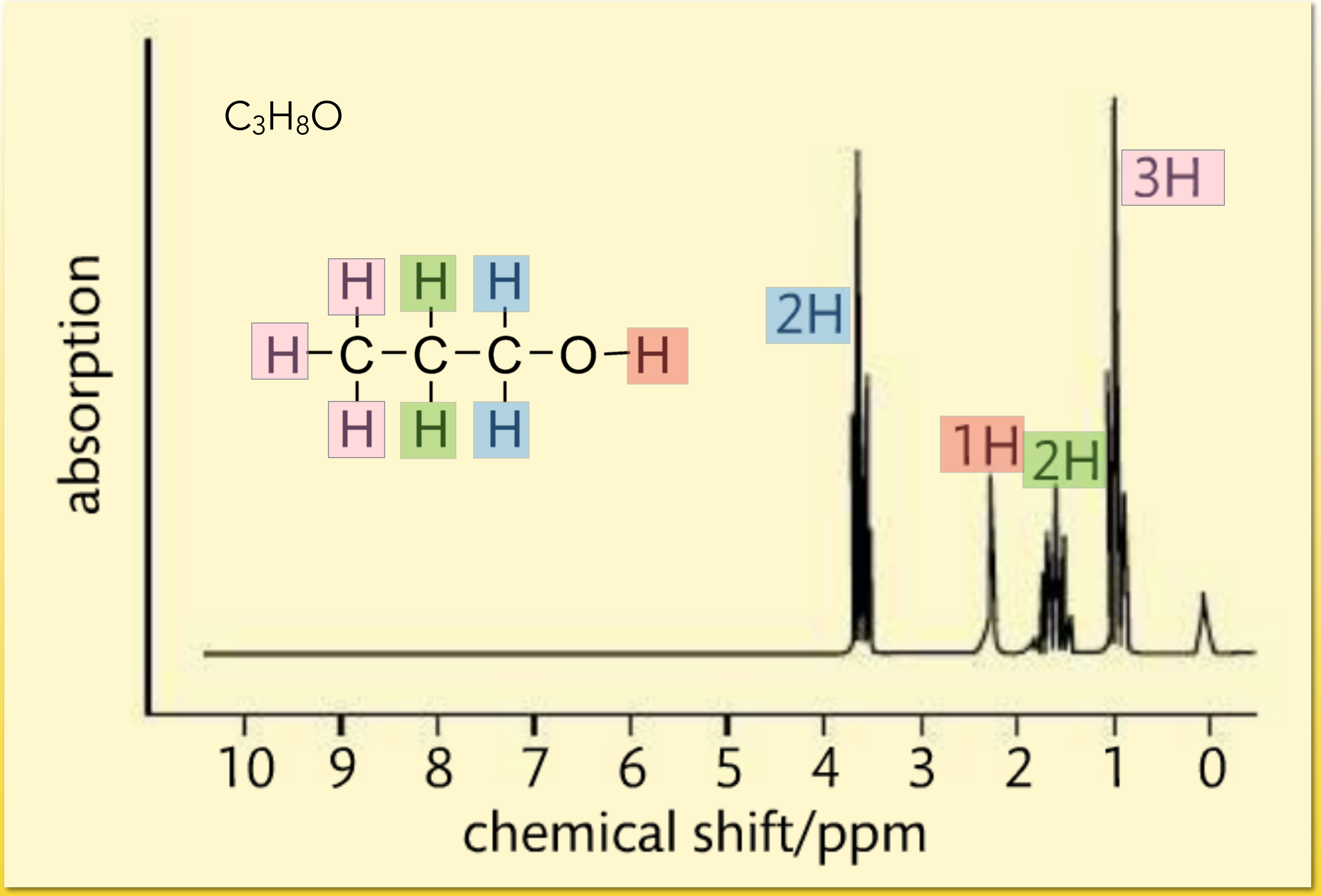
Example

- The [1]H NMR spectrum of a compound which has the molecular formula C_3H_8O is shown here.





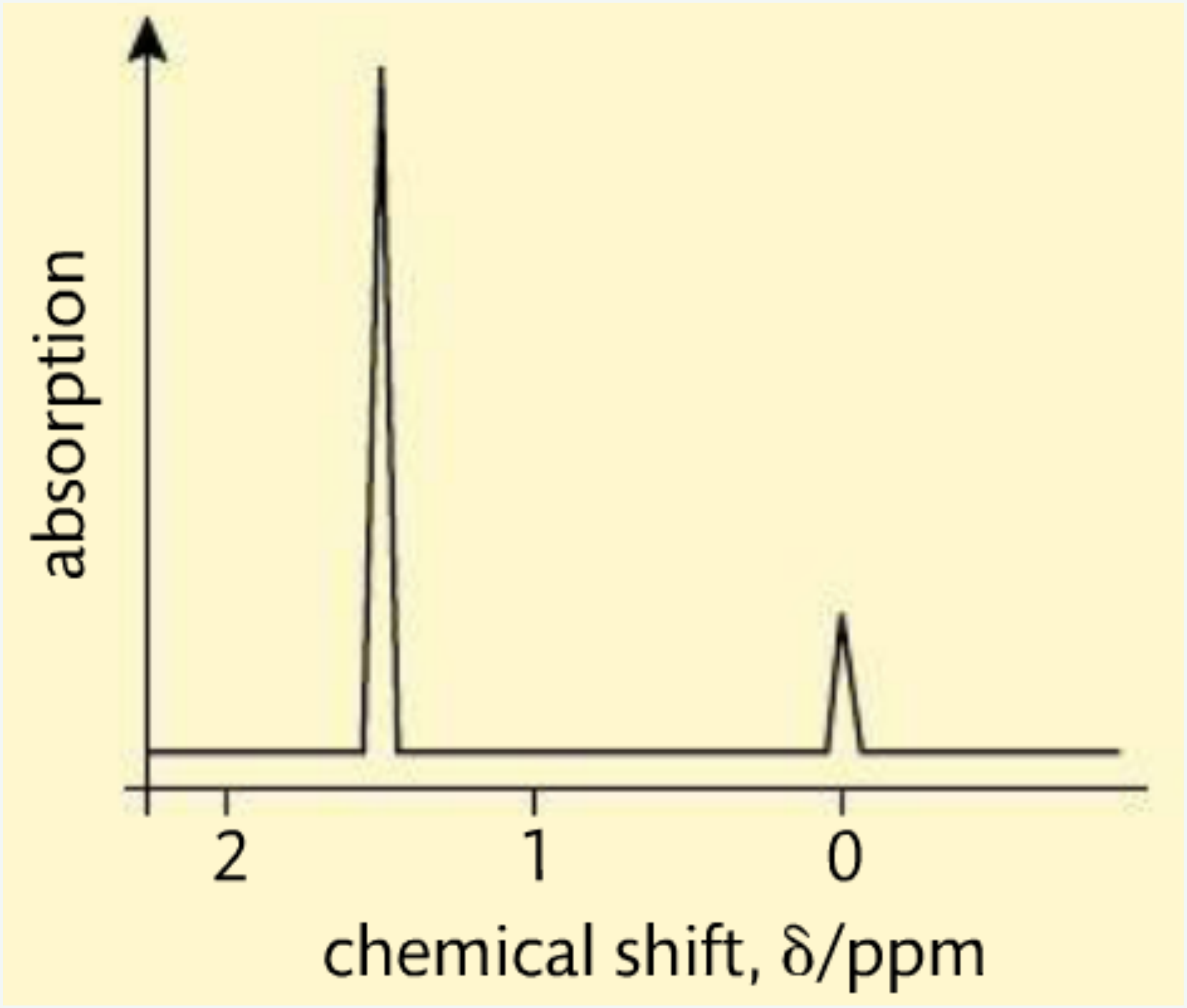
1. Draw structural formulas and name 3 possible isomers
2. What is responsible for the peak at 0 ppm?
3. Identify the unknown compound from the number of peaks.
4. Identify the group responsible for the signal at 0.9 ppm.

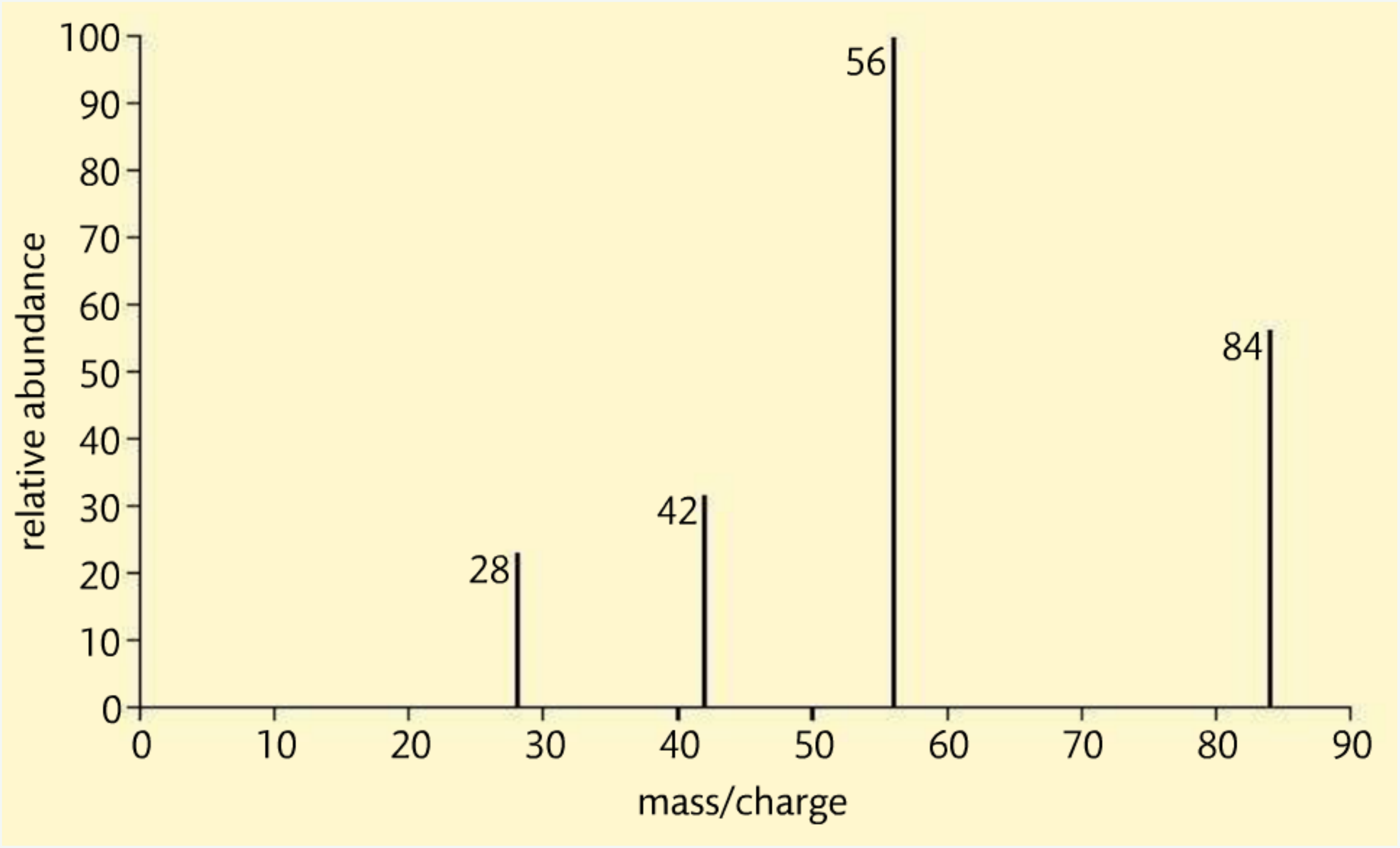


C3H8O
H
H
H
H–C–C–C–O–H
H
H
H
2H
1H
2H
3H
absorption
10
9
8
7
6
5
4
3
2
1
0
chemical shift/ppm

Combining Analytical Techniques

	% composition by mass
C	85.6
H	14.4





- Deduce IHD and molecular formula (Mass Spec)
- Is a CH_3 group present? (Mass Spec)
- The infrared (IR) spectrum shows one absorption close to 2900 cm^{-1}, but there is no absorption close to 1600 cm^{-1}. State what can be deduced from this.
- Deduce molecular structure. (^1H NMR)