

# Organic Chemistry Part One: Spectroscopy

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## Section 1: General Aspects

Spectroscopy: A set of techniques in which the response of molecules to the input of energy is measured.

*i.e.*, supply electromagnetic radiation to compounds, and observe the interaction.

Emphasis in these lectures:

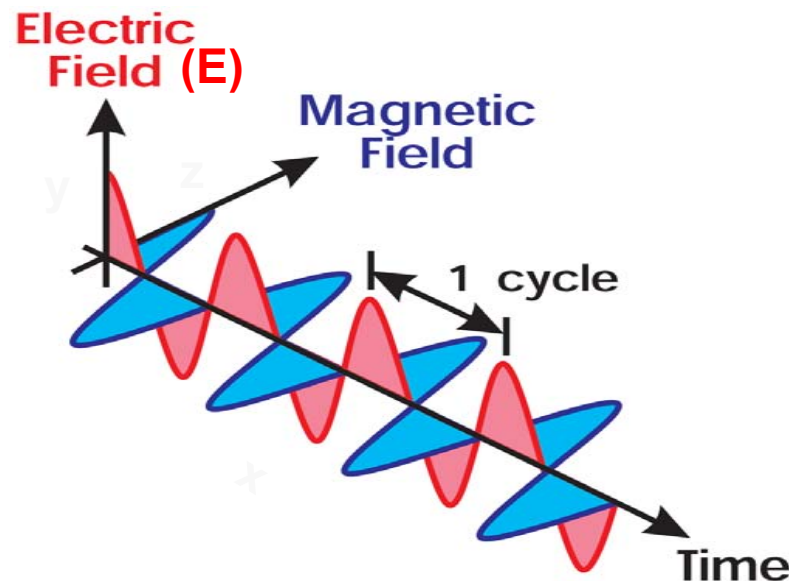
The interpretation of spectra, not physical aspects (see Physical Chemistry) or instrumentation (see Analytical Chemistry).

# ELECTROMAGNETIC RADIATION

## DUAL NATURE: *WAVES VS PARTICLES*

### 1. WAVE NATURE:

Travelling waves of varying *electric* (E) and *magnetic* (H) field strength.



E and H oscillate at right angles to each other and to the direction of propagation.

# ELECTROMAGNETIC RADIATION

QUANTITY	SYMBOL	UNITS
WAVELENGTH		m (SI) nm = $10^{-9}$ m (nm used in UV/vis)
VELOCITY		m s <sup>-1</sup> (SI)
FREQUENCY		s <sup>-1</sup> Hertz (Hz)
WAVENUMBER		m <sup>-1</sup> (SI) cm <sup>-1</sup> (used in IR)

## 2. PARTICLE NATURE:

“Photons”, each having a distinct energy given by:

$$E = h\nu \text{ (units: Joules, J)}$$

(h is Planck’s constant:  $6.626 \times 10^{-34}$  J s)

The regions of interest to us have  $E \approx 10^{-20}$  TO  $10^{-28}$  J.

Very small!

For a mole of photons,  
(where  $N_A$  is Avogadro’s number)

UNITS:

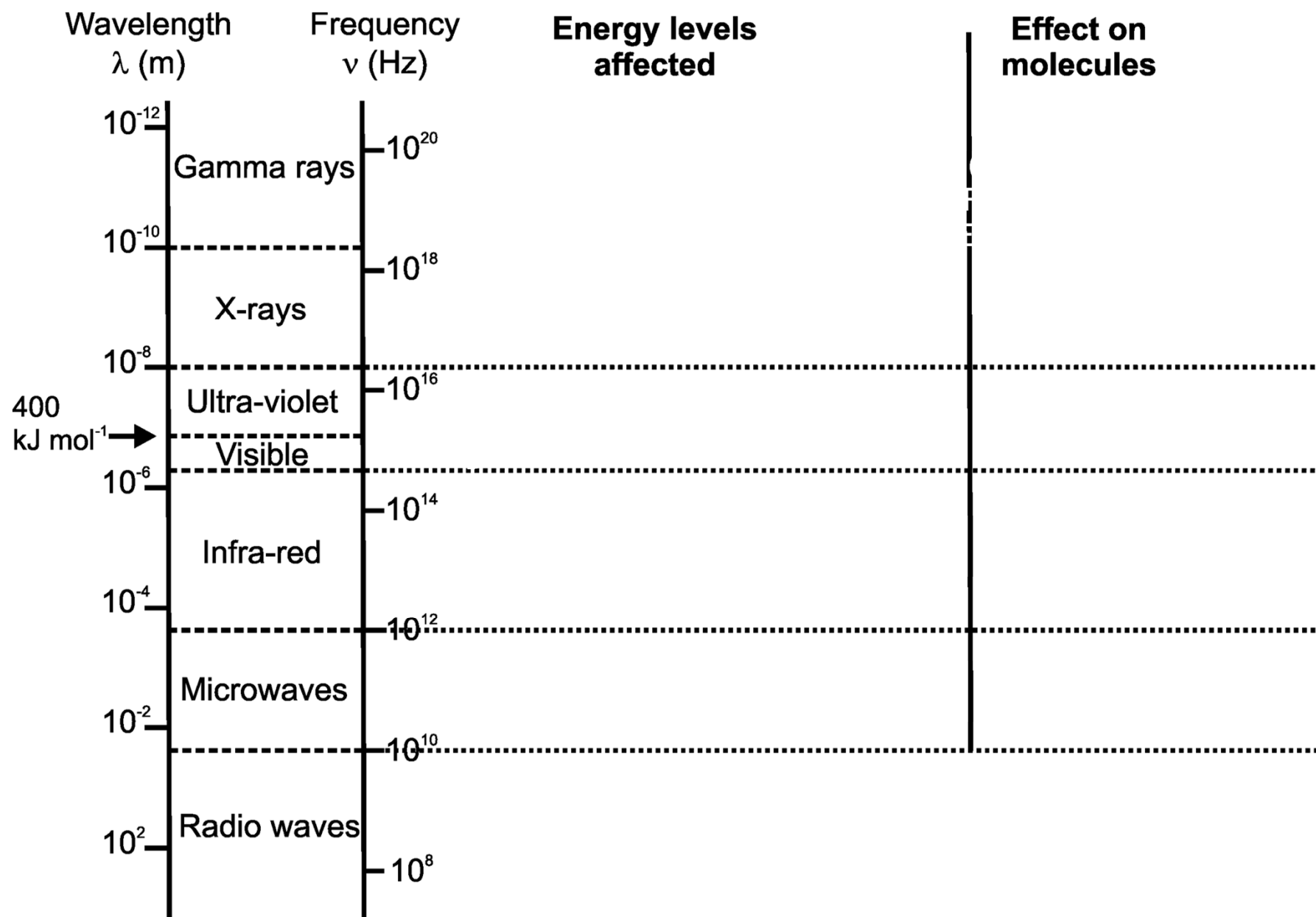
Note:

Spectroscopies of interest to us are *absorption* spectroscopies:

A molecule in a low energy state is excited to a higher energy state by *absorbing* a photon of energy. The change in energy is symbolised  $\Delta E$ .

(This is the typical situation in our common spectroscopies: IR, UV/vis, NMR)

# Regions of the electromagnetic spectrum:



## Obtaining spectra

1. Radiation of known wavelength passes through sample.
2. Sample *absorbs* energy.  $\therefore$  beam's intensity decreases as it emerges.



3. Detect the emerging beam and measure its intensity.
4. Repeat at other wavelengths.
5. "Graph" of intensity vs wavelength is a spectrum.  
(plural: spectra)



## Terms used in absorption spectroscopies

$I_0$  = Intensity of radiation                      passing through sample

$I$  = Intensity of radiation                      passing through sample

Transmittance,  $T$  =  
often expressed as %

Absorbance,  $A$  =

The Beer-Lambert law relates absorbance to concentration:

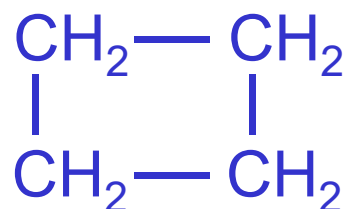
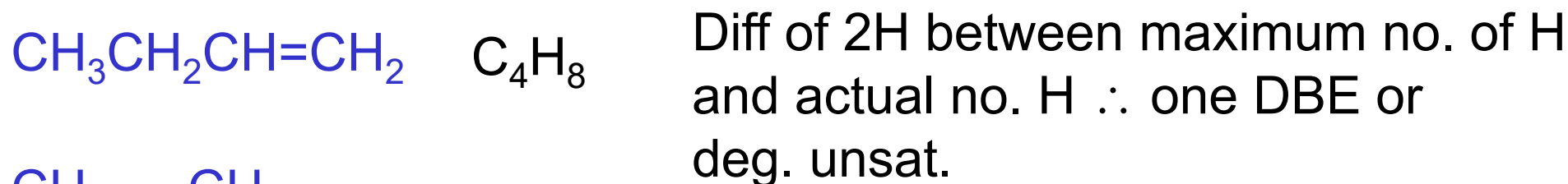
Where  $c$  = concentration of solution      ( $\text{mol L}^{-1}$ )  
    / or  $b$  = path length of solution      (cm)  
         $\epsilon$  = molar extinction coefficient      ( $\text{L mol}^{-1}\text{cm}^{-1}$ )

## Degree of unsaturation

Also called Double Bond Equivalence (DBE)

For a saturated hydrocarbon with  $n$  carbon atoms, the maximum possible number of H atoms is given by  $2n+2$  (Compound Formula:  $C_nH_{2n+2}$ ).

e.g.



So each degree of unsaturation represents

$$\text{DBE} = \frac{\text{theoretical maximum no. H} - \text{actual H} - \text{Hal} + \text{N}}{2}$$

In general, for a given compound:

The DBE can be calculated from the molecular formula thus:

$$\frac{[\text{theoretical maximum no. H } (2n+2) - \text{actual H} + \text{N} - \text{Hal}]}{2}$$

*e.g.*  $\text{C}_4\text{H}_6\text{BrNO}$        $\text{DBE} = \frac{10 - 6 + 1 - 1}{2}$

2 DBE  $\therefore$  either: 2 double bonds  
or 2 rings  
or one of each  
or one triple bond

Now suggest possible functional groups:

## Degree of unsaturation example

A compound has the formula  $\text{C}_8\text{H}_7\text{Br}$

1. Work out the double bond equivalence
2. Propose a structure for the compound

DBE =

For example

OR

OR

OR

## Section 2: Infra-red (IR) Spectroscopy

### Basics

1. Typical operating range of instruments:

$\lambda$ :  $2.5 \times 10^{-6} \text{ m}$  to  $2.5 \times 10^{-5} \text{ m}$

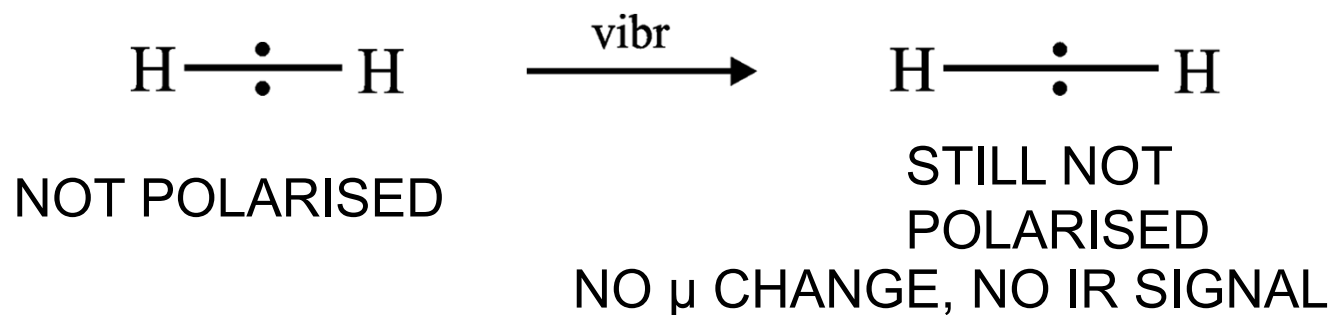
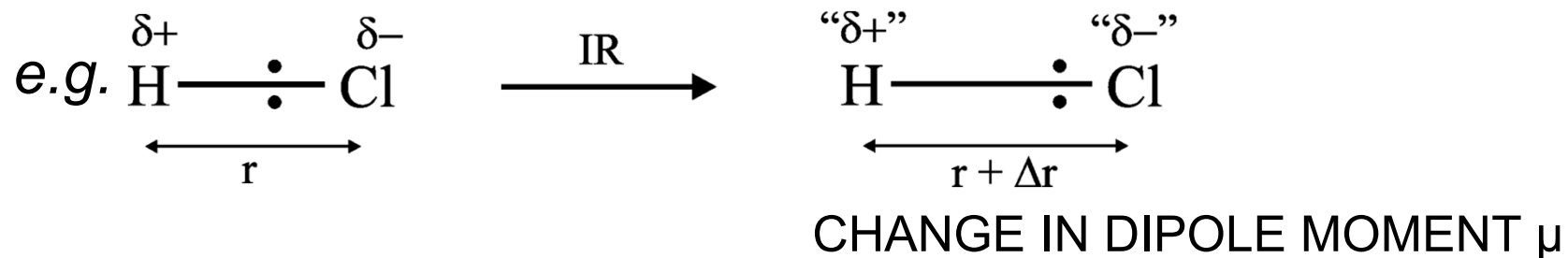
$\bar{\nu}$ :

2. Infra-red radiation induces transformations in molecules.

3. Electric component of radiation is involved  
i.e. not magnetic

4. The size of the changes during vibration.

(If the doesn't change, there won't be an IR signal)



The larger the change in dipole moment, the stronger the signal

Information from IR spectra = *information about bonds*:

(a) Quantitative information:

$\approx$  BOND STRENGTHS

(b) Qualitative Information:

– *What functional groups are present?*

e.g. CH vs OH vs NH

**C=O**      vs      **C=C**

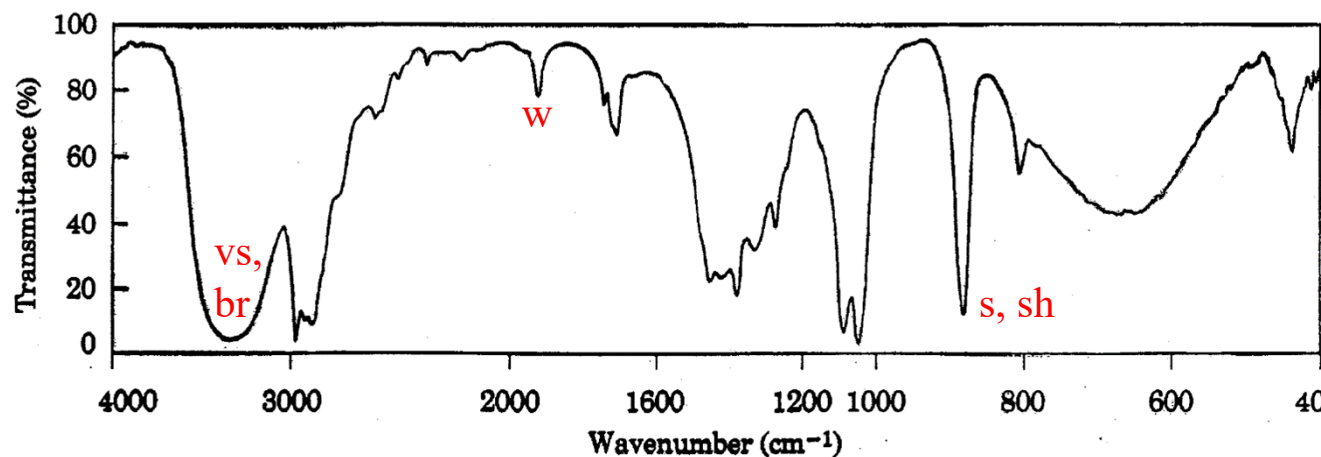
$$\text{C} \equiv \text{C} \quad \text{vs} \quad \text{C} \equiv \text{N}$$

Most important in IR are the bonds that stretch more or less independently of the rest of the molecule. This happens when:

- The bond is much stronger than others nearby
- The bond is between atoms that are much closer than their neighbours



# Interpreting IR spectra



Look at:

- Peak Intensities And Shapes

very strong

strong

medium

weak

sharp

broad

- Peak Positions ( $\bar{\nu}$  values)

Most important for us:

What determines peak position?

## Position of IR signal (i.e. $\bar{\nu}$ value) depends on:

Consider a bond X—Y

Treat like a spring X——Y

Frequency of oscillation for X—Y is given by

HOOKE'S LAW:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{SO} \quad \bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

where  $k =$

( $\approx$  measure of bond strength)

and  $\mu =$

$$\mu = \frac{M_x M_y}{M_x + M_y}$$

where  $M_x, M_y =$  atomic  
mass of X, Y

For C-C bond: 6.0

For C-H bond: 0.92

## Hooke's law

From  $\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$

One can see that:

$$\bar{\nu} \propto k^{1/2}$$

and

$$\bar{\nu} \propto \mu^{-1/2}$$

In other words:

- Strong bonds absorb at wavenumbers
- Bonds with heavier atoms absorb at  $\bar{\nu}$

<i>e.g.,</i>	C—C	C=C	C≡C
Bond energy	348	611	837
$\bar{\nu}$	800-1200	1600-1650	≈2200
	C=O	P=O	
$\mu$	6.86	10.55	
$\bar{\nu}$	1650-1800	1000-1300	

## Some facts about vibrations

1. Vibrations can be:

Bond length changes

Bond angle changes

Stretching requires more energy than bending  
*i.e.* at a higher  $\bar{\nu}$  than bending

2. Polyatomic molecules:

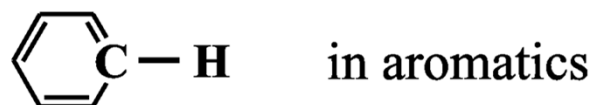
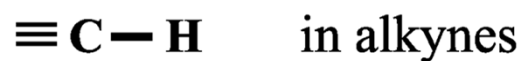
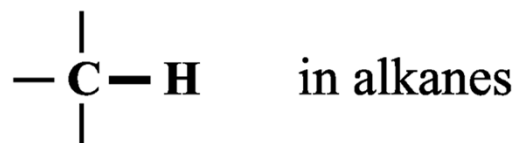
What happens in a bond influences what happens  
in neighbouring bonds                      A knock - on effect

Independent combinations of vibrational motion are called  
*normal modes of vibration* (see example later).

## Adjacent bonds influence position of signals

*e.g.*, C — CH BONDS

$\bar{\nu}$  (cm<sup>-1</sup>)



Result: different functional groups have very characteristic IR absorption signals!

Average positions from many examples are listed in correlation tables or charts (see course book)

## Normal modes of vibration - examples



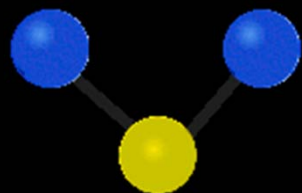
Symmetrical  
stretch



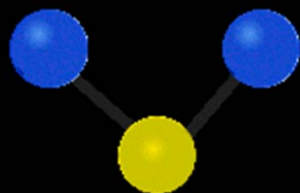
Asymmetrical  
stretch



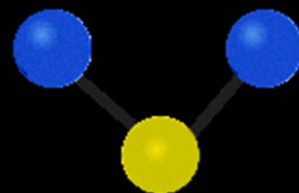
Scissoring



Rocking

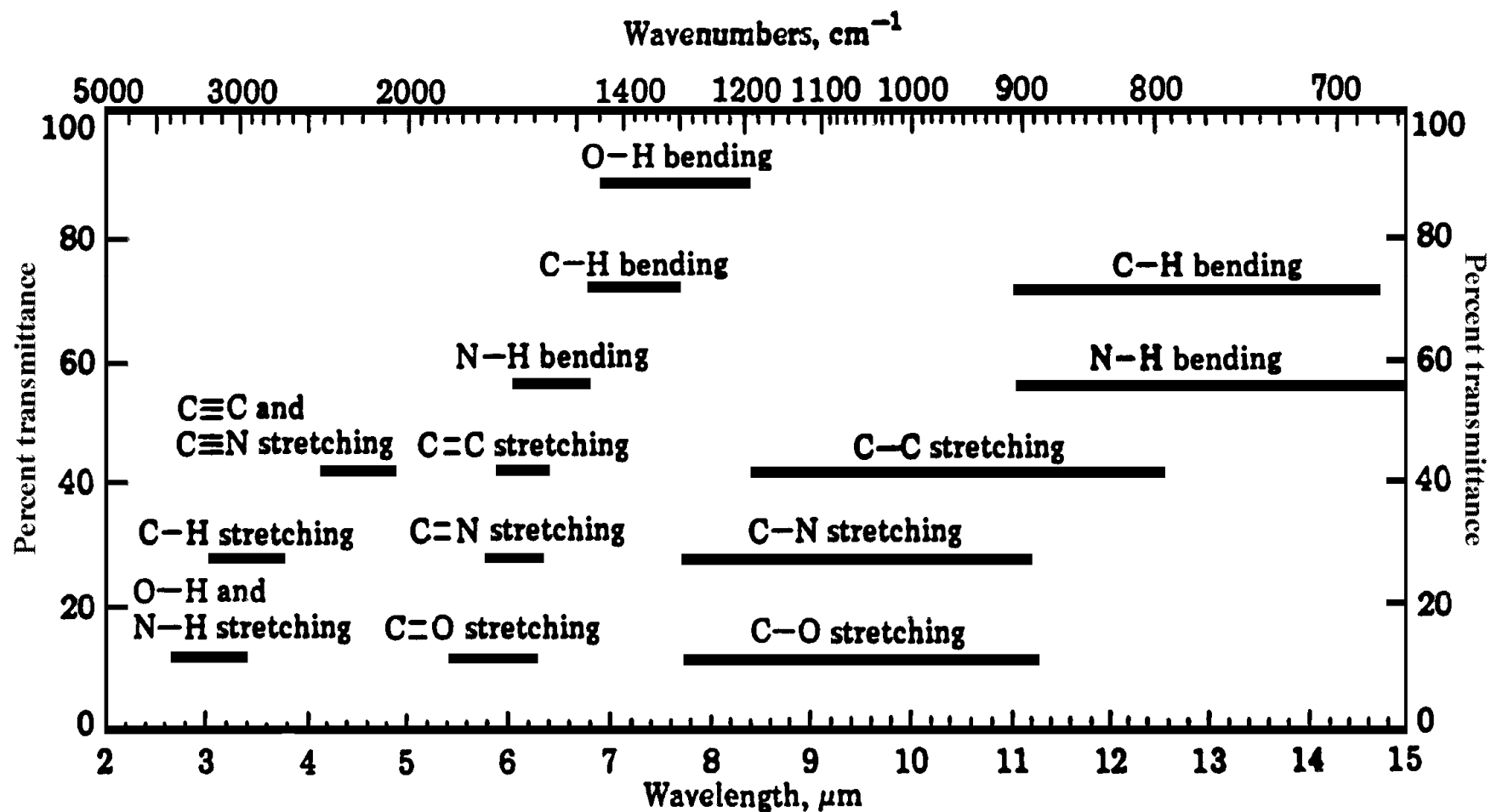


Wagging

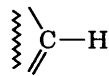
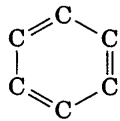


Twisting

# Example of an IR correlation chart



# Example of an IR correlation table

<i>Functional group class</i>	<i>Band position (cm<sup>-1</sup>)</i>	<i>Intensity of absorption</i>
<b>Alkanes, alkyl groups</b>		
C—H	2850–2960	Medium to strong
<b>Alkenes</b>		
=C—H	3020–3100	Medium
C=C	1640–1680	Medium
<b>Alkynes</b>		
≡C—H	3300	Strong
—C≡C—	2100–2260	Medium
<b>Alkyl halides</b>		
C—Cl	600–800	Strong
C—Br	500–600	Strong
C—I	500	Strong
<b>Alcohols</b>		
O—H	3400–3650	Strong, broad
C—O	1050–1150	Strong
<b>Aromatics</b>		
	3030	Medium
	1600, 1500	Strong
<b>Amines</b>		
N—H	3300–3500	Medium
C—N	1030, 1230	Medium
<b>Carbonyl compounds<sup>a</sup></b>		
C=O	1680–1750	Strong
<b>Carboxylic acids</b>		
O—H	2500–3100	Strong, very broad
<b>Nitriles</b>		
C≡N	2210–2260	Medium
<b>Nitro compounds</b>		
NO <sub>2</sub>	1540	Strong

<sup>a</sup>Acids, esters, aldehydes, and ketones.



# What should you memorise?

4000

1500

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STRETCHING VIBRATIONS

STRETCHES AND BENDS

OTHER C—X e.g. C-O  
STRETCHES C-F, C-Cl

FINGERPRINT REGION -  
USEFUL IN MATCHING  
SPECTRA

Try to assign everything above  $1500\text{ cm}^{-1}$

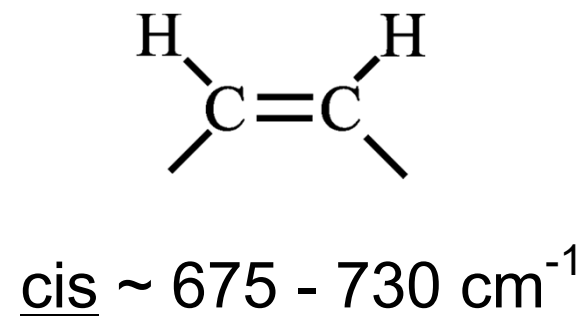
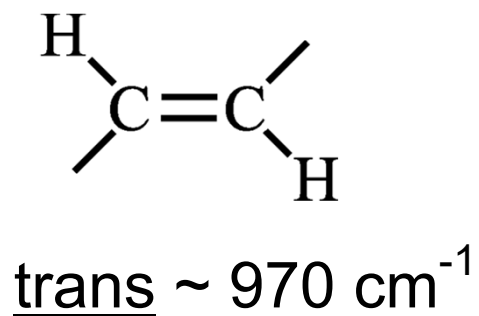
Note: complete assignment of every signal is difficult, if not impossible!

## Useful information from the fingerprint region

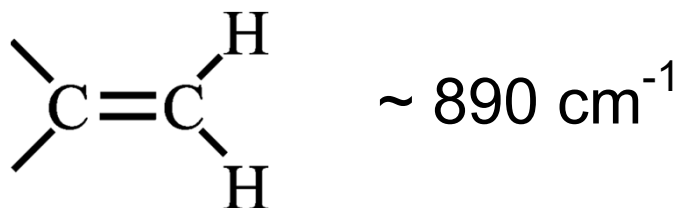
Some specific substitution patterns have characteristic bending vibrations

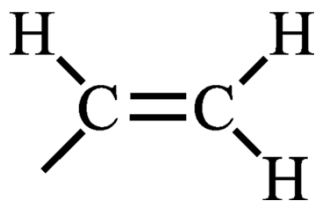
2 × H ATOMS:

Vicinal H  
(Neighbouring)



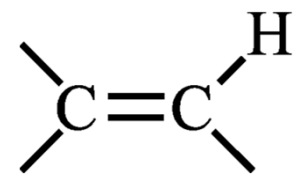
Geminal H  
(Twinned)





3 × H ATOMS

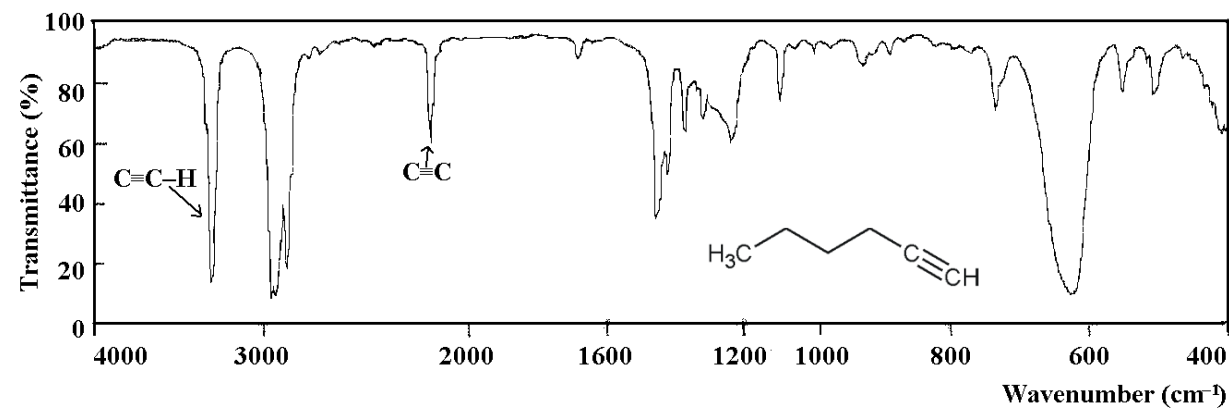
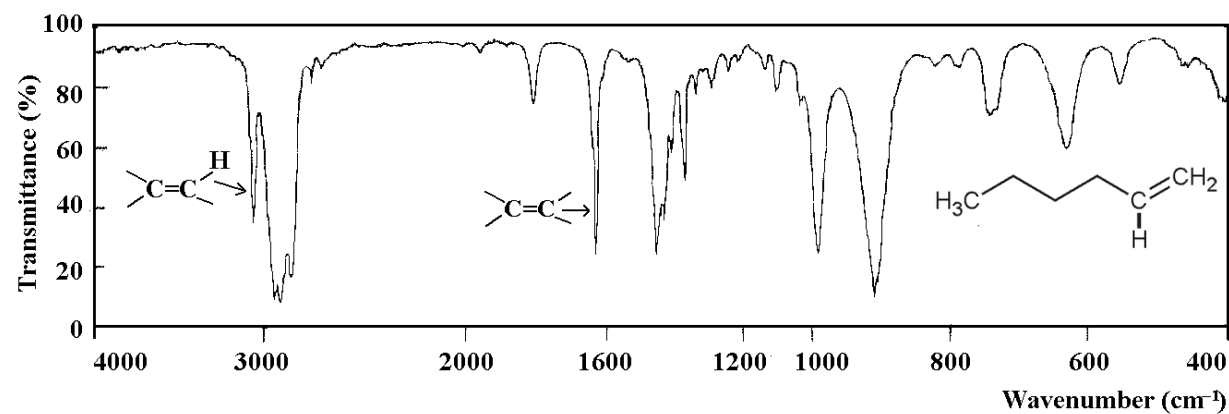
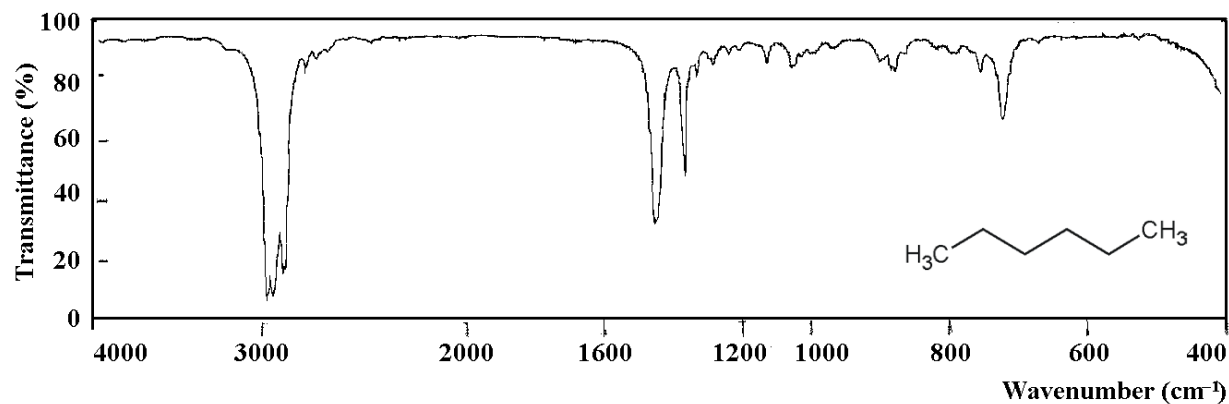
2 BANDS, ~ 900, ~ 990 cm<sup>-1</sup>



1 × H ATOMS

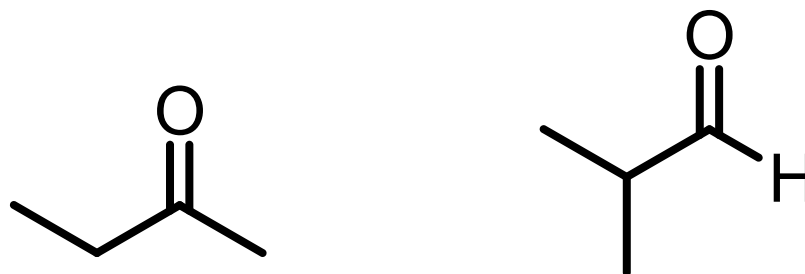
~ 790 – 840 cm<sup>-1</sup>

# IR SPECTRA OF (a) HEXANE; (b) 1-HEXENE; (c) 1-HEXYNE



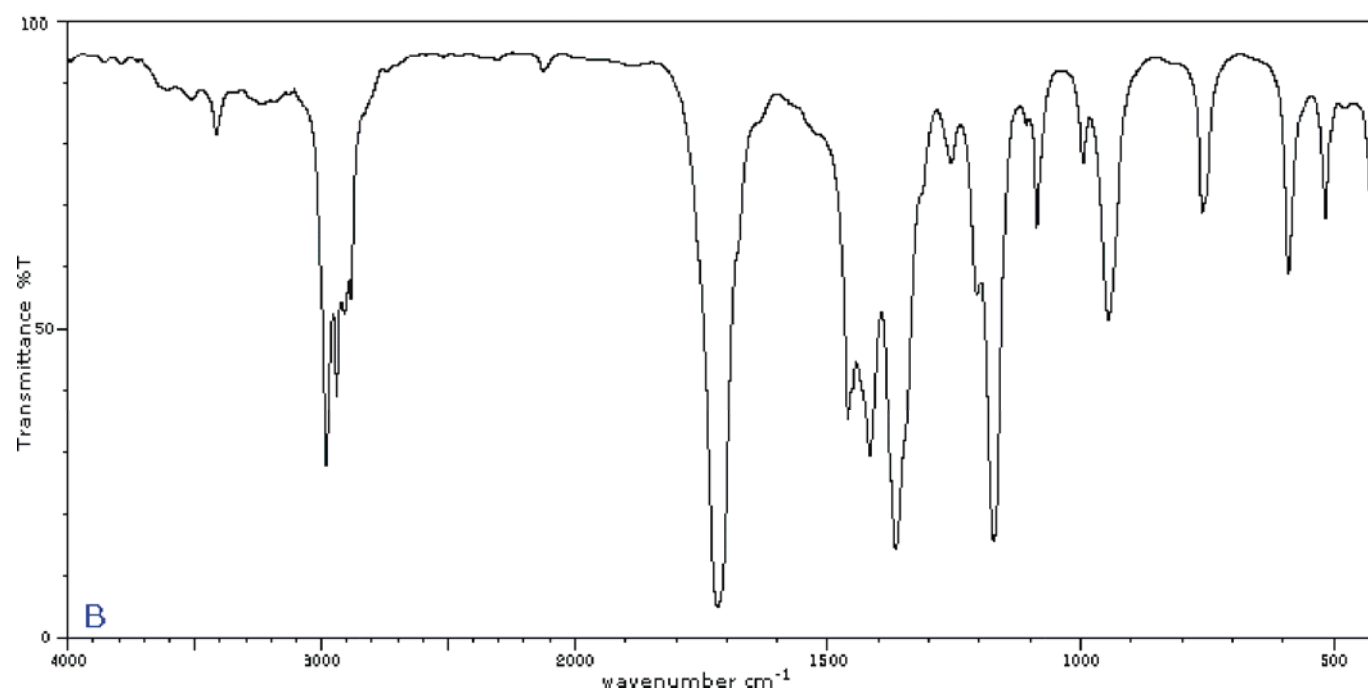
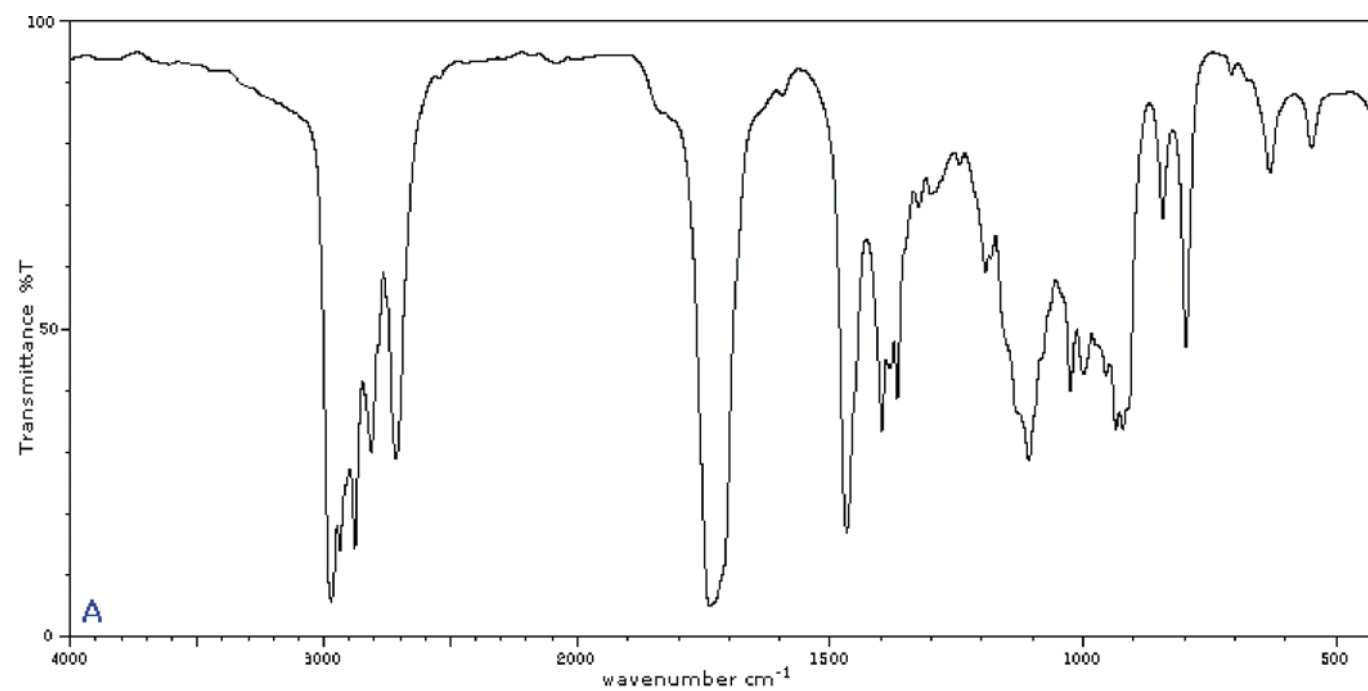
# IR LECTURE EXAMPLE:

Using the data from the table provided, decide which isomer belongs with which spectrum:



## Typical IR Absorption Frequencies for Aldehydes and Ketones

Stretching Vibrations			Bending Vibrations		
Range (cm <sup>-1</sup> )	Intensity	Assignment	Range (cm <sup>-1</sup> )	Intensity	Assignment
2690-2840(2 bands)	med	C-H (aldehyde C-H)	1350-1360	str	α-CH <sub>3</sub> bending
1720-1740	str	C=O (saturated aldehyde)	1400-1450	str	α-CH <sub>2</sub> bending
1710-1720	str	C=O (saturated ketone)	1100	med	C-C-C bending
1690	str	aryl ketone			
1675	str	α, β-unsaturation			
1745	str	cyclopentanone			
1780	str	cyclobutanone			



## Section 3: Electronic (Ultra-violet/Visible) Spectroscopy (Uv-vis)

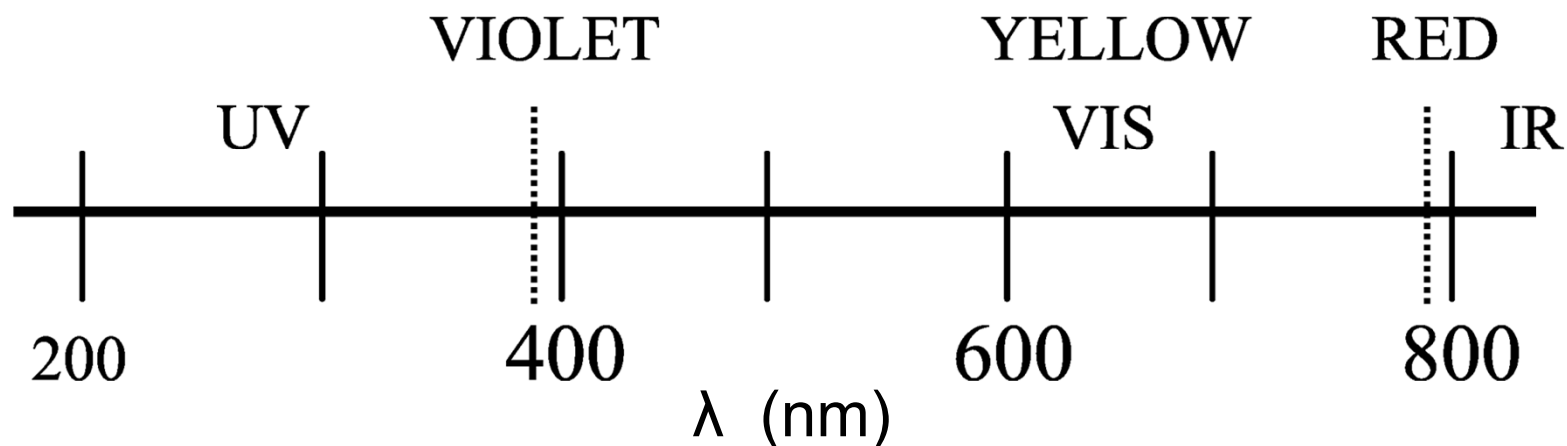
The oldest of the common spectroscopic techniques.

Fairly simple, comparatively cheap instruments.

Gives information about *structure*:  $\therefore$  useful in both organic and inorganic chemistry.

Useful tool for analysis (e.g. Use of the Beer-Lambert law for determining concentrations).

## WAVELENGTHS?



- Ordinary light (e.g. sunlight) contains *all* wavelengths in the visible (VIBGYOR) and near IR/UV regions:

If a compound \_\_\_\_\_ light at a particular wavelength, it will  
other wavelengths.



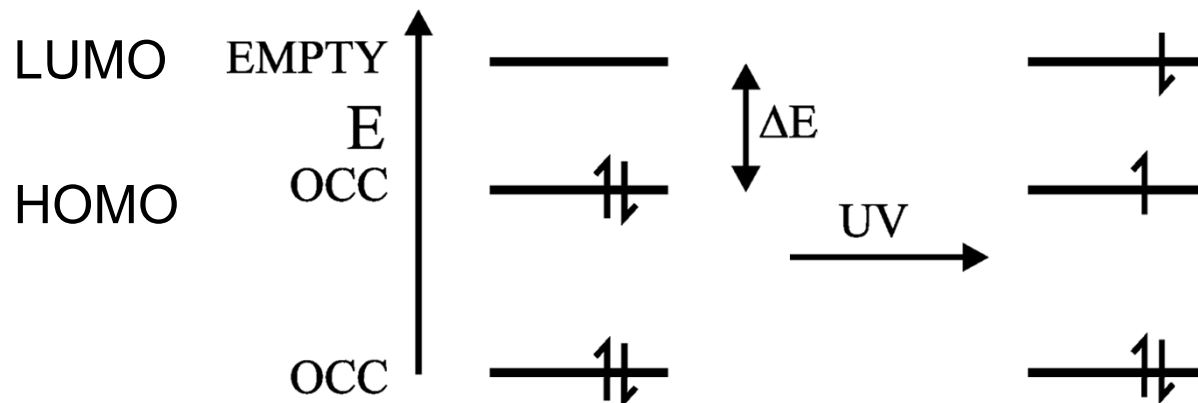
Correlation between Wavelength of Absorbed Radiation and Observed Color		
Absorbed light		Observed (transmitted) color
Wavelength [nm]	Corresponding color	
400	violet	yellow-green
425	indigo blue	yellow
450	blue	orange
490	blue-green	red
510	green	purple
530	yellow-green	violet
550	yellow	indigo blue
590	orange	blue
640	red	blue-green
730	purple	green

- *Monochromatic* radiation is used in UV-vis spectroscopy:

*i.e.*, scan at specific wavelengths across the  $\lambda$  range; measure absorption at each  $\lambda$  value.

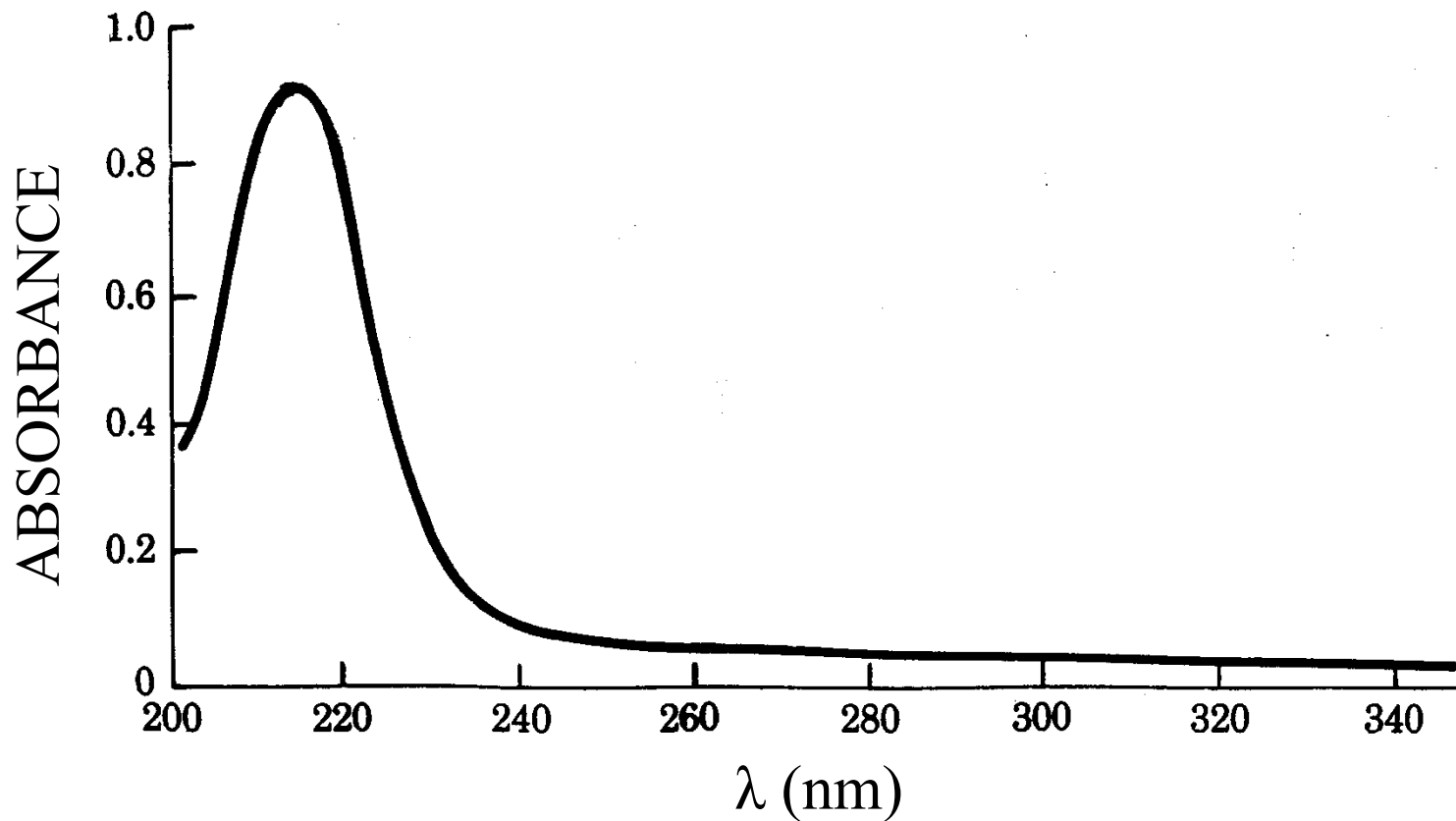
## Principles

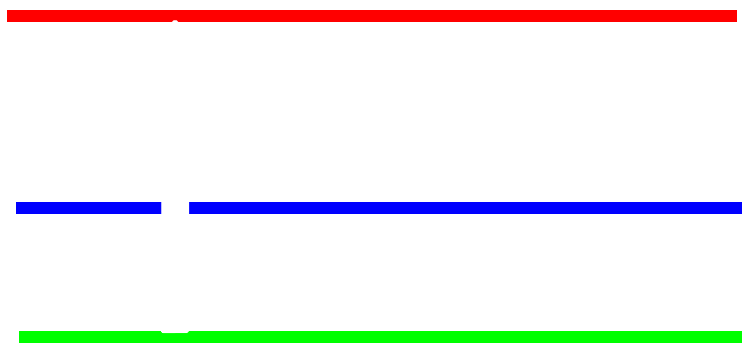
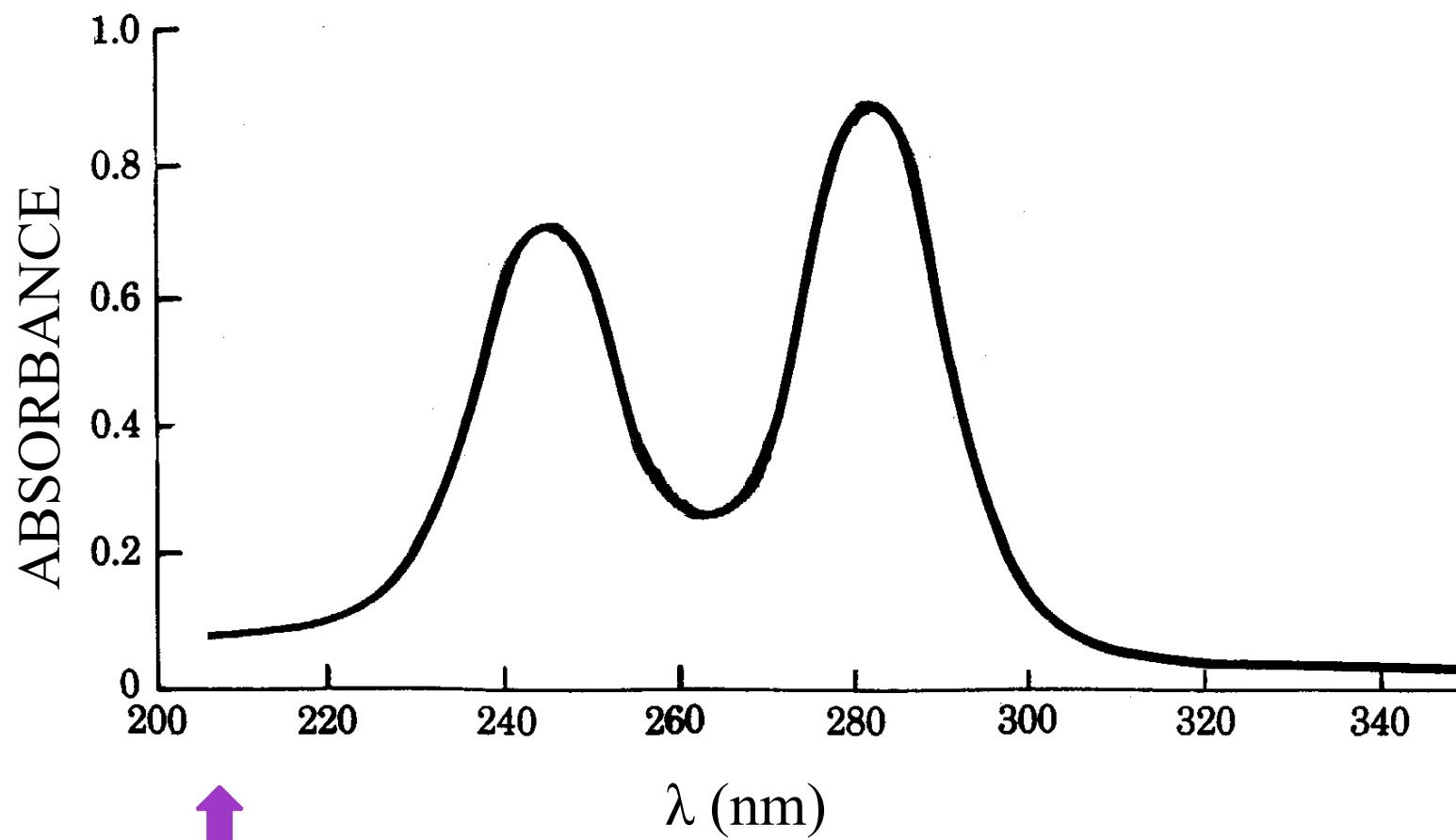
- Excite an electron from an *occupied* molecular orbital into a *vacant* orbital



- $\Delta E = hc/\lambda$ , *i.e.*,  $\Delta E$  determines the wavelength of absorption.
- Absorption is in visible range (400–800 nm) – compounds are coloured  
e.g., chlorophyll,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , transition metal ions
- near UV* range (200-400 nm) – conjugated organics, aromatics, many inorganics.
- far UV* range (<200 nm) – simple organics, and inorganics. e.g.,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , alkanes, alkenes. Need special instruments

- Simultaneous changes in vibration & rotation lead to a spread of  $\Delta E$  values: one sees broad bands, not sharp lines.
- Typical UV-vis spectrum:

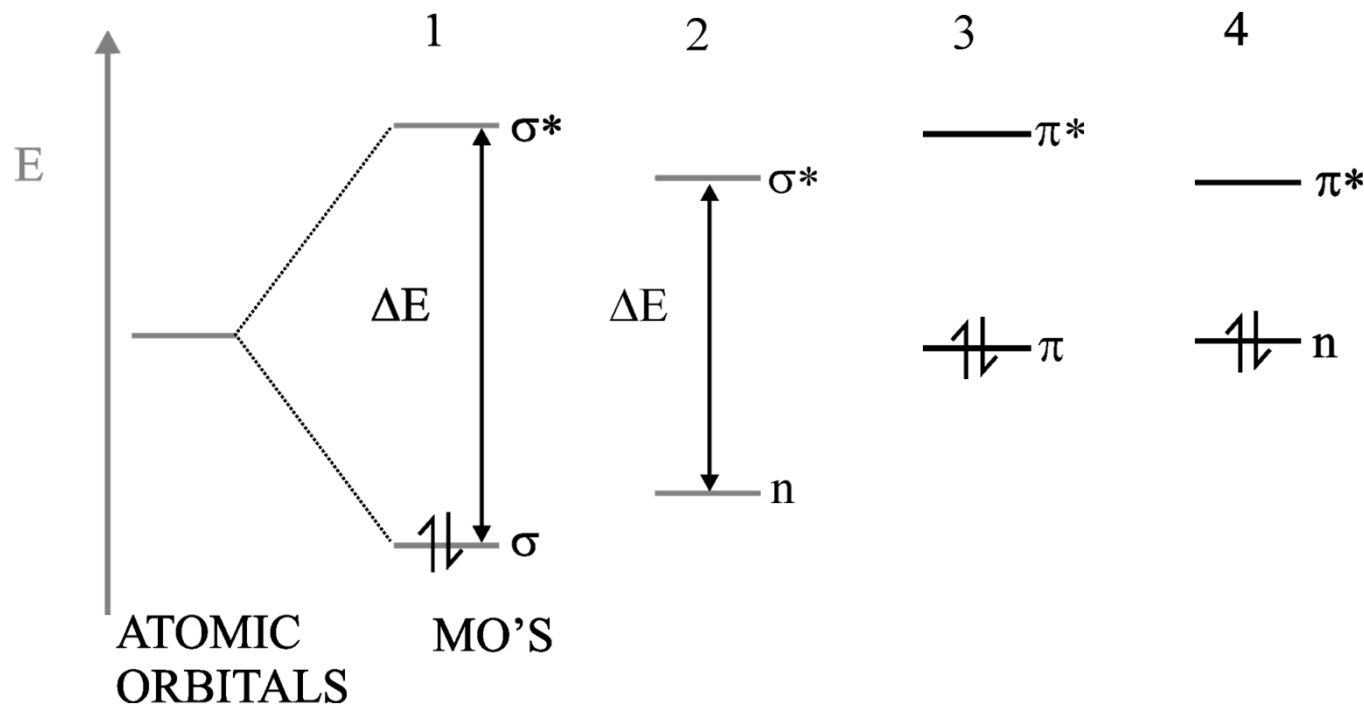




# What orbitals are involved?

- bonding and antibonding sigma orbitals  
e.g., simple saturated compounds.
- bonding and antibonding pi orbitals  
e.g., alkenes, alkynes, aromatics
- orbitals with non-bonded electrons, *i.e.*, lone pairs  
e.g.,
- occupied or vacant d orbitals  
e.g. transition metals

# Relative energies



Possible transitions (in order of decreasing  $\Delta E$ ):

1. large  $\Delta E$ ,  $\lambda_{\text{MAX}} < 200 \text{ nm}$
2. *e.g.* in 150 – 200 nm
3.  $\lambda_{\text{MAX}}$  range 200 - 300 nm
4. *e.g.* in smallest  $\Delta E$

This is a generalisation - depends on exact energy of different orbitals

Other important electronic transitions (commonly seen in inorganic chemistry):

5.  $d \rightarrow d$

electronic transitions from occupied to vacant d orbitals in transition metals.

6. Bands arising from *charge transfer complexes*

*e.g.*, when ligands bind to metals, electrons on ligand are excited into empty orbitals on metal



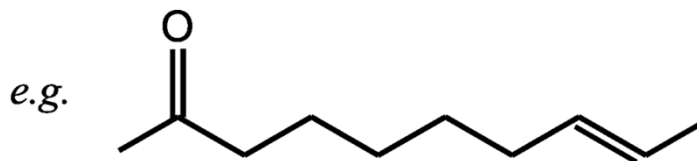
# Chromophores

The part of the molecules that contain the electrons responsible for the observed absorption.

*e.g*

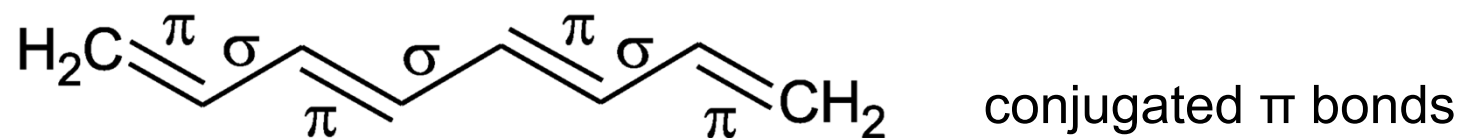
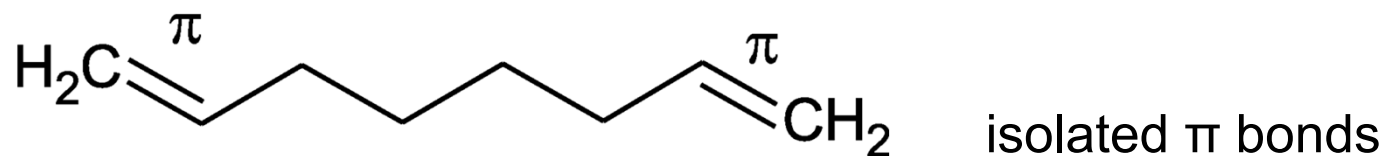
$$\begin{array}{llll} \dot{\lambda}_{\text{MAX}} & \sim 170 \text{ nm } (\pi \rightarrow \pi^*) & \sim 190 (\pi \rightarrow \pi^*) & \sim 195 (\text{n} \rightarrow \sigma^*) \\ & & \sim 280 (\text{n} \rightarrow \pi^*) & \end{array}$$

- Chromophores remote from one another absorb independently:  
∴ should see more than one band

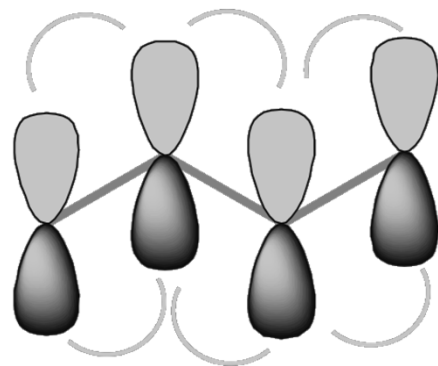




- Conjugated  $\pi$ -electron systems are special

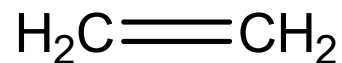


- conjugation in  $\pi$ -electron systems *lowers*  $\Delta E$  of both  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. Why?



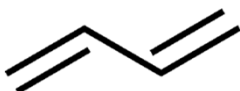
electrons less tightly held  $\therefore$  easier to excite.

*e.g.,*

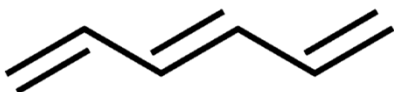


$\lambda_{\text{max}} (\pi \rightarrow \pi^*)$

171 nm



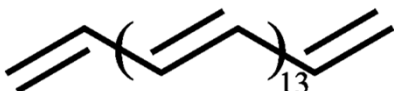
217 nm



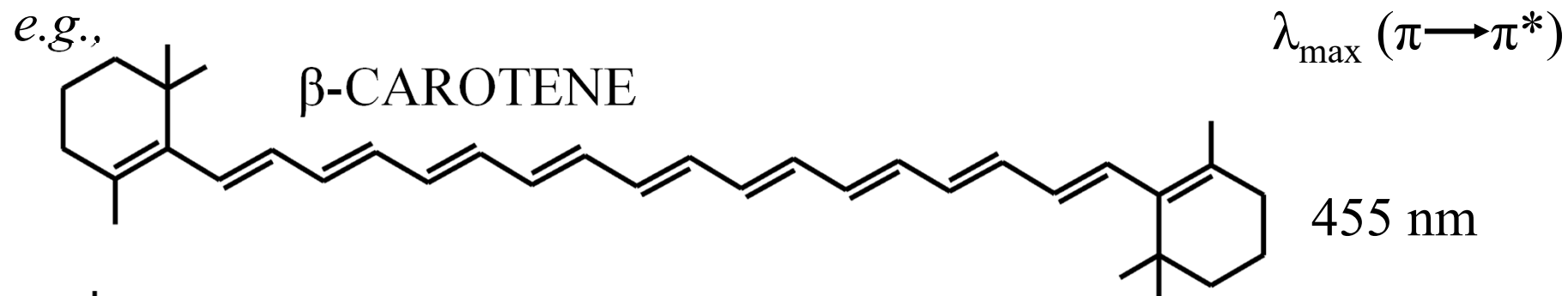
263 nm

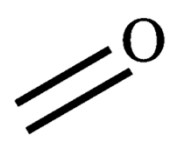
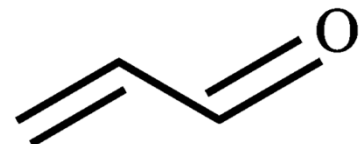
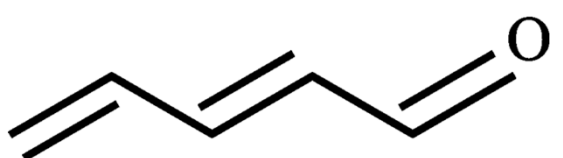


415 nm



504 nm



	$\lambda_{\max}$ $\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
	188	280 nm
	210	315 nm
	270	350 nm
	STRONG	WEAK

simple additivity rules allow one to predict  $\lambda_{\max}$  for conjugated systems bearing various substituents – “Woodward rules”

## Quantitative use of UV-vis

N.B. Use of Beer-Lambert law for finding concentration of compounds in solution

$A$  = Absorbance,  $b$  = path length (cm),  $c$  = conc. ( $\text{mol } \ell^{-1}$ ),  
 $\epsilon$  = molar extinction (absorptivity) coefficient ( $\ell \text{ mol}^{-1} \text{cm}^{-1}$ )

Size of  $\epsilon$  is related to the probability of transition

Typical  $\epsilon$  values for:

- Conjugated dienes
- Conjugated polyenes
- Saturated compounds
- $n \rightarrow \pi^*$
- Metal  $d \rightarrow d$

N.B. Solvents in which spectra are recorded also affect  $\lambda_{\text{max}}$  and  $\epsilon$  values  
(Solvation, H-bonding)

## UV-vis lecture exercise

The UV/vis spectrum of a solution (conc. =  $2.5 \times 10^{-5}$  M) has two prominent peaks.

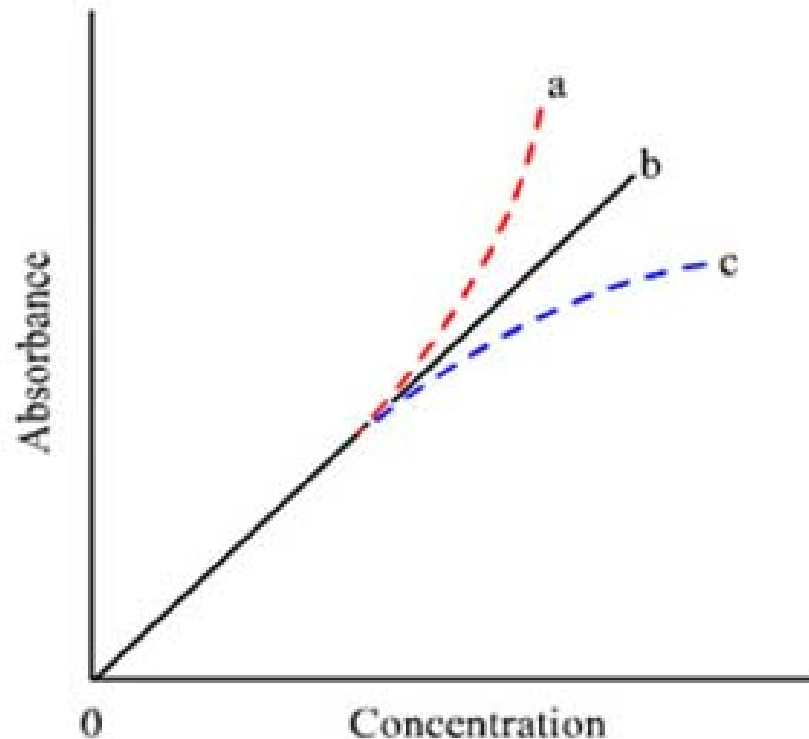
The first at 400 nm has an absorbance of 0.8, and the second at 550 nm has an absorbance of 0.1.

The measurement was conducted in a cuvette with a pathlength of 0.02 m.

Calculate the extinction coefficient for both peaks.

# Use Beer-Lambert law

For better result, would use a range of Absorbance vs conc. values



Slope =

Must use linear part of plot  
At high concentrations –  
deviation from linearity

## Section 4: Nuclear Magnetic Resonance Spectroscopy (NMR)

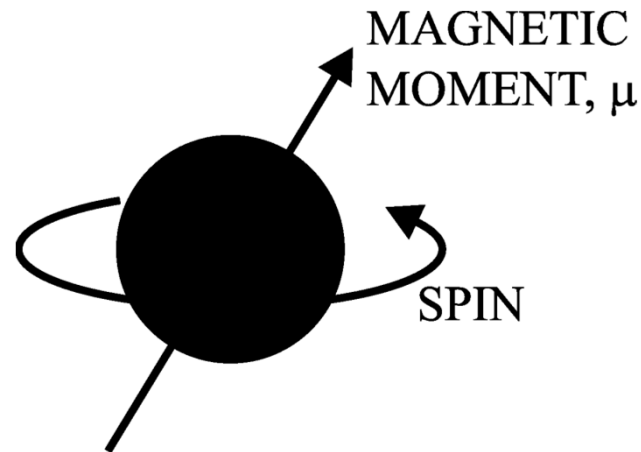
Involves atomic nuclei, which are:

- charged
- spinning about an axis

They have a property called  
Net effect: they behave like

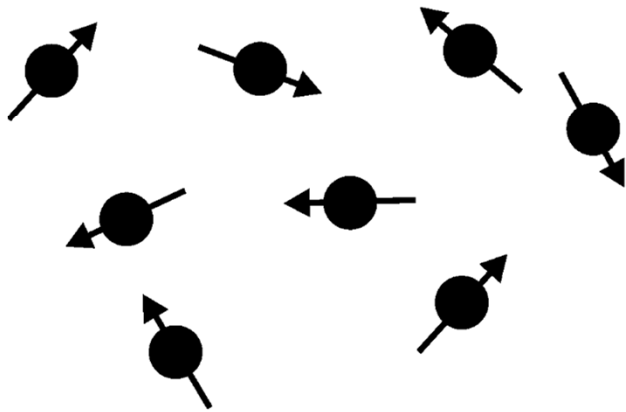
So: place them in an external magnetic field ( $H_0$ ), and they will interact with it.

Nucleus:



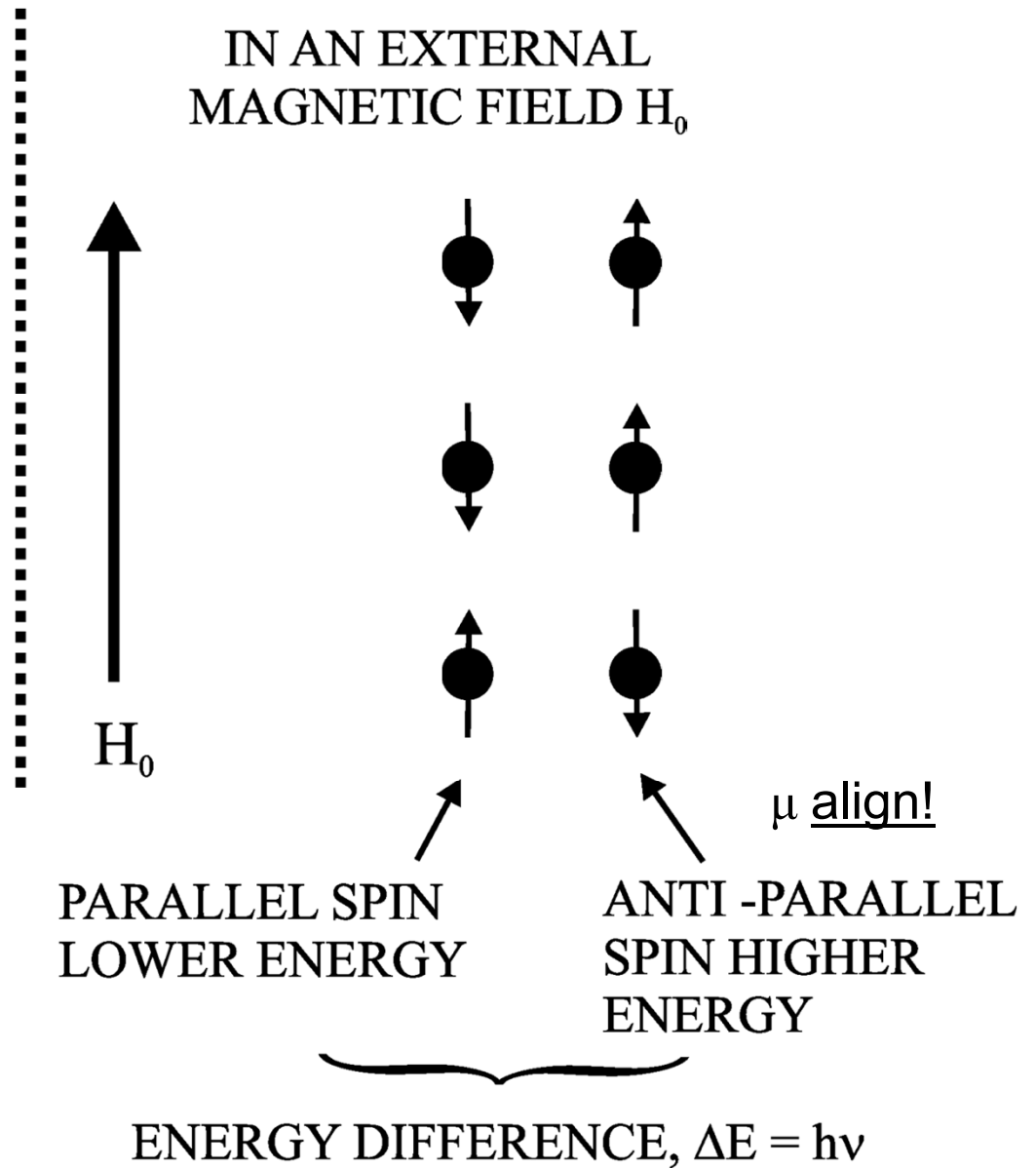
Spin is a fundamental property of nature like electric charge or mass

NO EXTERNAL  
MAGNETIC FIELD

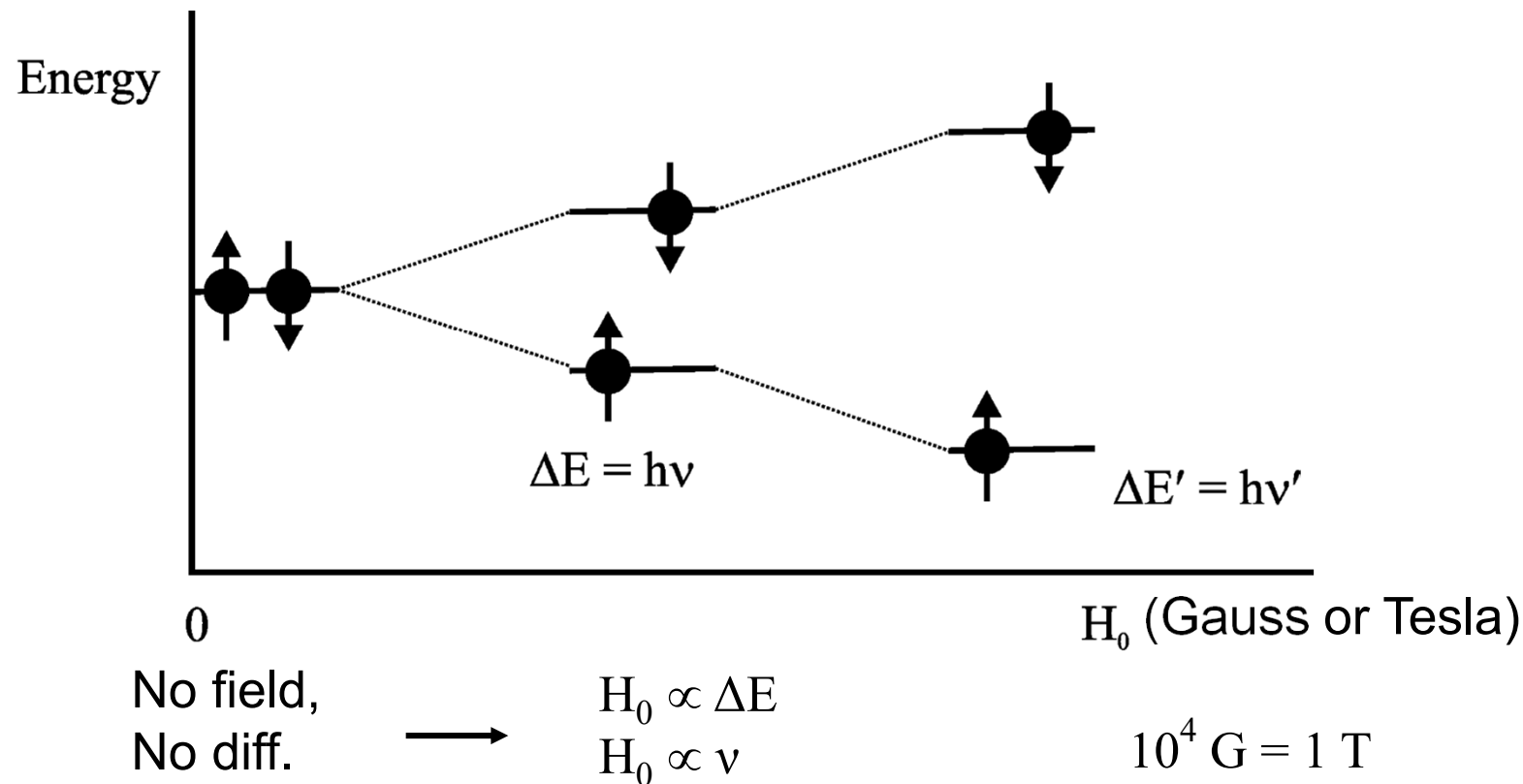


Random orientations of  $\mu$

IN AN EXTERNAL  
MAGNETIC FIELD  $H_0$







The stronger the magnet, the bigger

- $\Delta E$  is very small!  $\sim 10^{-5} \text{ J mol}^{-1}$  Radiowave region
- Need very little energy to get a “spin flip”

EQUILIBRIUM BETWEEN  $\downarrow$  &  $\uparrow$

AT 1 TESLA: IF  $\downarrow$  = 1000000 NUCLEI

10 000 Gauss  $\uparrow$  = 1000006 NUCLEI

- Very powerful magnets are needed  
(typical  $H_0 = 141 - 200$  kG or  $1.41 - 20$  T)  
*cf.* earth's magnetic field:  $\sim 1$  Gauss

# What nuclei show nuclear magnetic resonance?

Inactive nuclei have:

- number of protons (atomic number) *and*
- mass number (no. protons plus neutrons)

e.g.

Spin quantum number  $I = 0$  these nuclei are inactive

All other nuclei are NMR-active!

Isotopes – diff  
no. of neutrons!

$I \neq 0, \quad I = 1/2, 1, 3/2, 2, \dots$

Nuclei with  $I = 1/2$  have two allowed values of spin:  
+1/2 and -1/2 (two possible energy levels  $2 + 1 = 2$ )

NUCLEUS	SPIN	NATURAL ABUNDANCE	SENSITIVITY
H			
H = D			
C			
F, P			
Al			

Different nuclei need different energies to achieve resonance (different  $\Delta E$  gaps) – their absorptions are in different regions of the spectrum.

*$\therefore$  You can only observe one nucleus at a time!*

e.g. If  $H_0 = 14100$  Gauss (=1.41 Tesla):

NUCLEUS	$\Delta E$ (kJ mol <sup>-1</sup> )	$\nu$ (Hz)	$\lambda$ (m)
H	$\approx 24 \times 10^{-6}$	$60 \times 10^6$ (60 MHz)	5
C	$\approx 6 \times 10^{-6}$	$15 \times 10^6$ (15 MHz)	20
N	$\approx 24 \times 10^{-6}$	$6 \times 10^6$	50

For observing  $^1\text{H}$ , typically:

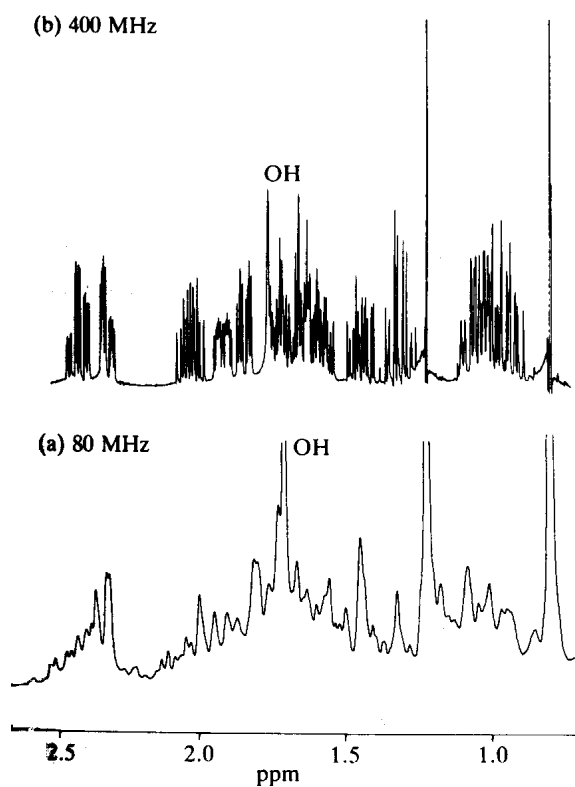
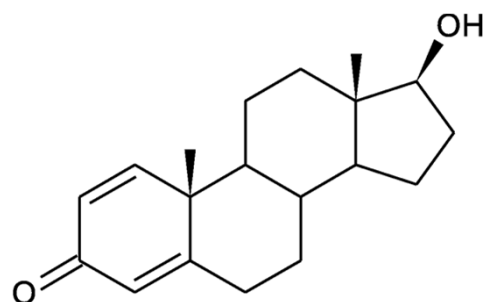
Electromagnets:            14 100 Gauss  
                                     = 60 MHz

Superconducting magnets:   up to 900 MHz for  $^1\text{H}$ !

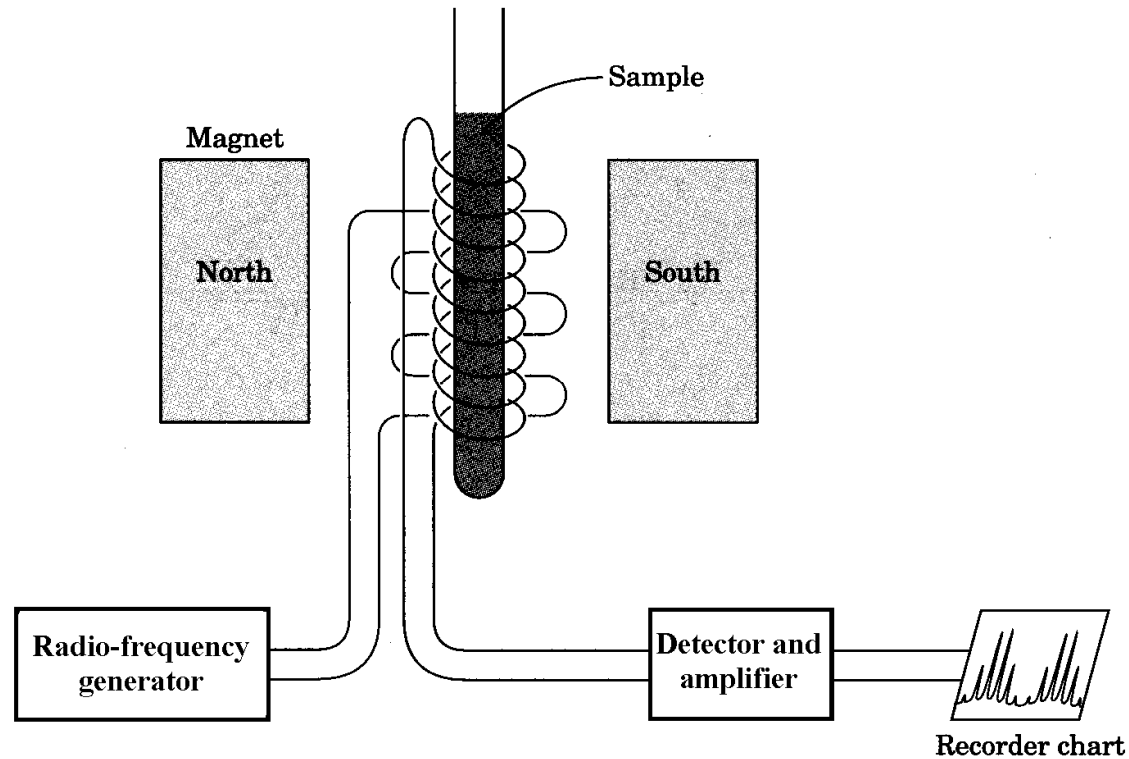
Advantages of large  $H_0$ :

But : more expensive : our 300 MHz cost ~R2 million in 2002

e.g.  $^1\text{H}$  NMR spectrum of dehydrotestosterone



# Typical instrument



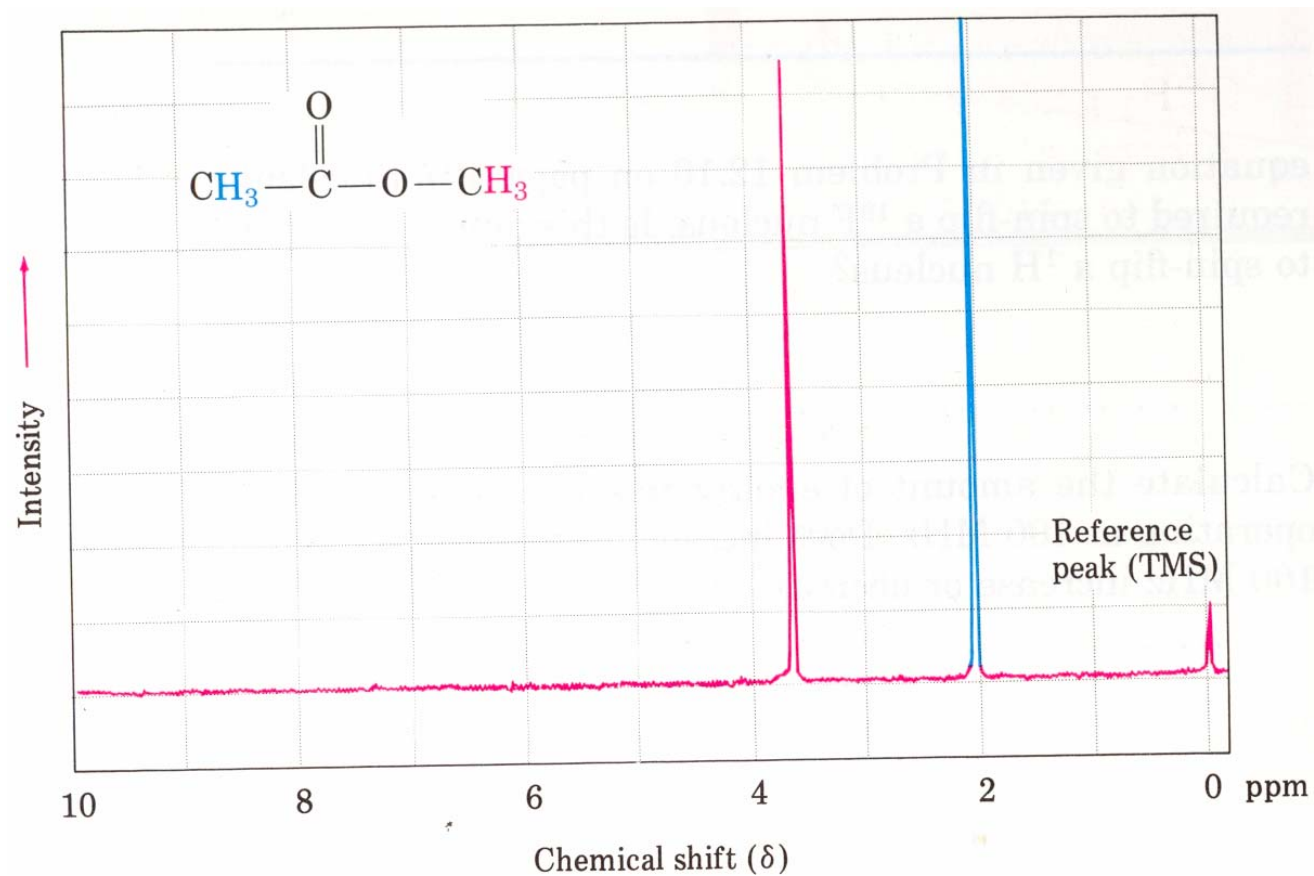
## Sample preparation

- tube spins rapidly (for homogeneity)
- sample is in solution

For  $^1\text{H}$  NMR, avoid solvents with H!!

# Simple NMR spectrum

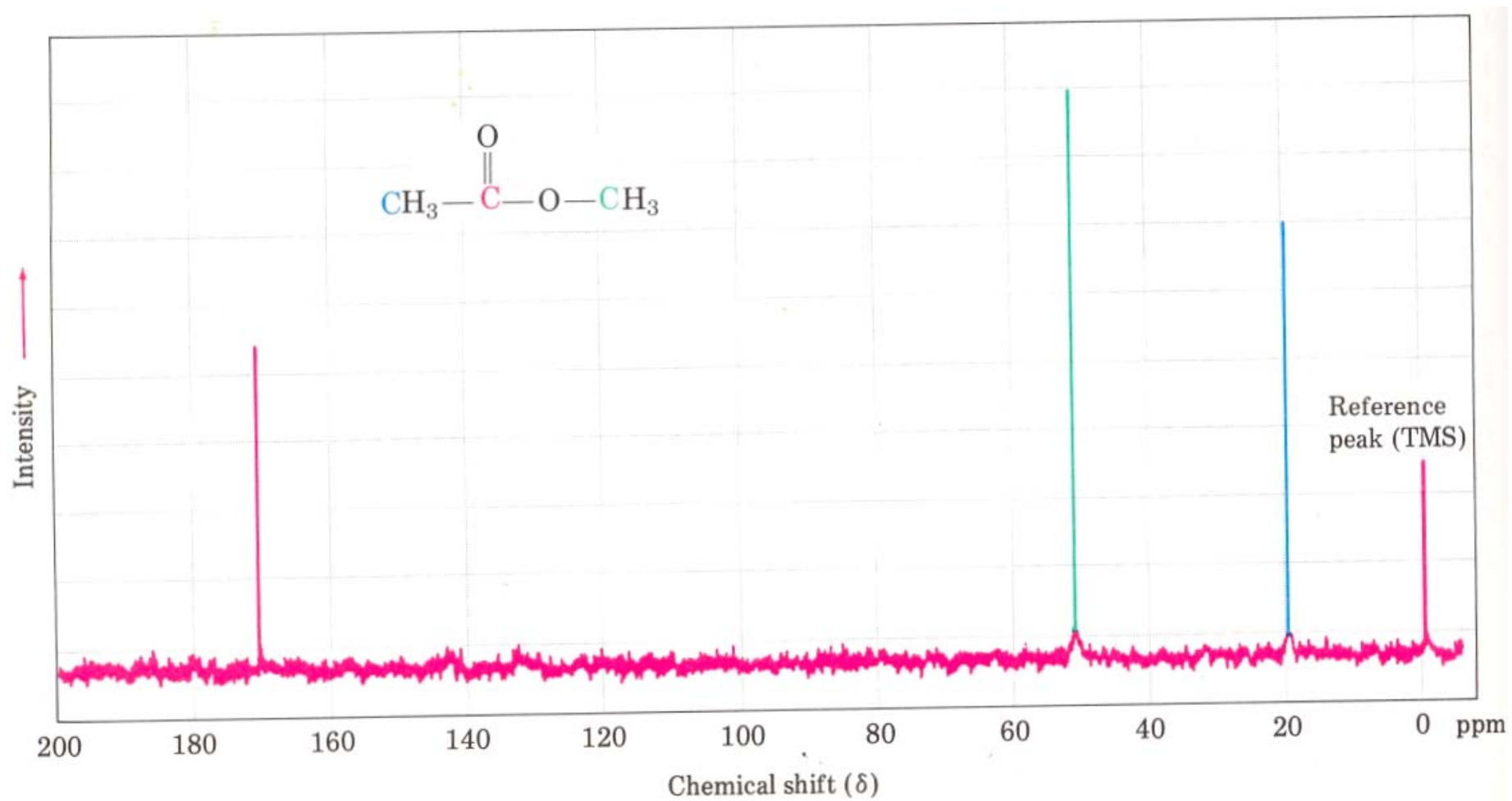
$^1\text{H}$  spectrum of methyl acetate



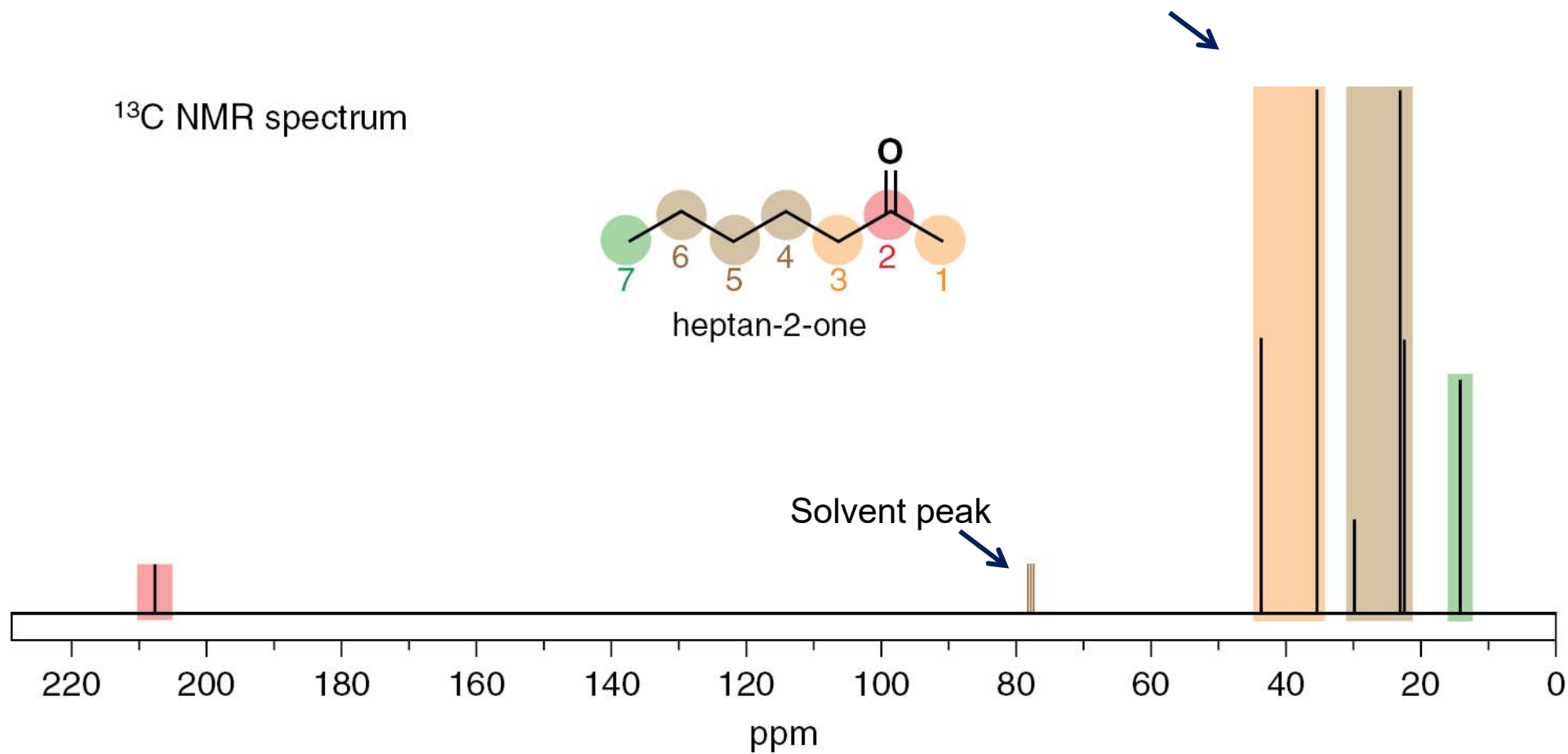
Two things to note immediately:



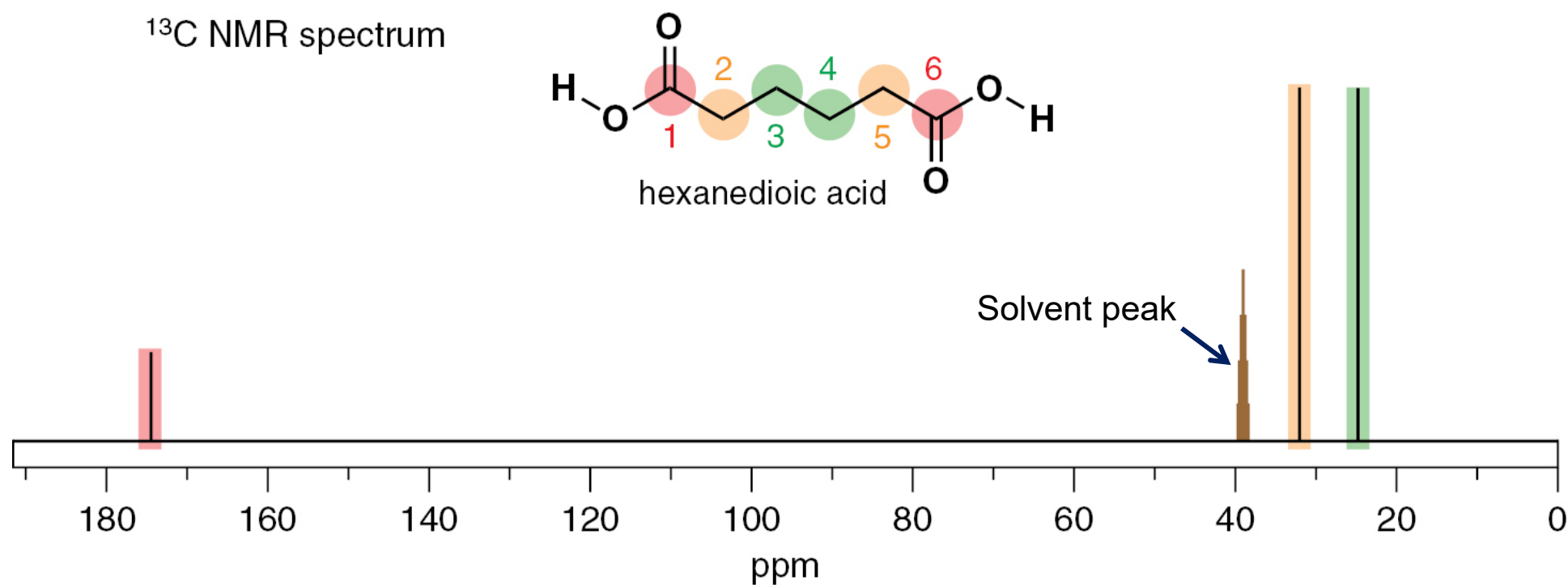
# $^{13}\text{C}$ spectrum of methyl acetate



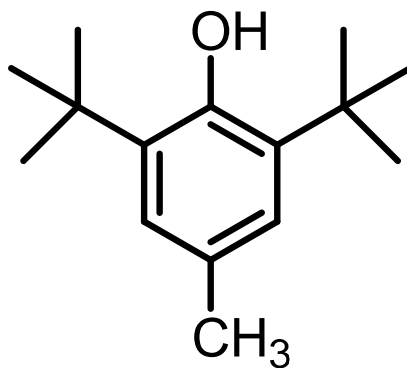
# Equivalent versus non-equivalent chemical environments ( $^{13}\text{C}$ )



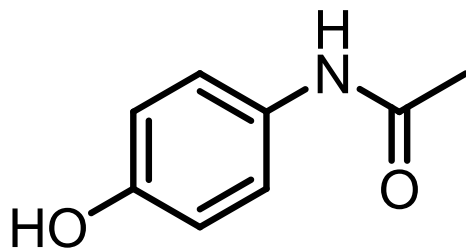
# Equivalent versus non-equivalent chemical environments ( $^{13}\text{C}$ )



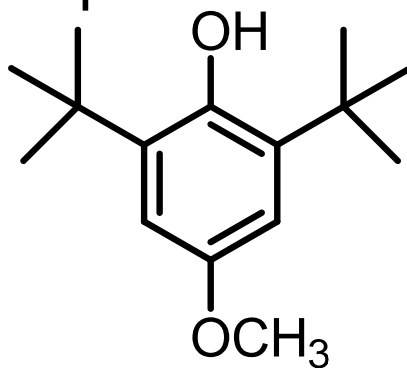
Equivalent versus non-equivalent chemical environments ( $^{13}\text{C}$ )



## Equivalent versus non-equivalent chemical environments ( $^{13}\text{C}$ )



Equivalent versus non-equivalent chemical environments ( $^1\text{H}$ )



## NMR spectroscopic signals

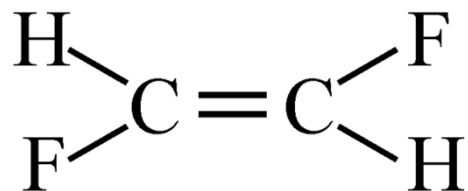
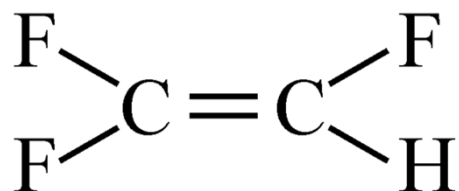
The of signals depends on of the nuclei.

The of signals depends on how many nuclei are in environments.

### Equivalent nuclei

	$^{13}\text{C}$	$^1\text{H}$
$\text{CH}_4$		
$\text{H}_3\text{C}-\text{CH}_3$		
$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_3$		

More examples:





## NMR spectroscopic signals

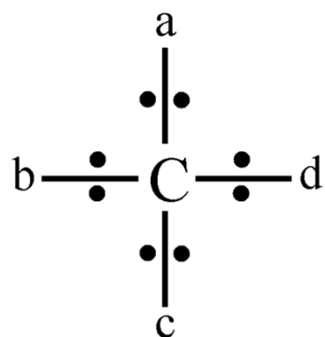
In an NMR spectrum we look for:

For a particular nucleus, we know that  $\Delta E$  depends on the strength of the applied field,  $H_0$

So why do nuclei of the same type (eg.  $^{13}\text{C}$ ) absorb energy at different frequencies??

## Position of signal: influence of shielding

$H_0$



$\Delta E$  for  $^{13}\text{C}$  nucleus depends on  $H_0$  — but ...

Circulating electron clouds set up tiny *local magnetic fields* that *oppose*  $H_0$ .

$\therefore$  Carbon nucleus “sees”

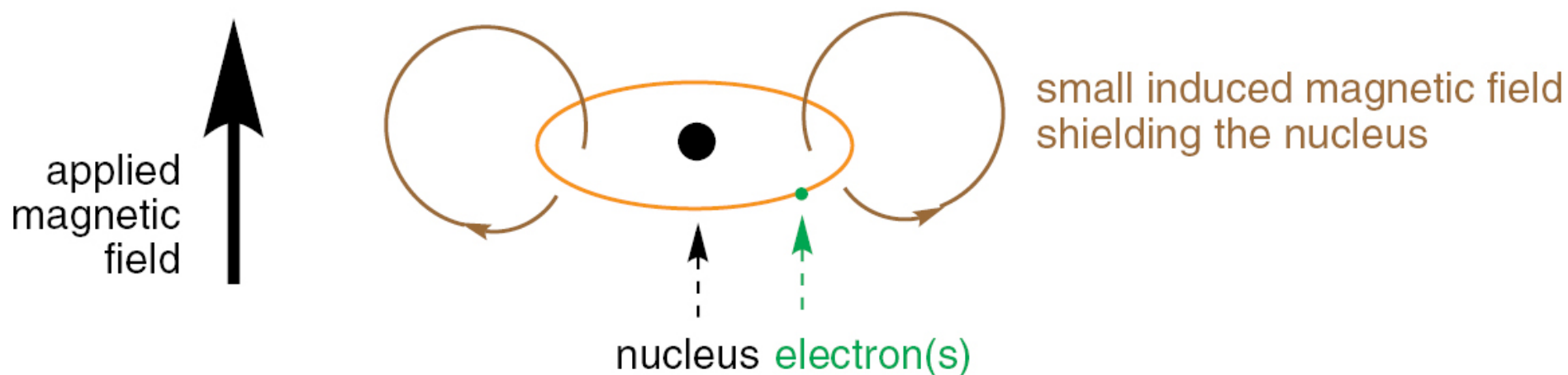
$$(H_0 - H_{\text{electrons}}) = H_{\text{overall}}$$

Electron clouds shield nucleus from  $H_0$  (the denser the cloud, the more the shielding).

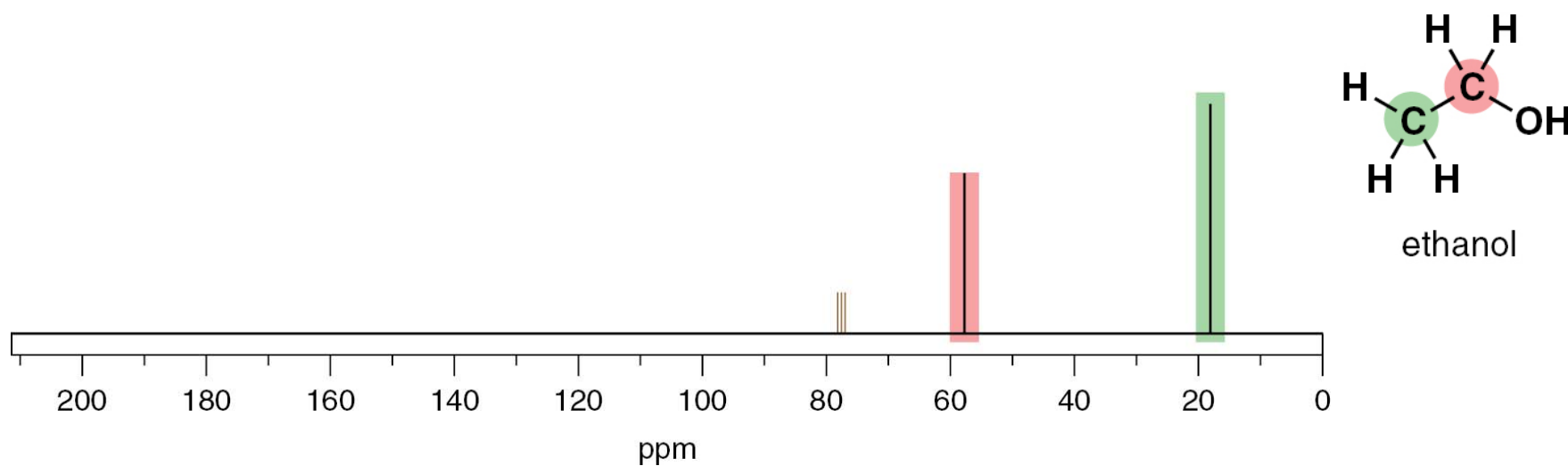
Each nucleus experiences a different magnetic field, even though the external field is the same and therefore :

# Shielding

shielding of nuclei from an applied magnetic field by electrons:



$^{13}\text{C}$  NMR spectrum of ethanol



## Chemical shift

The position (on the x axis) at which the nucleus absorbs (*i.e.*, where the signal is found) is known as the *chemical shift*.

Scale: The  $\delta$  (delta) scale is defined as follows:

= 1 part per million (ppm) of the instrument's operating frequency.

So at 60 MHz       $= 60 \times 10^6 \text{ Hz}$       1  $\delta$  unit =

at 300 MHz       $= 300 \times 10^6 \text{ Hz}$       1  $\delta$  unit =

at 750 MHz       $= 750 \times 10^6 \text{ Hz}$       1  $\delta$  unit =

$\therefore$  scale *automatically compensates* for the type of instrument used.

A universal scale

Define  $\delta = 0$  ppm for a reference compound:

(TMS)

$\delta = 0$  for  $^1\text{H}$  NMR

$\delta = 0$  for  $^{13}\text{C}$  NMR

$\delta = 0$  for  $^{29}\text{Si}$  NMR

$\delta$  values for all other C & H compounds are then quoted relative to  $\delta$  (TMS) = 0 ppm.

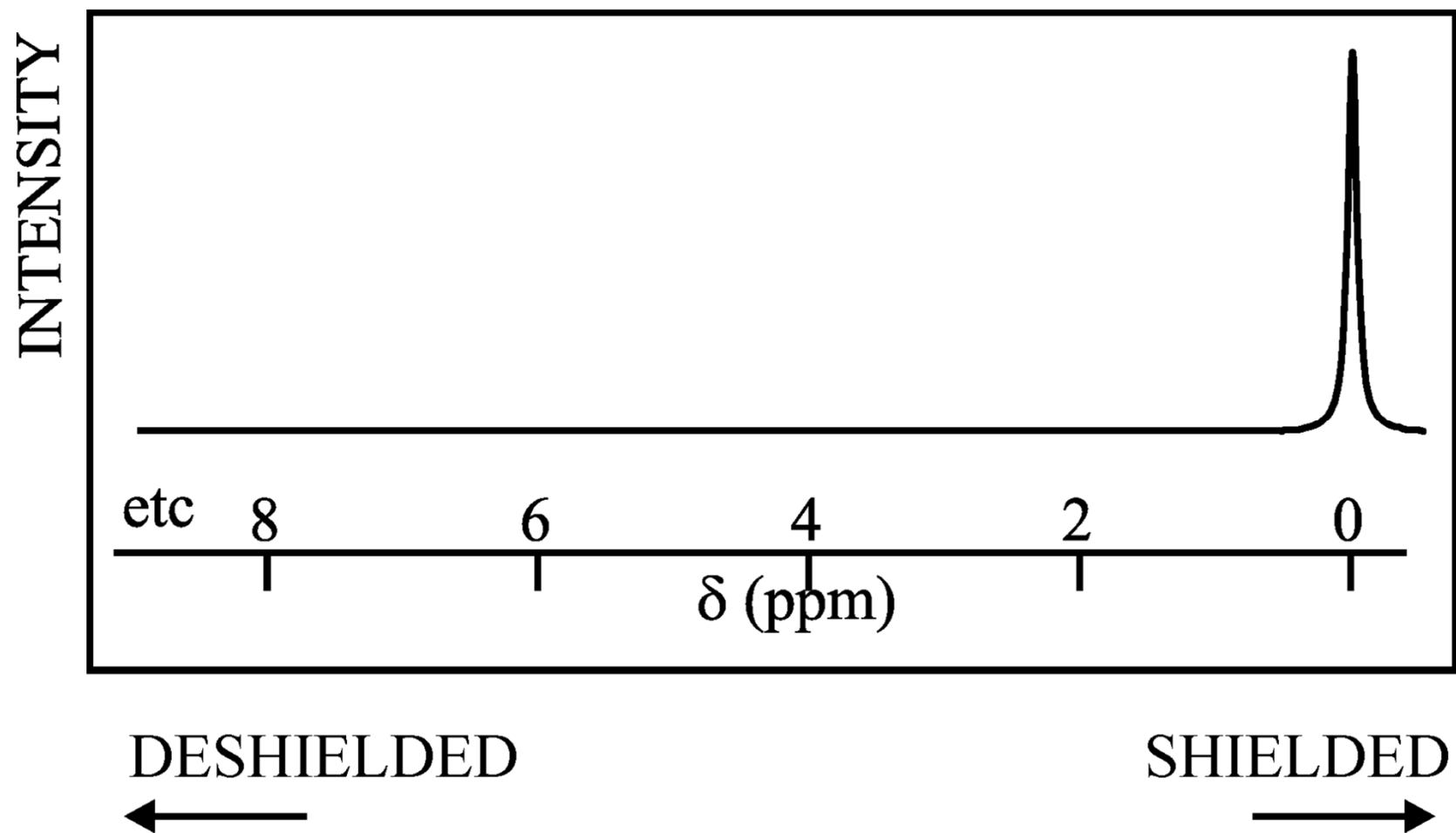
$$\delta = \frac{\text{frequency (Hz)} - \text{frequency TMS (Hz)}}{\text{instrument operating frequency (MHz)}}$$

Typical  $\delta$  ranges:

$^1\text{H}$	$0 < \delta < 10$
$^{13}\text{C}$	$0 < \delta < 220$

Typical  $\delta$  ranges for functional groups are listed in correlation tables and charts (see tutorial book)

# The NMR spectrum



*e.g.* shielding

1. C            shielded (deshielded)

2. H            shielded

H also experiences some “pull”

higher chemical shift (higher  $\delta$  number)

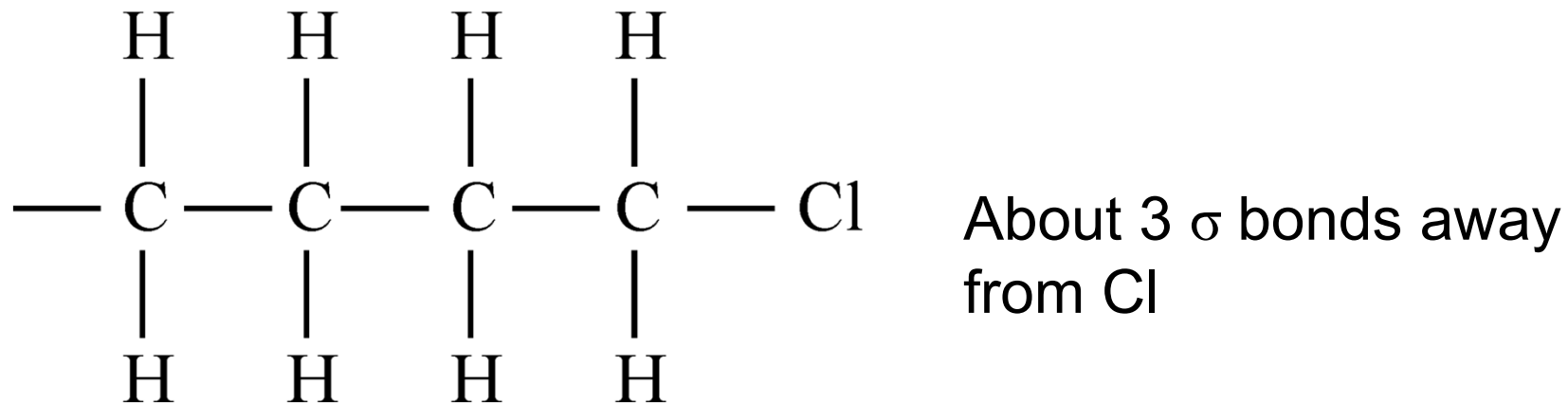
1. C            shielded

2. H            shielded

lower chemical shift (lower  $\delta$  number)

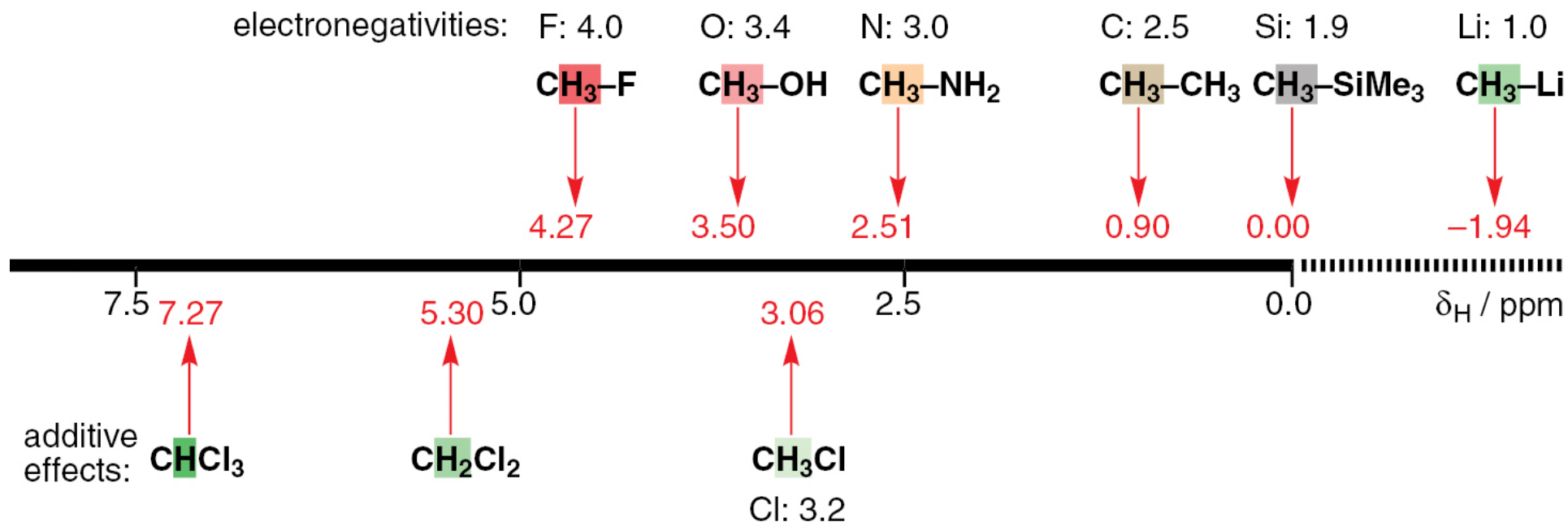
Inductive effects: electronic effects transmitted through neighbouring  $\sigma$  bonds

How far down the chain can inductive effects extend?

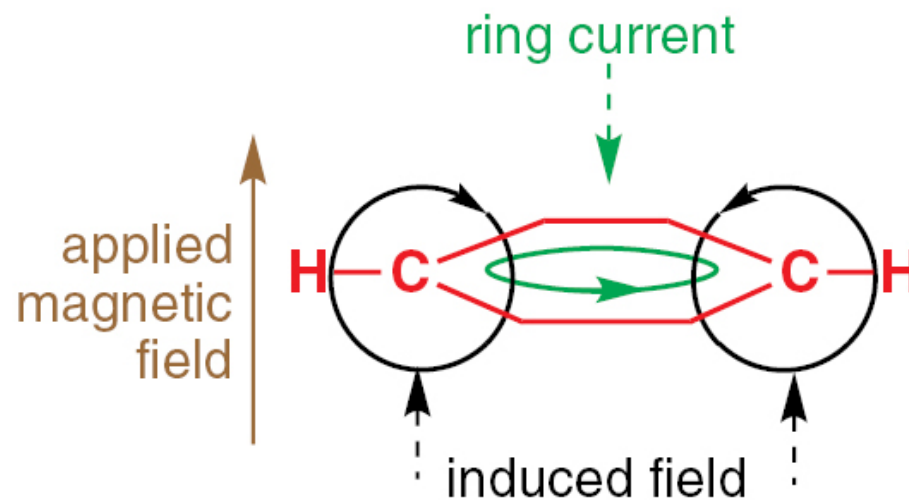
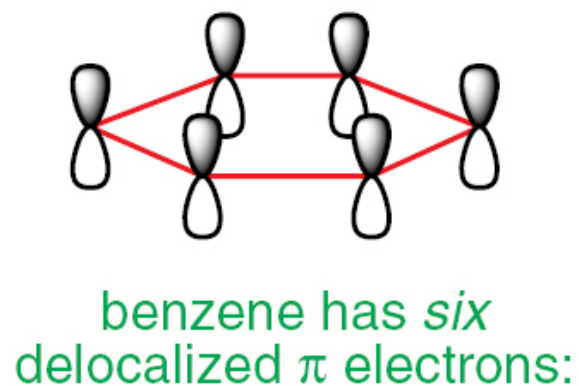
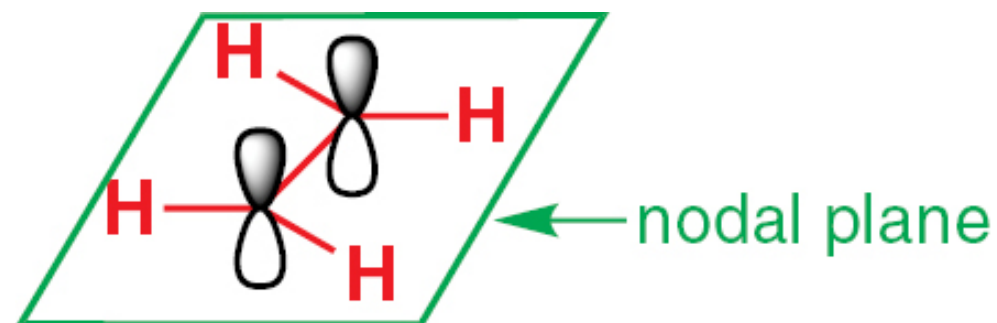
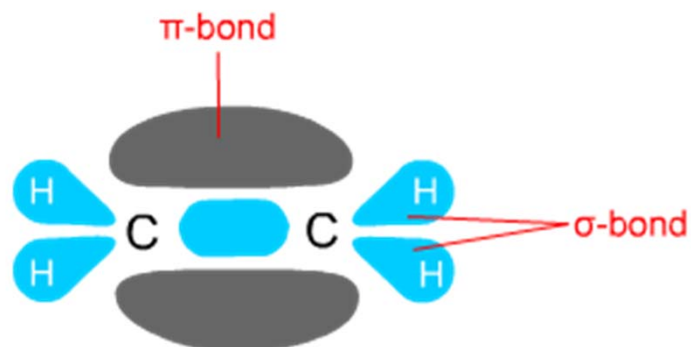




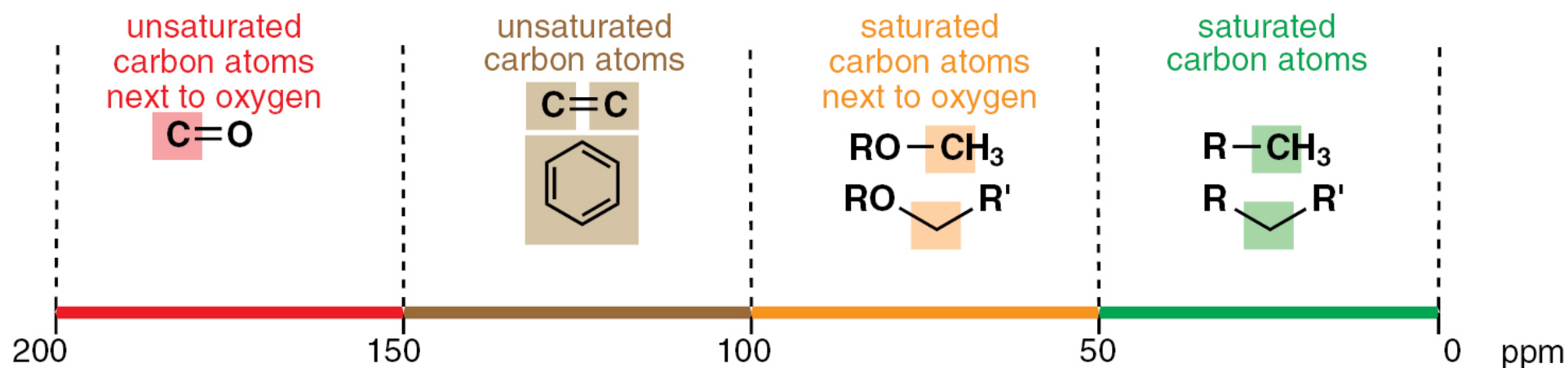
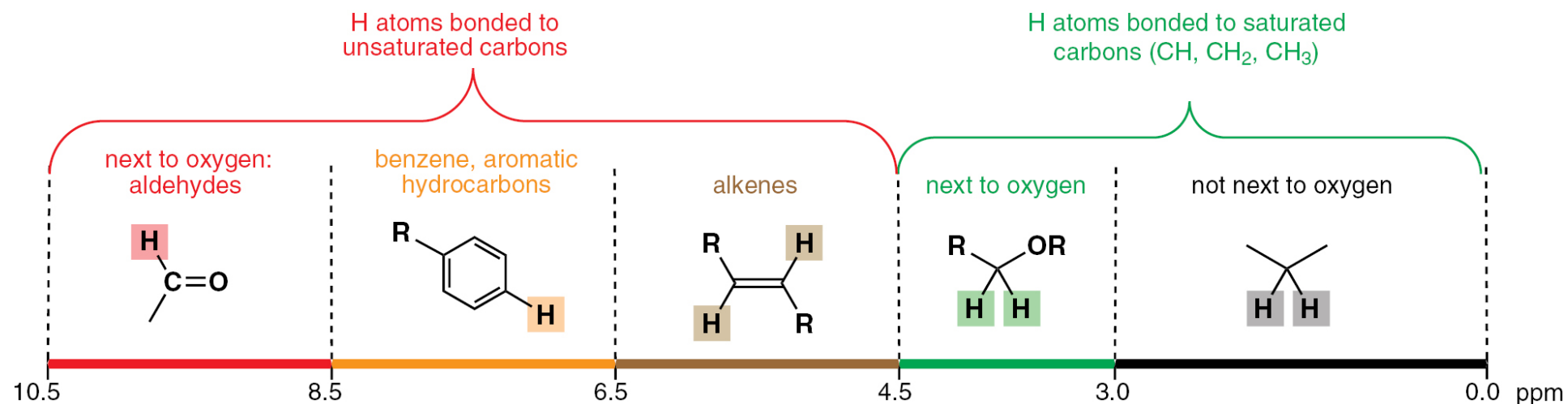
# The effect of electronegativity on chemical shift



# The effect of unsaturation on chemical shift



# Typical chemical shift values

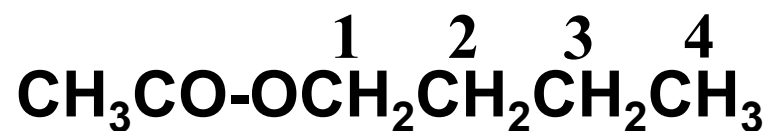
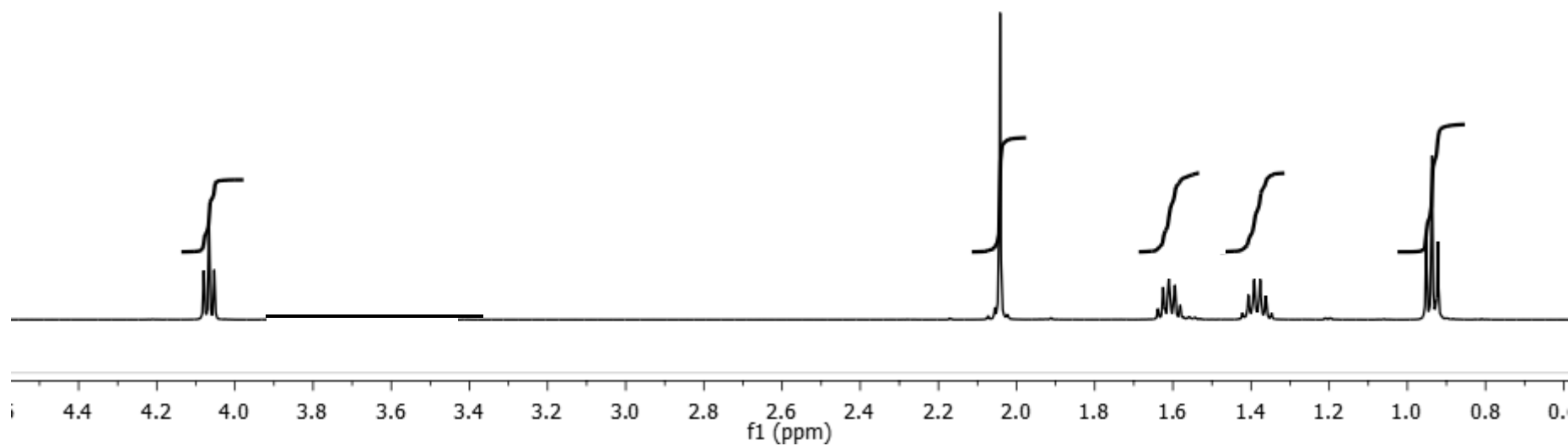
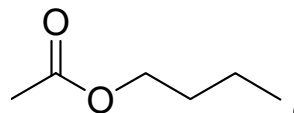


## Integration of signals

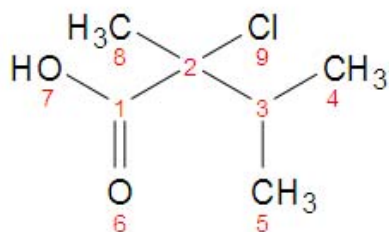
1. Area under peaks    number of  $^1\text{H}$  nuclei causing the signals
2. Instrument can *integrate* peak areas. Integral is plotted as “steps”



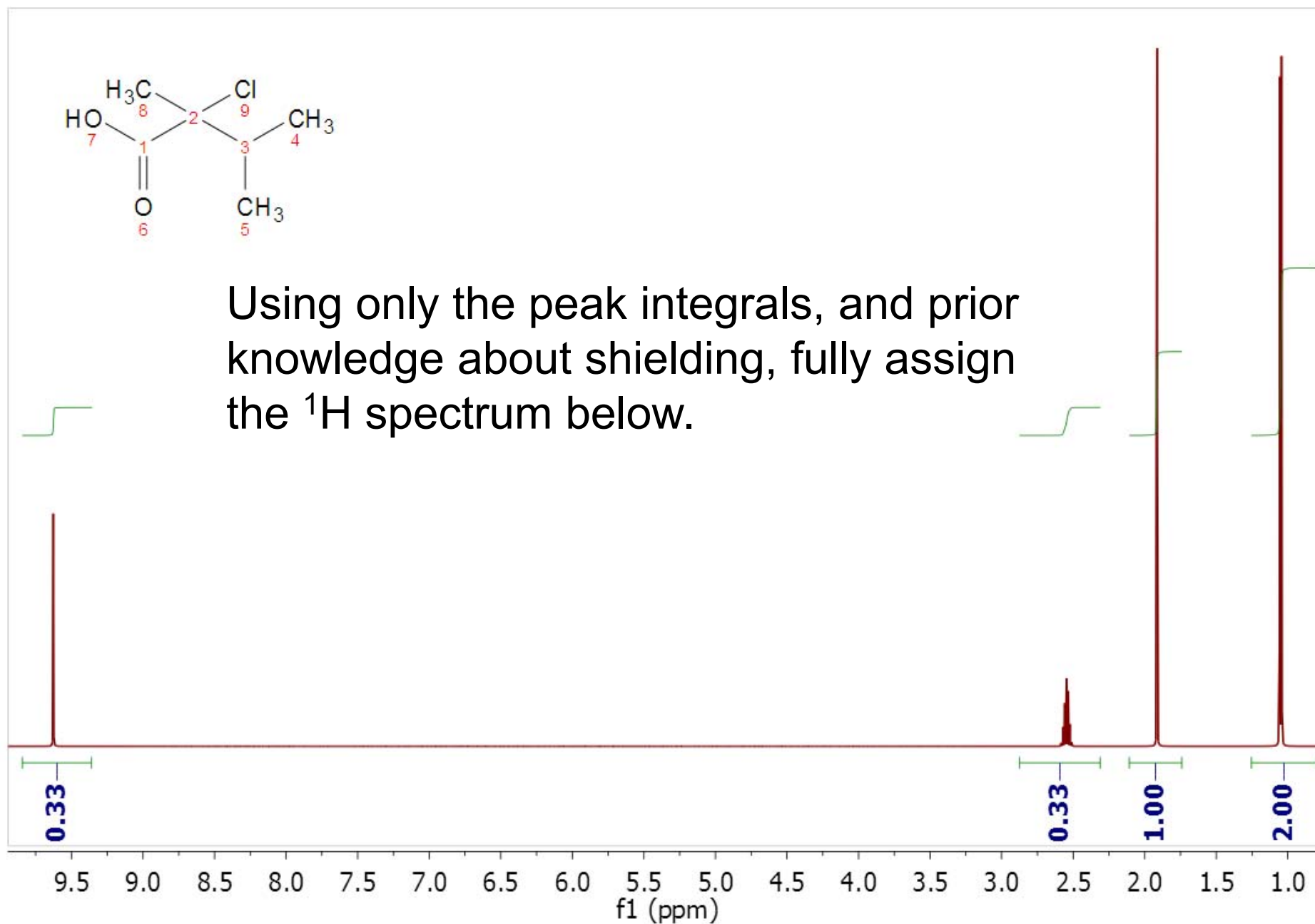
3. Heights of step
4. Integration works with  $^1\text{H}$ , but *fails* with most other nuclei.



If you don't know the formula, then ratio of step heights  $\propto$  ratio of H in compound.

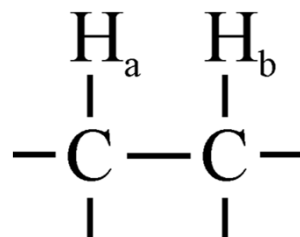


Using only the peak integrals, and prior knowledge about shielding, fully assign the <sup>1</sup>H spectrum below.



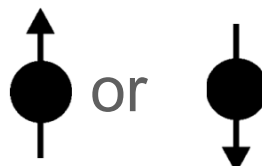
## Spin-spin coupling

Applied  
field

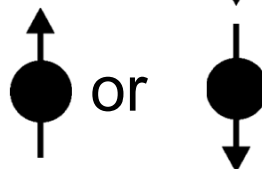


Effect of  
neighbours

$H_a$  can “sense” if  $H_b$  is



$H_b$  can “sense” if  $H_a$  is



$H_a$  “sees” environments of  $H_b$

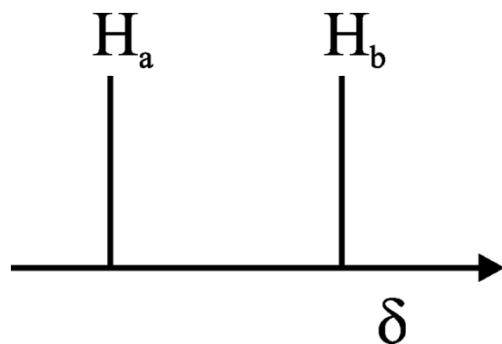
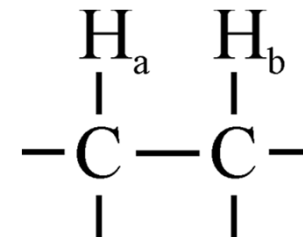
$H_b$  “sees” environments of  $H_a$

Result:

$H_a$  signal is split into two by  $H_b$

$H_b$  signal is split into two by  $H_a$

*i.e.*, don't see



instead, see:



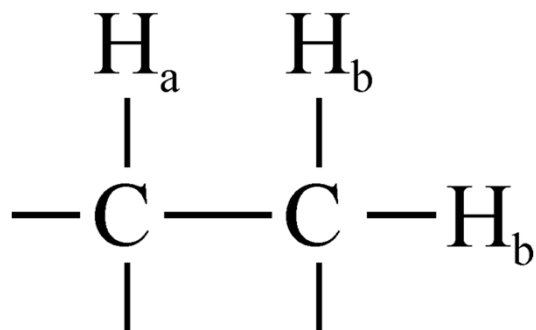
## How much splitting?

Depends on the number of equivalent neighbours: the signal of a proton with  $n$  equivalent neighbouring protons is split into

For  $^1\text{H}$ :

Neigh- bours	Split?	Appearance
0		
1		
2		
3		
$n$		

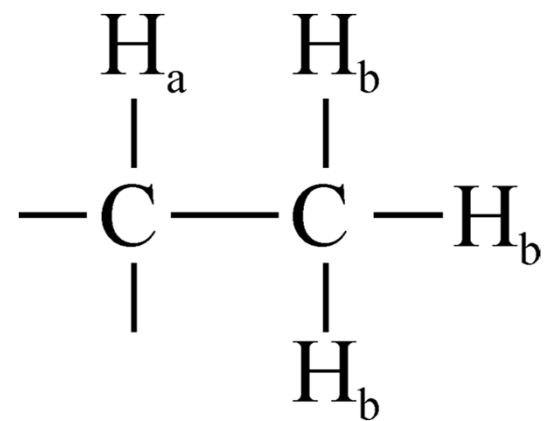
What does  $H_a$  “see” next to a  $CH_2$ ?



If  $H_a$  has two neighbours:  $H_a$  “sees”:

Magnetic  
moment

What does  $H_a$  “see” next to a  $CH_3$ ?

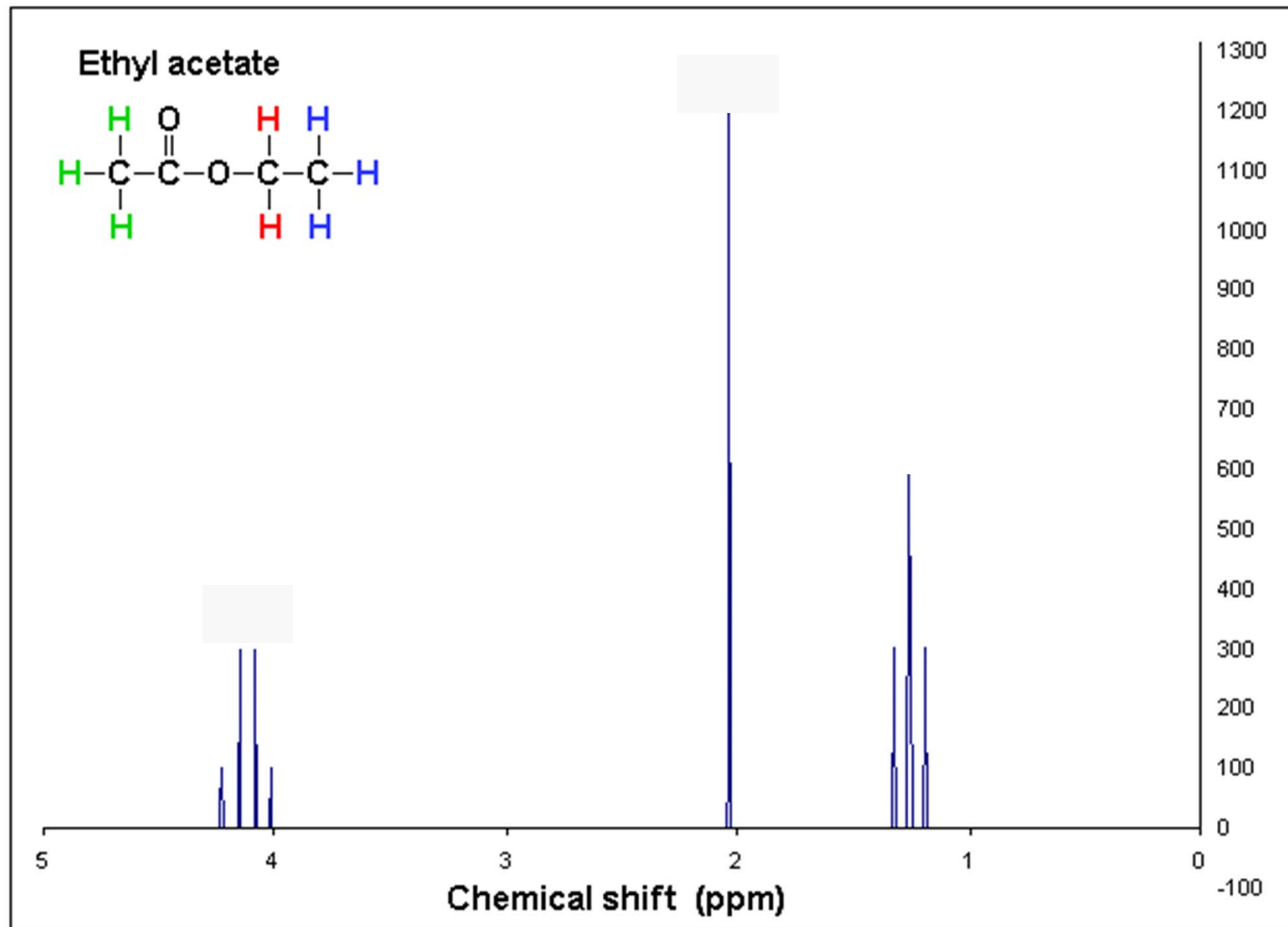


*e.g.* triplet

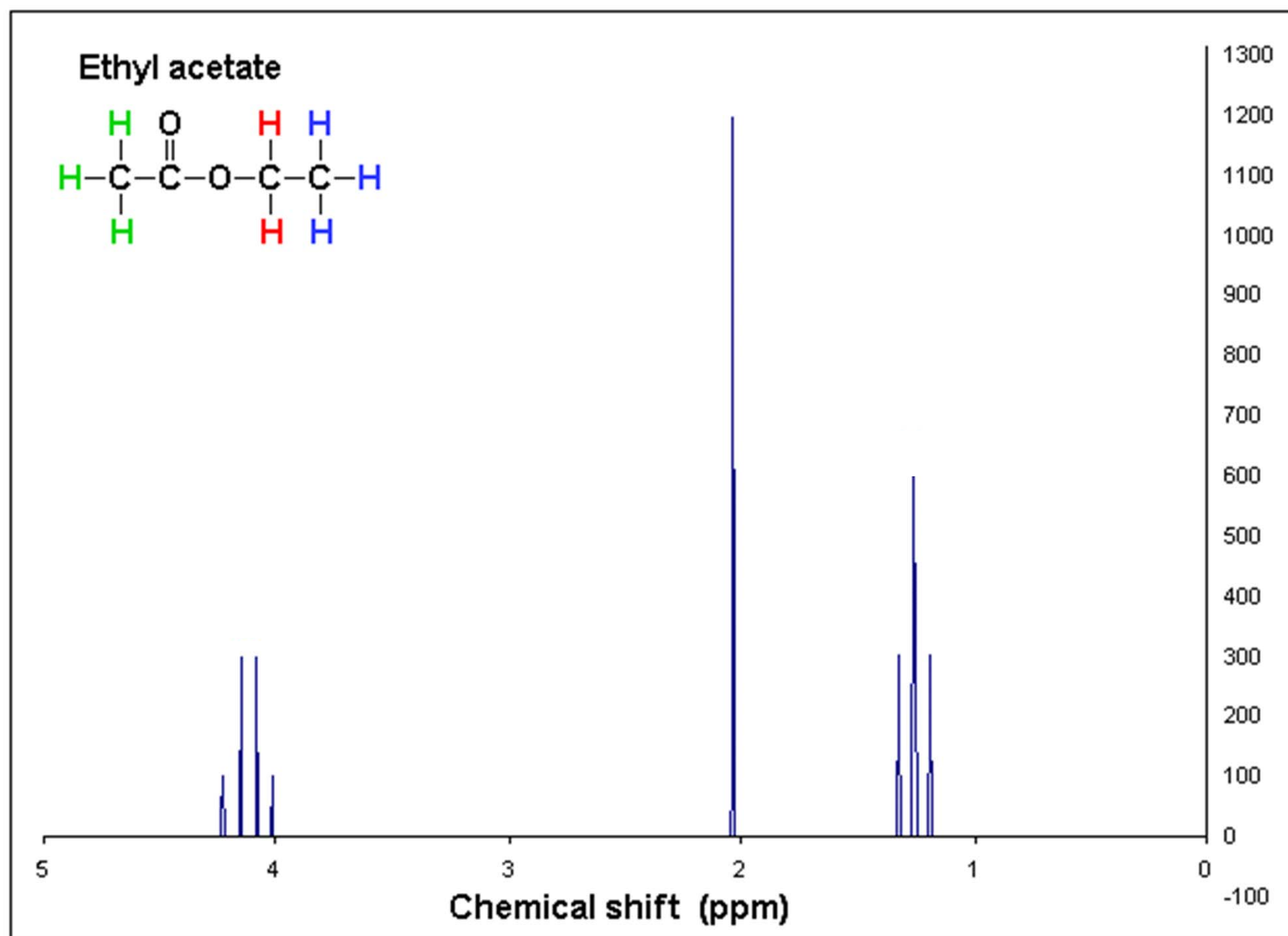
1. Lines are equally spaced
2.  $J$  = coupling constant in Hz
3.  $J$  is a measure of the degree to which coupled nuclei interact.
4. Typical  $J_{\text{H-H}}$  : 0 – 18 Hz

$J$  is independent of field strength

e.g. Ethyl acetate



e.g. Ethyl acetate

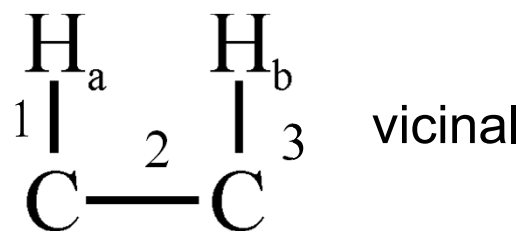


## How far away are coupled nuclei?

1. Chemically equivalent nuclei do not couple!

e.g.

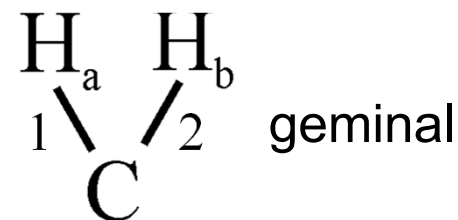
2.  $^1\text{H}$  must be attached to C to show coupling



$^3J_{ab}$  – coupling observed

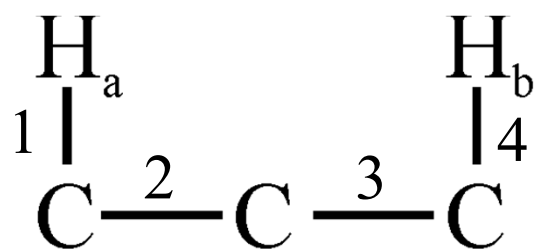


= H 3 bonds (or atoms)  
away



$^2J_{ab}$  – coupling observed only if  
 $\text{H}_a$  &  $\text{H}_b$  not equiv.

e.g.



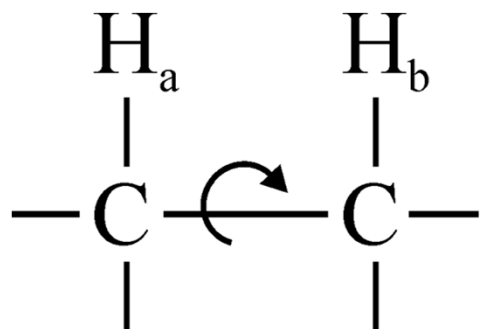
${}^4J_{ab}$  – coupling seldom observed,  
(special cases)



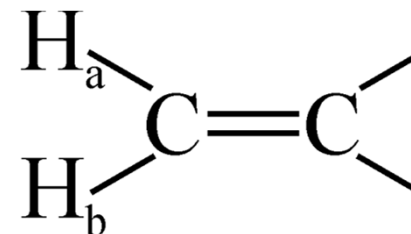
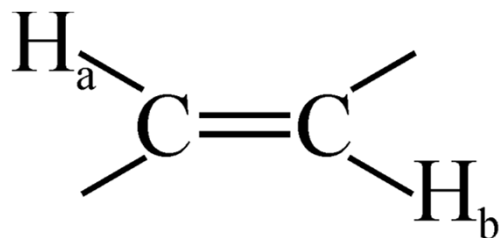
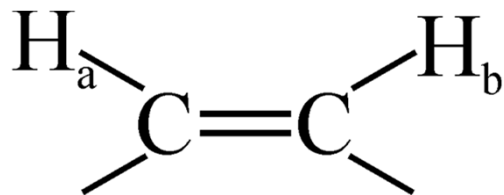
## Size of $J$ ?

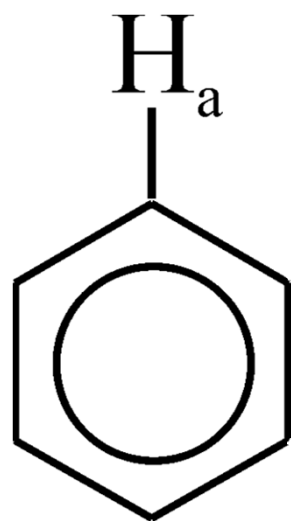
Depends on geometry of system

1. If free rotation is possible:



2. Rigid systems – no rotation:

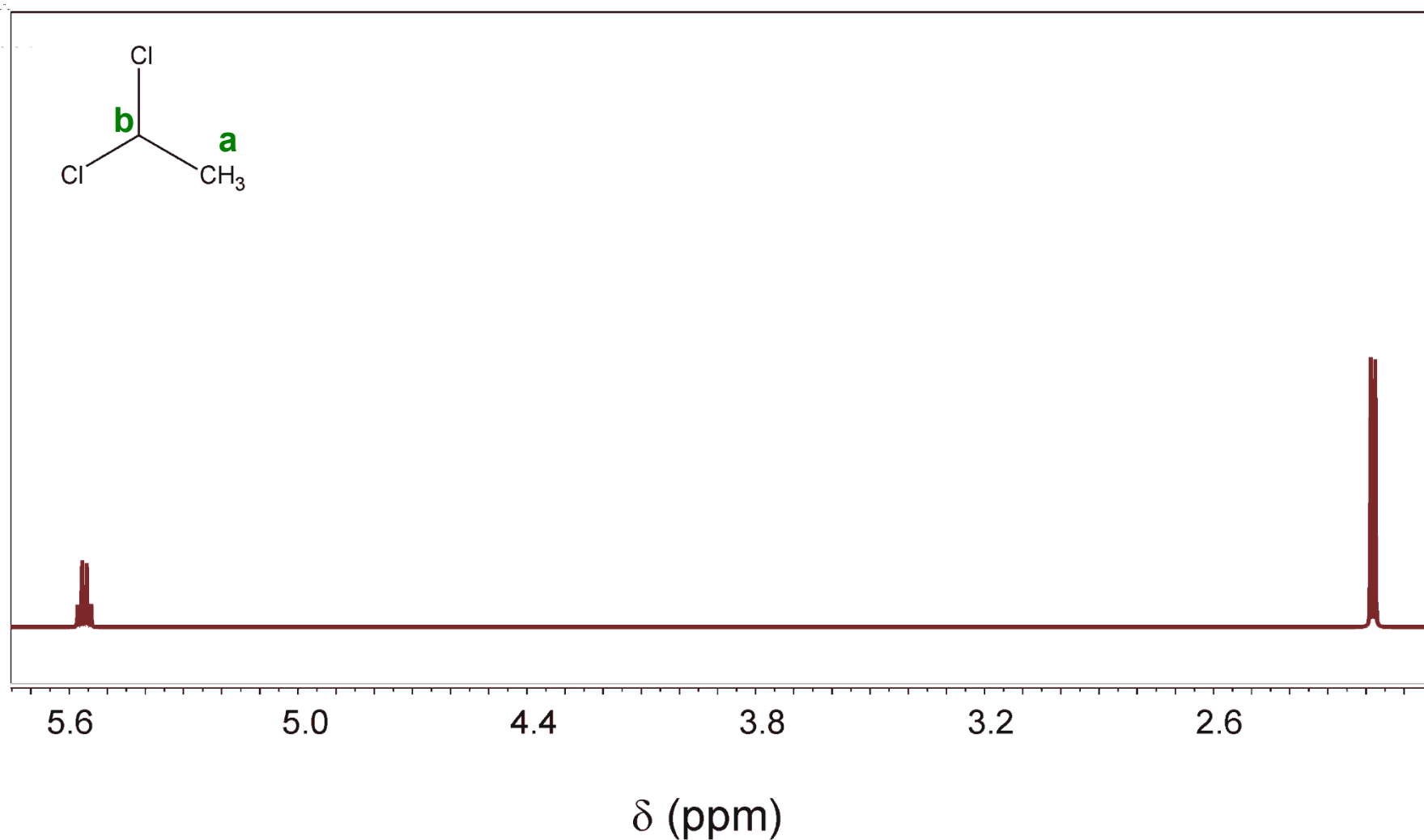




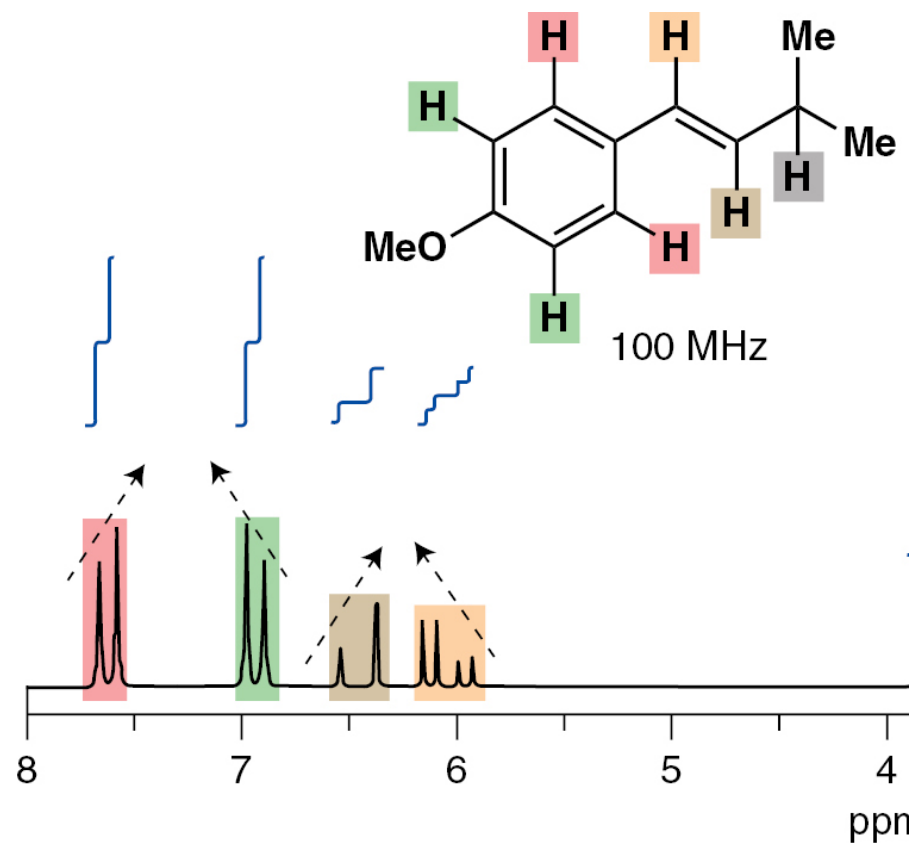
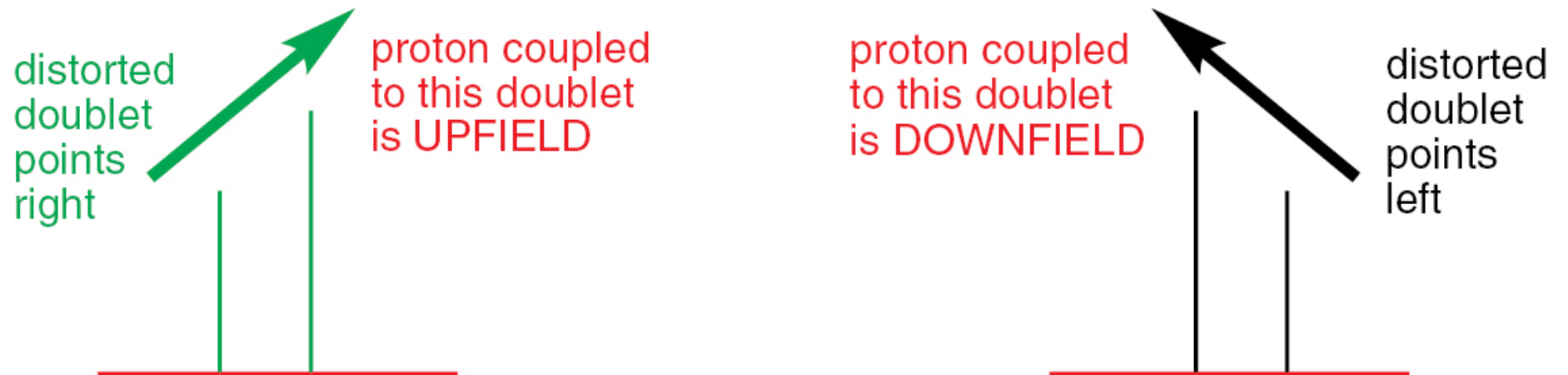
## How is $J$ calculated?

The magnitude of  $J$  can be calculated by  $\times$  the separation of the lines in  $\delta$  (ppm) units by the resonance frequency of the spectrometer in MHz.

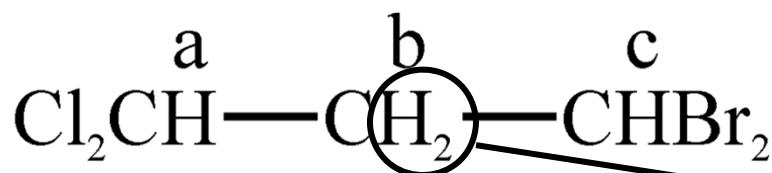
## More on $J$



If  $\text{H}_a$  and  $\text{H}_b$  are coupled, then the spacing between the lines is equal,



## Coupling to several neighbours



see:



??



See  $3 \times {}^1\text{H}$  signals

split by both a and c

Pattern depends on the size of  $J_{\text{ab}}$  &  $J_{\text{bc}}$

### Two cases:

1.  $J_{\text{ab}} \gg J_{\text{bc}}$

Splitting “tree”

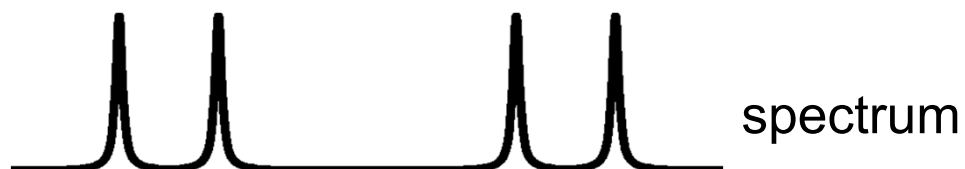
if no coupling

doublet

effect of  $\text{H}_\text{a}$

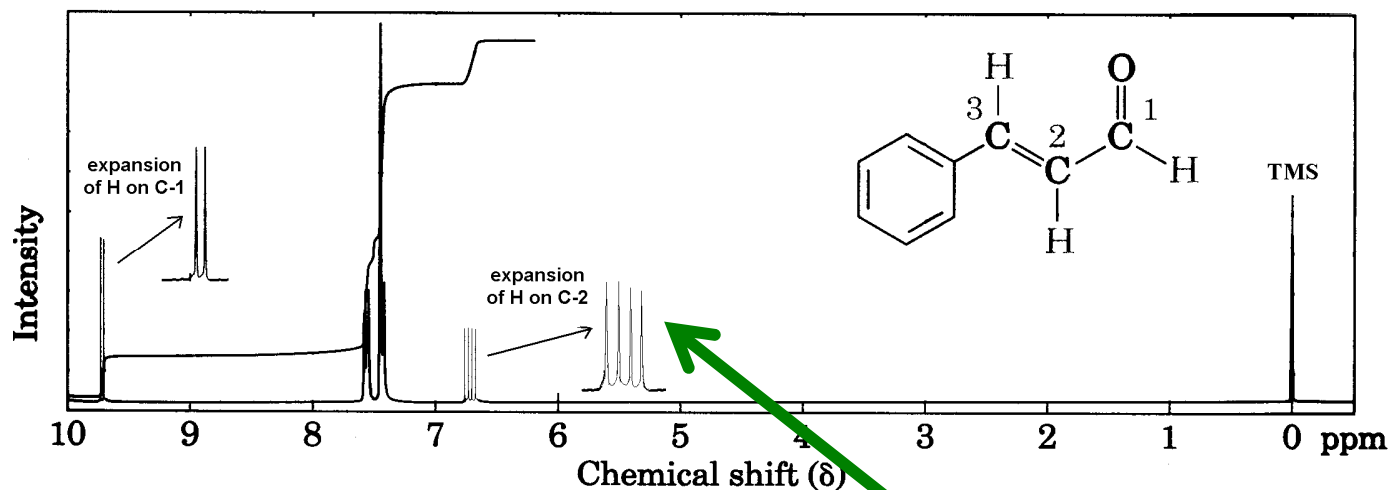
double  
doublet

effect of  $\text{H}_\text{c}$



2.  $J_{\text{ab}} \approx J_{\text{bc}}$

## e.g. $^1\text{H}$ NMR spectrum of cinnamaldehyde



Tree diagram for proton on C-2

NB. This is not a quartet

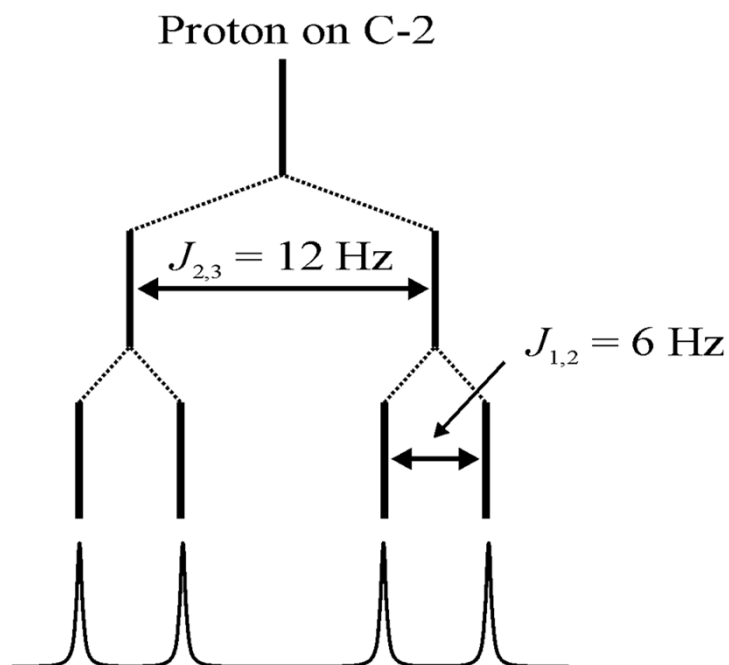
if no coupling, see s

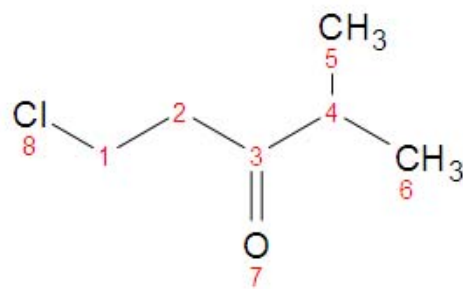
but

H-3 splits H-2 into d with  $J = 12$  Hz

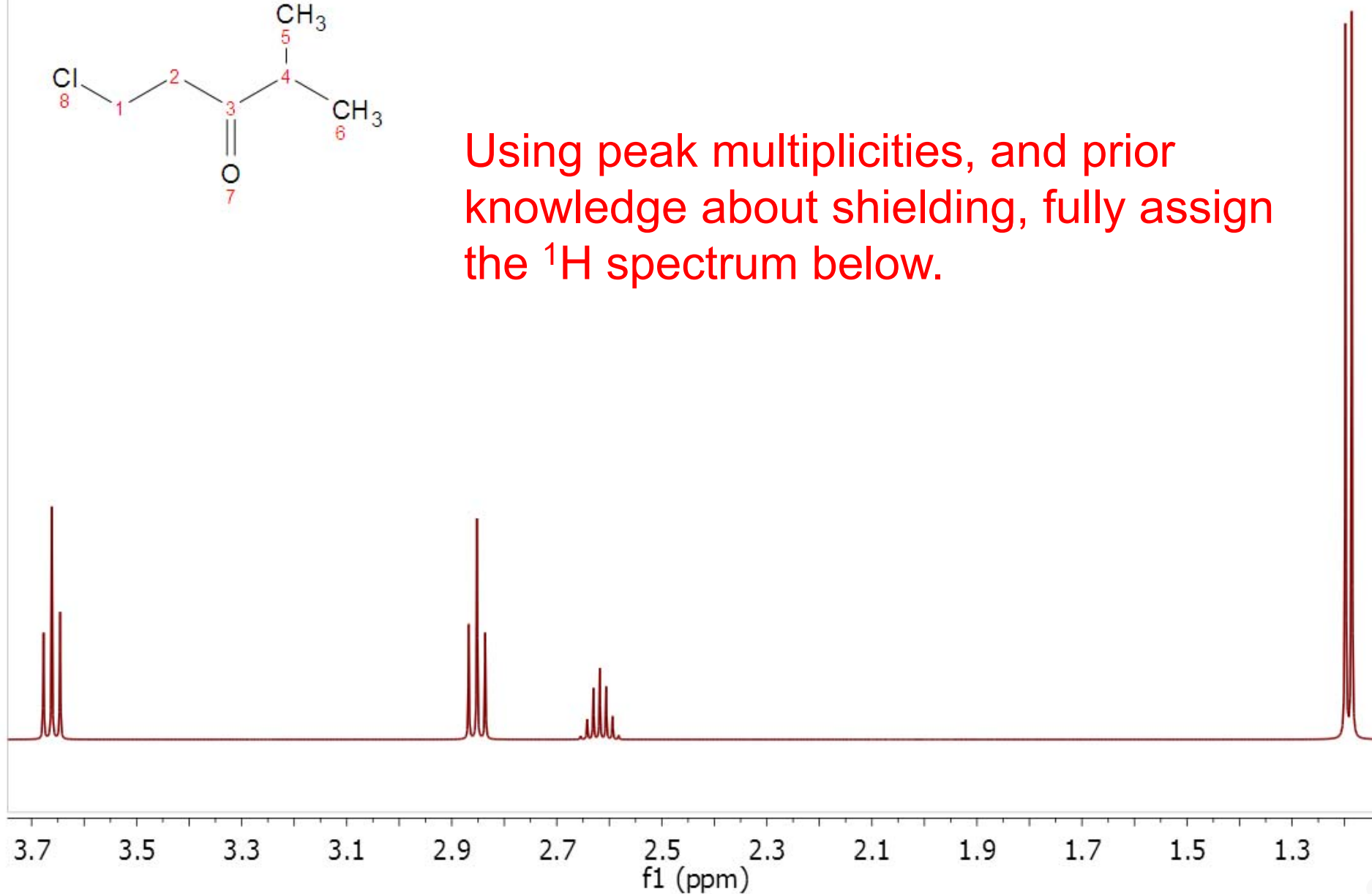
then

H-1 splits each line again into d, this time with  $J = 6$  Hz



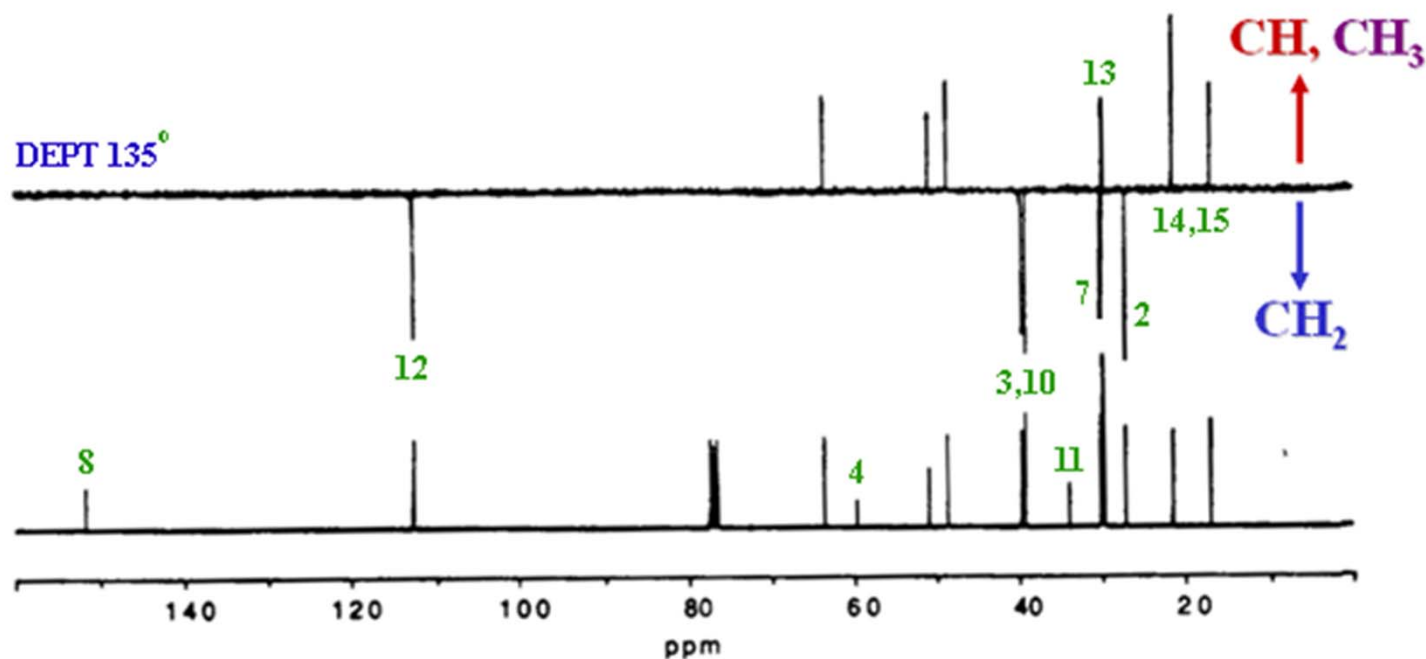


Using peak multiplicities, and prior knowledge about shielding, fully assign the  $^1\text{H}$  spectrum below.





## DEPT spectra



Usually DEPT-135:

CH and CH<sub>3</sub> signals are up and CH<sub>2</sub> signals are down,  
quaternary carbon signals disappear

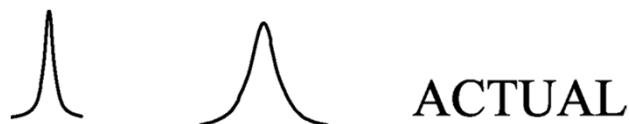
## $^1\text{H}$ attached to N, O, *etc.*

1. Hydrogen bonding is possible
2. There is \_\_\_\_\_ of H between molecules

### 3. Results:

- Peaks are often broad
- $\delta$  values can vary greatly
- Positions also depend on *solvent & concentration*
- Very seldom see coupling

*e.g.*  $\text{CH}_3\text{—OH}$



## Locating $^1\text{H}$ attached to N, O, *etc.*

One can take advantage of H exchange between molecules to *locate* H attached to N or O

- Add  $\text{D}_2\text{O}$  to the sample

OH signal vanishes!

e.g. tut four, problem 9

NB. This also happens for  $\text{NH}_2$  or NH signals!!

# Interpreting $^1\text{H}$ NMR spectra: a summary

Look at four things:

1. Number of signals

Gives information about non-equivalent nuclei

2. Chemical shift ( $\delta$ ) of signals

Gives information about environment of nuclei and possible functional groups. *Use correlation tables and charts!*

3. Integration (area under each signal)

Gives information about the number of H responsible for each signal.

4. Splitting patterns

Gives information about the number of H on the *neighbouring C*

# Interpreting $^{13}\text{C}$ NMR spectra: a summary

Look at three things:

1. Number of signals

Gives information about non-equivalent nuclei

2. Chemical shift ( $\delta$ ) of signals

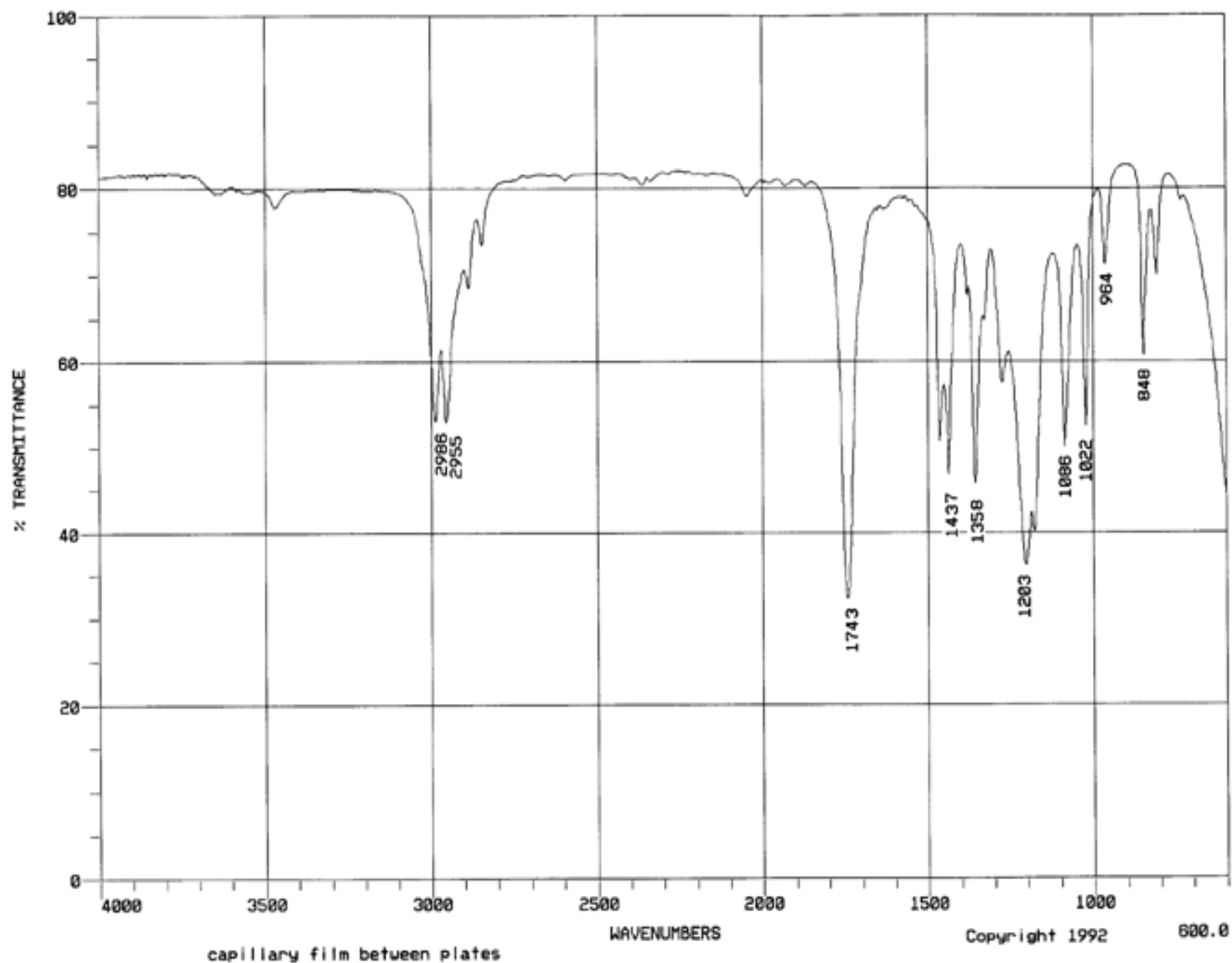
Gives information about environment of nuclei and possible functional groups. *Use correlation tables and charts!*

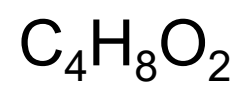
3. Off-resonance data (if provided)

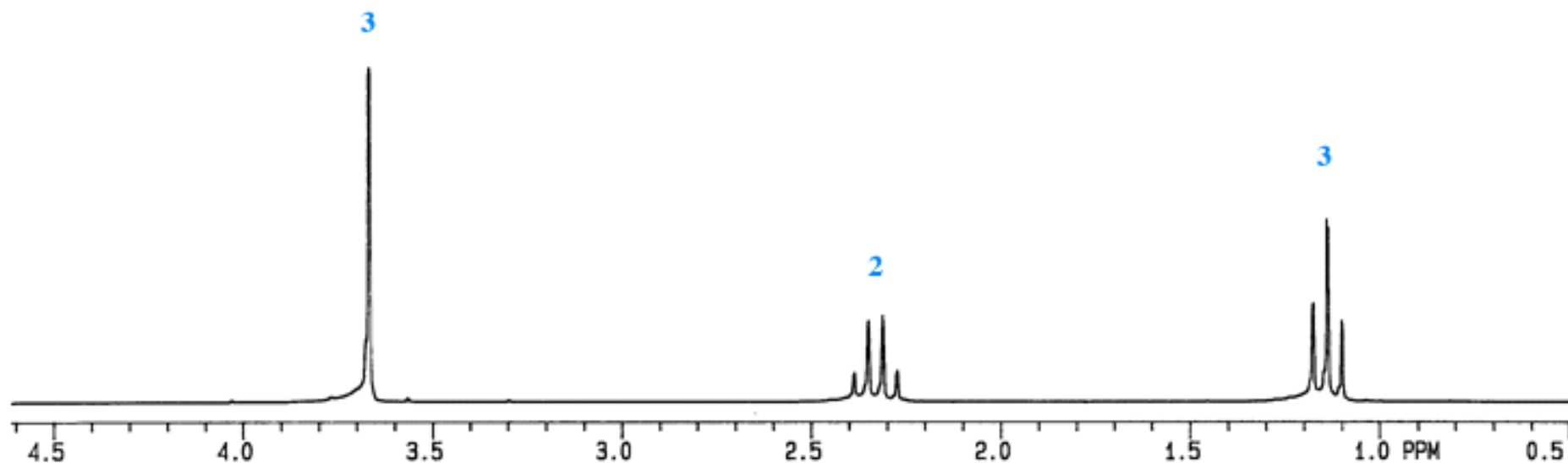
Gives information about the number of h on each carbon atom

*N.B.*  $^{13}\text{C}$  NMR signals are not integrated!

Molecular formula  $\text{C}_4\text{H}_8\text{O}_2$ . IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are given.

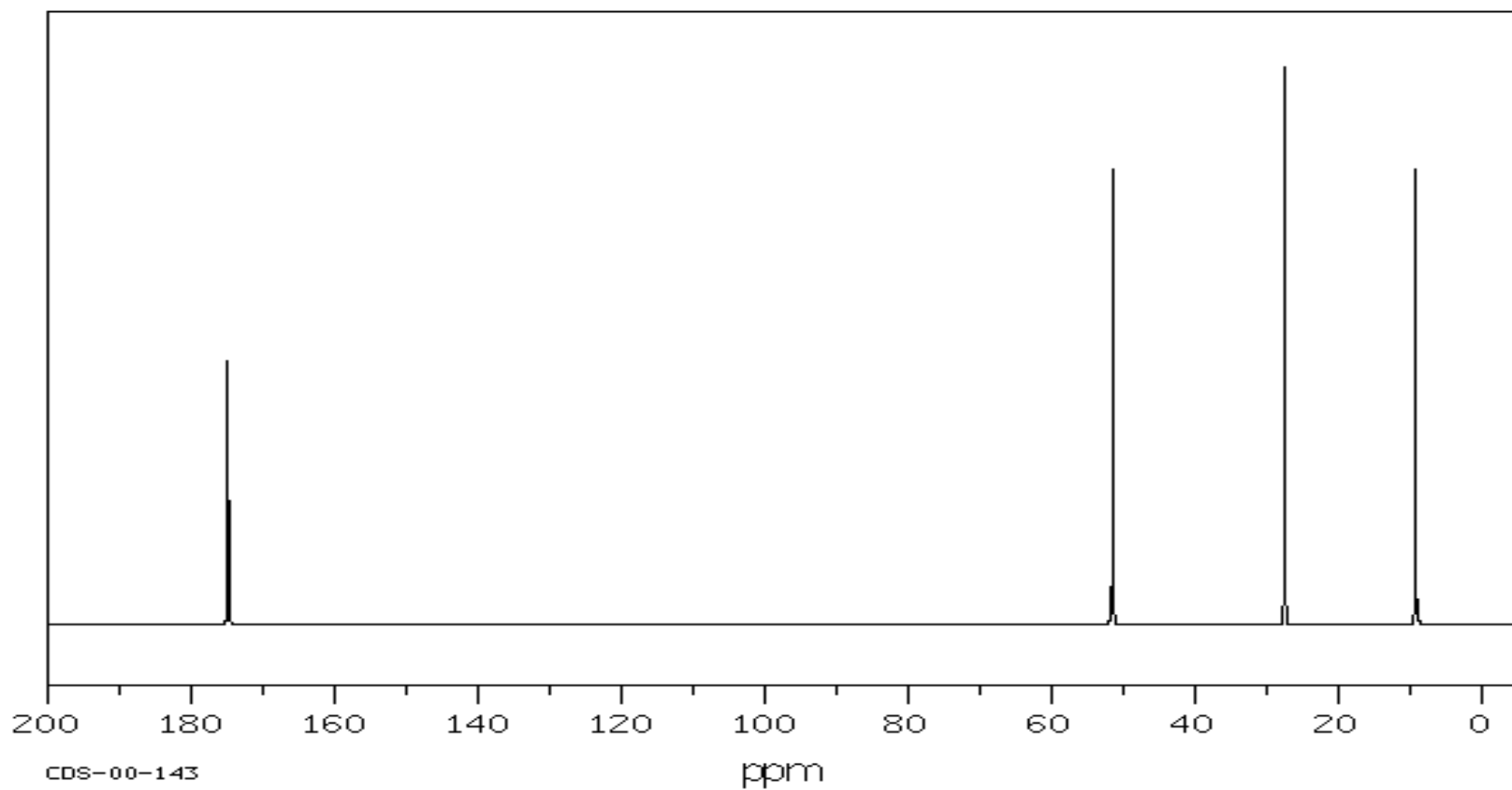






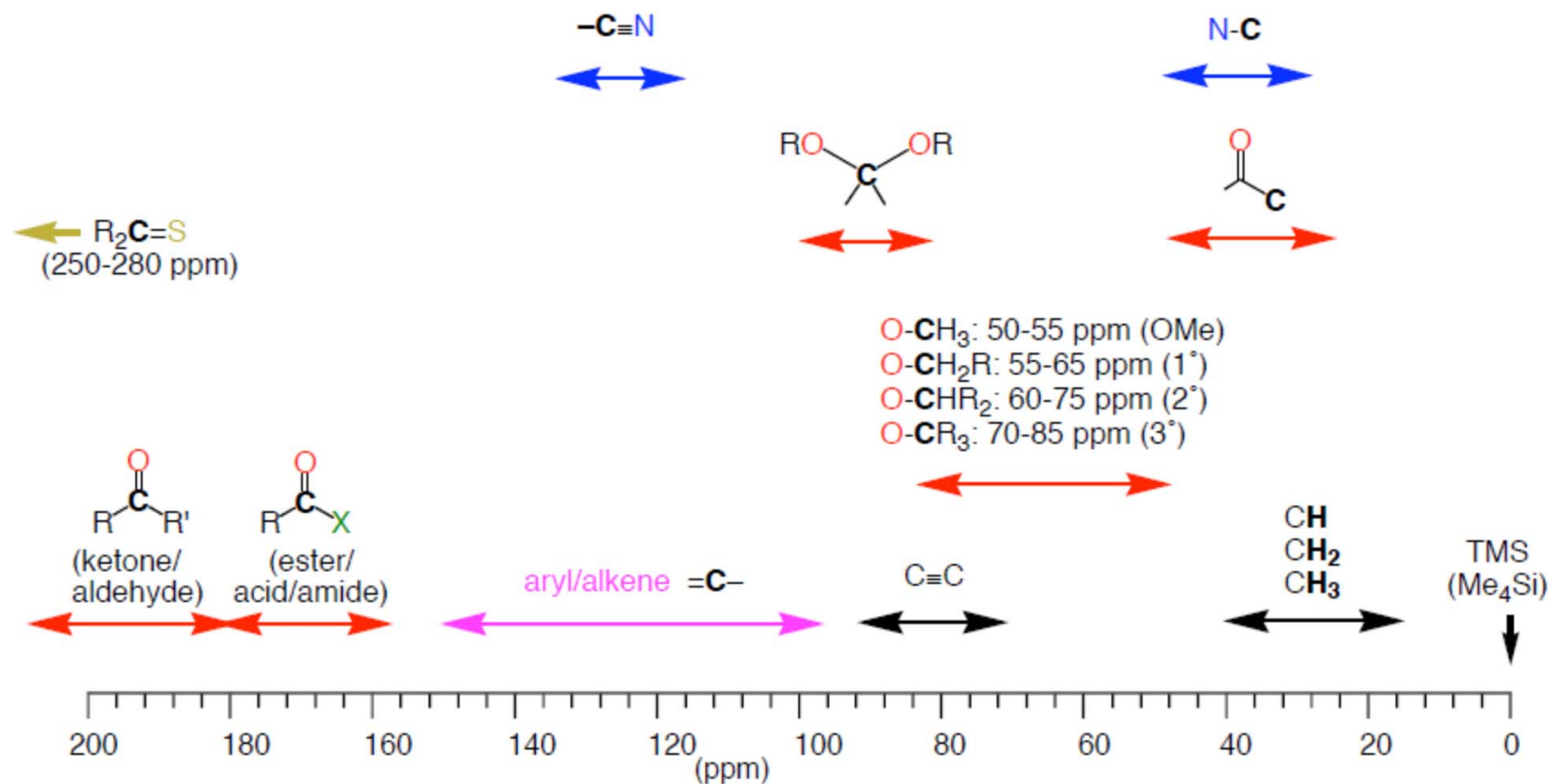
	Signal 1	Signal 2	Signal 3
Chemical shift ( $\delta$ ) /ppm			
Number of H (integration)			
Multiplicity			
No. of H on adjacent C			
Assignment			





	Signal 1	Signal 2	Signal 3	Signal 4
Chemical shift ( $\delta$ ) /ppm				
Assignment				

# $^{13}\text{C}$ Correlation Chart



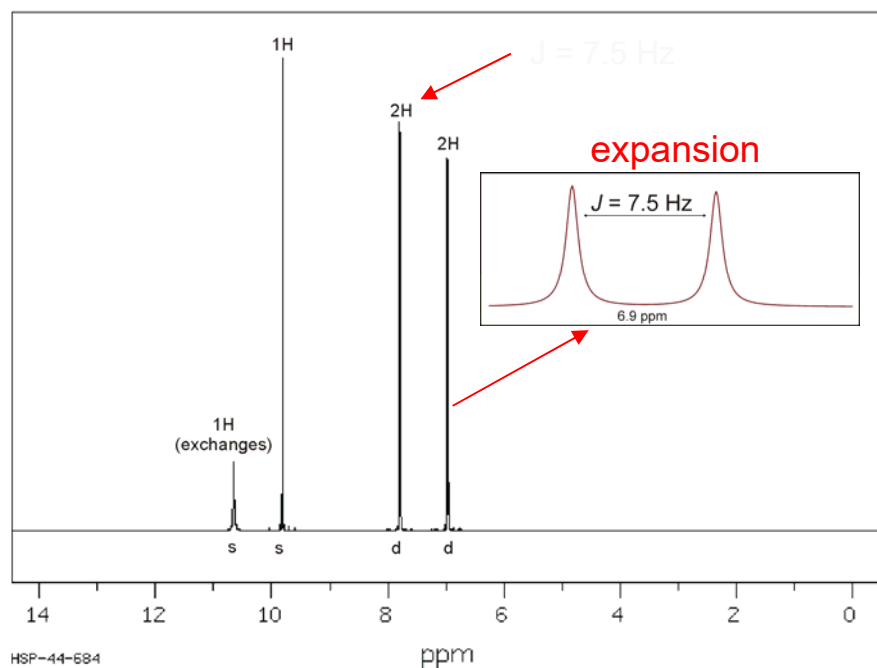
# Spectroscopy lecture example:

Given: Molecular formula :  $\text{C}_7\text{H}_6\text{O}_2$

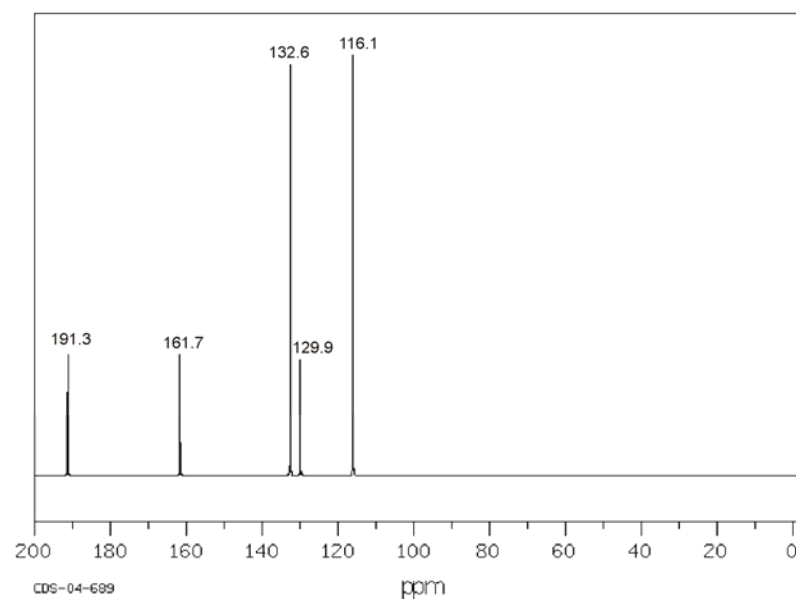
IR Spectrum : Strong, broad band at  $3239\text{ cm}^{-1}$

Strong, sharp peak at  $1698\text{ cm}^{-1}$

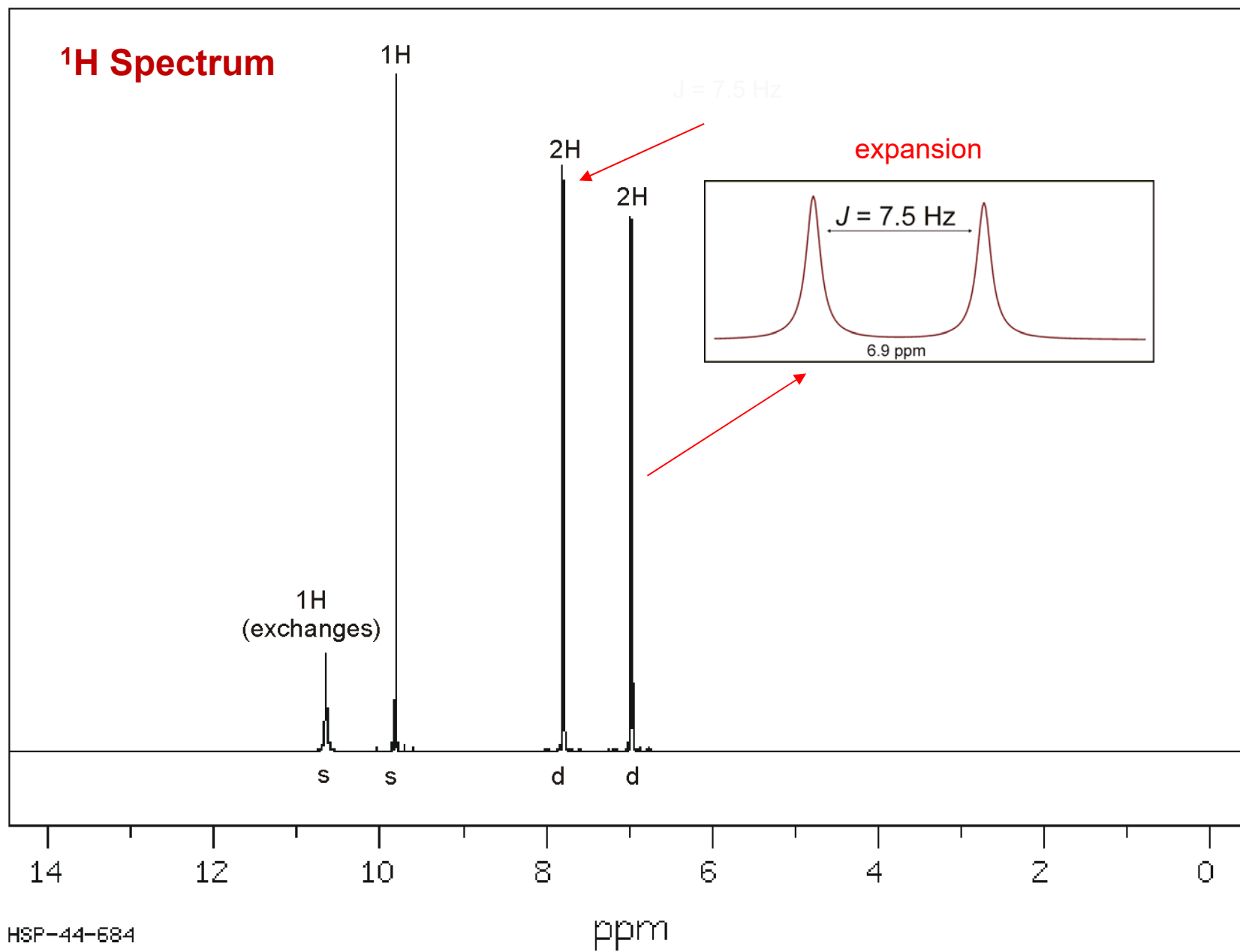
## $^1\text{H}$ NMR Spectrum



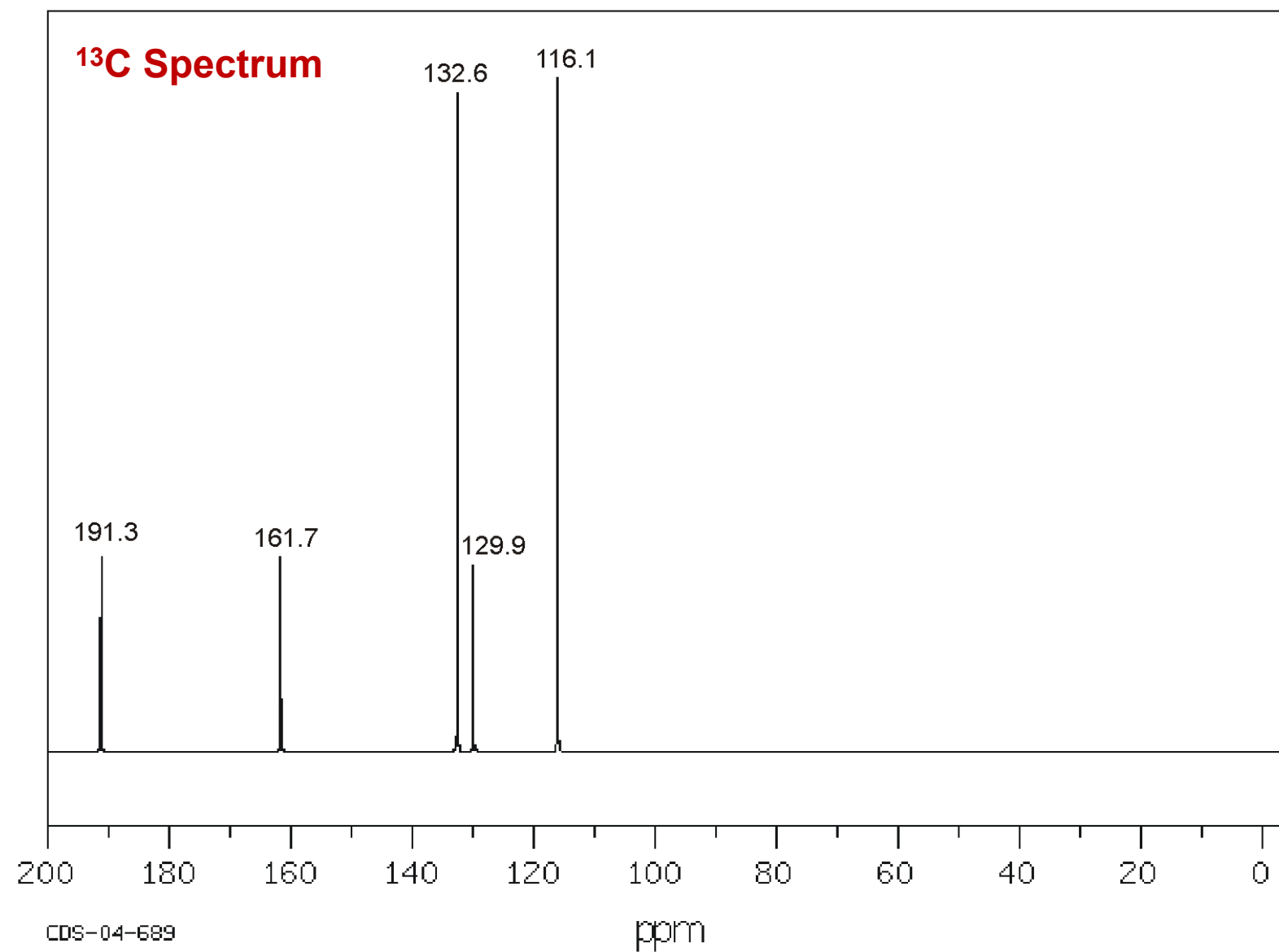
## $^{13}\text{C}$ NMR Spectrum



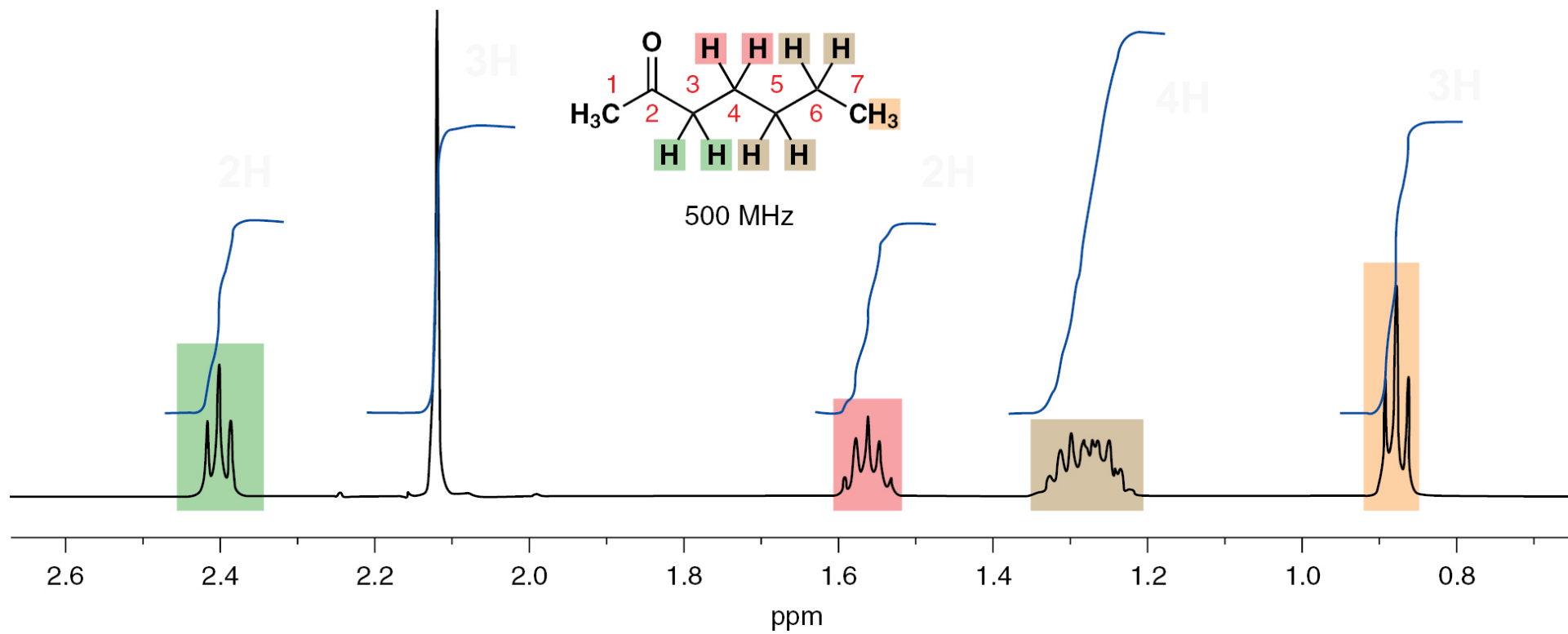
Determine the structure, and FULLY assign the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra



$^1\text{H}$ NMR	Signal 1	Signal 2	Signal 3	Signal 4



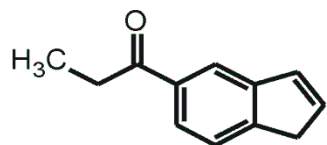
$^{13}\text{C}$ NMR	Signal 1	Signal 2	Signal 3	Signal 4	Signal 5
Chemical Shifts (ppm )					
Assignment					



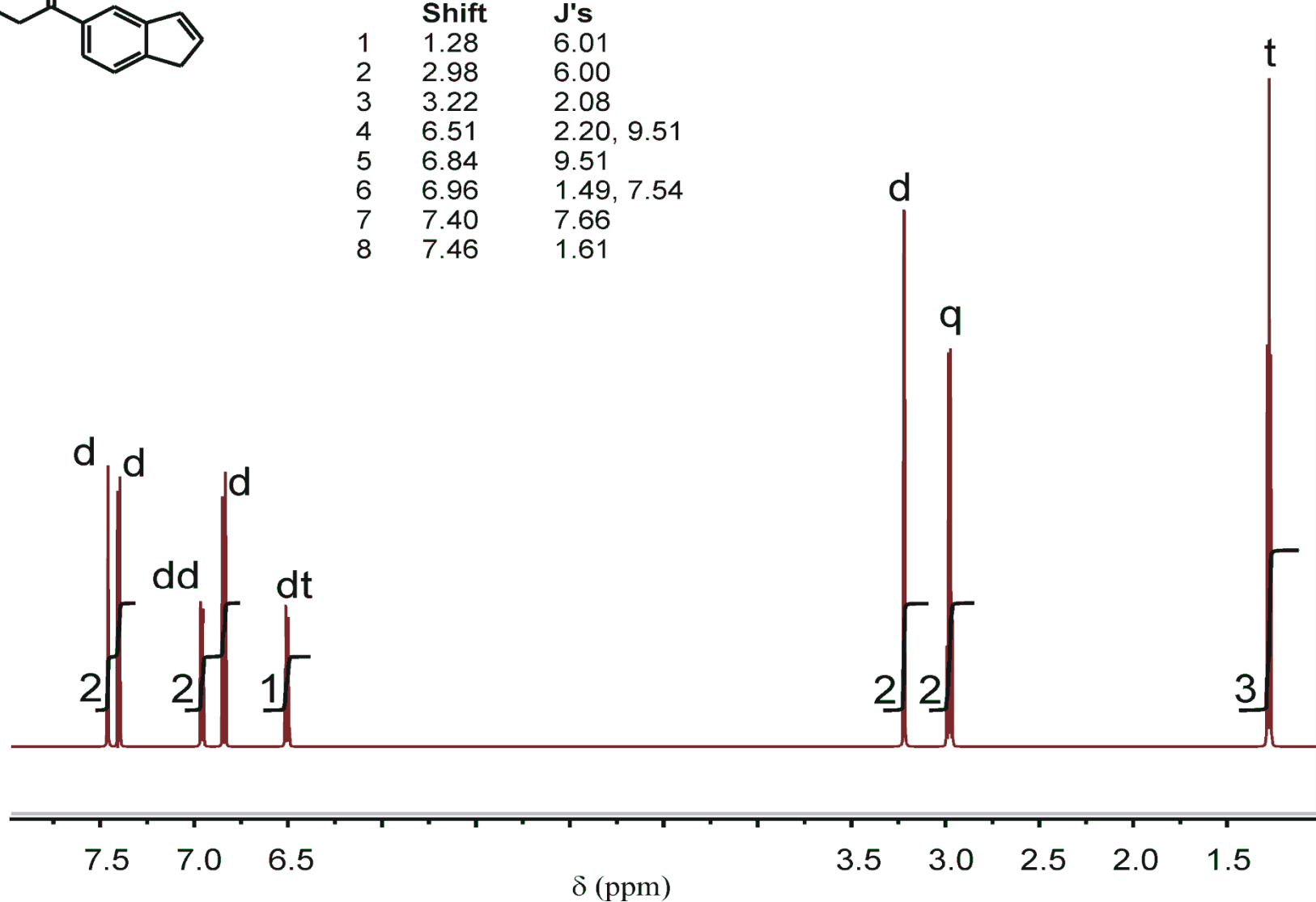


# Spectroscopy example:

FULLY assign the  $^1\text{H}$  spectrum below:



	Shift	J's
1	1.28	6.01
2	2.98	6.00
3	3.22	2.08
4	6.51	2.20, 9.51
5	6.84	9.51
6	6.96	1.49, 7.54
7	7.40	7.66
8	7.46	1.61



## Mass spectrometry (MS)

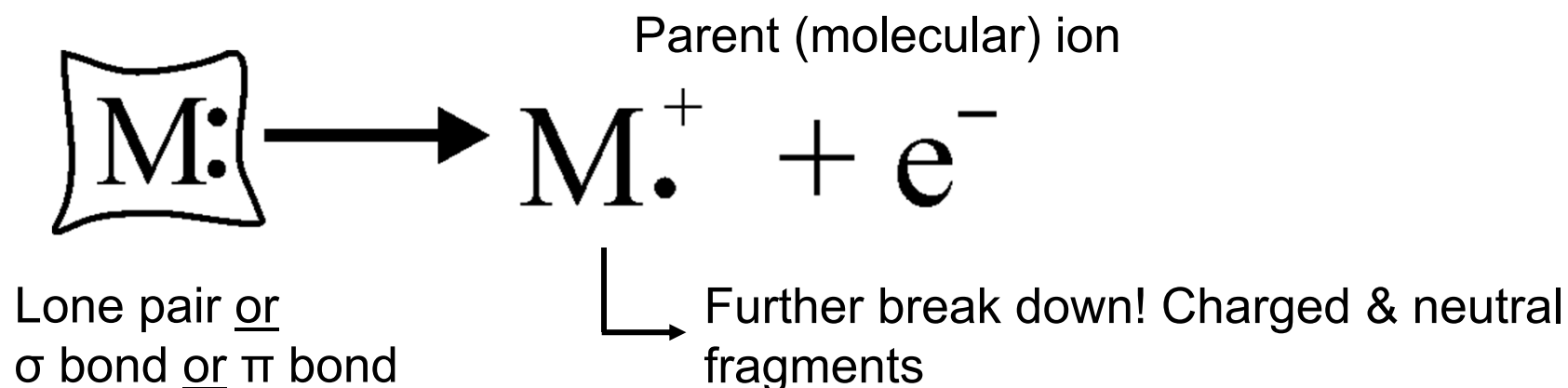
- Is *not* a spectroscopy! (Does not involve electromagnetic radiation)
- Is used for determining the
- Also get structural information by measuring the mass of when high-energy molecules break up.

## The ideas behind MS

- Blast molecules with a beam of *electrons* (usually

$$\sim 70 \text{ eV} = 6700 \text{ kJ mol}^{-1}$$

- These dislodge a from the molecule, leaving behind a

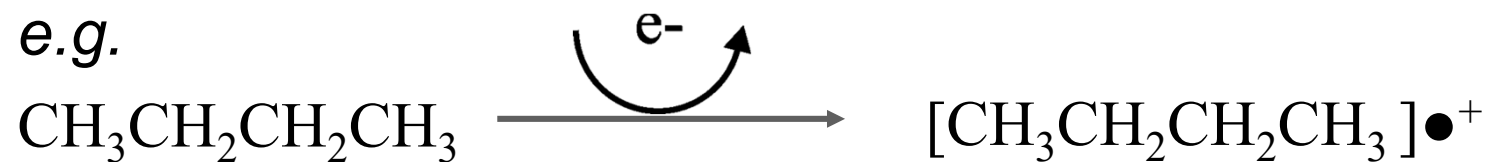


- the instrument detects all positively charged ions, and sorts them according to their

usually +1 charge

## Fragmentation

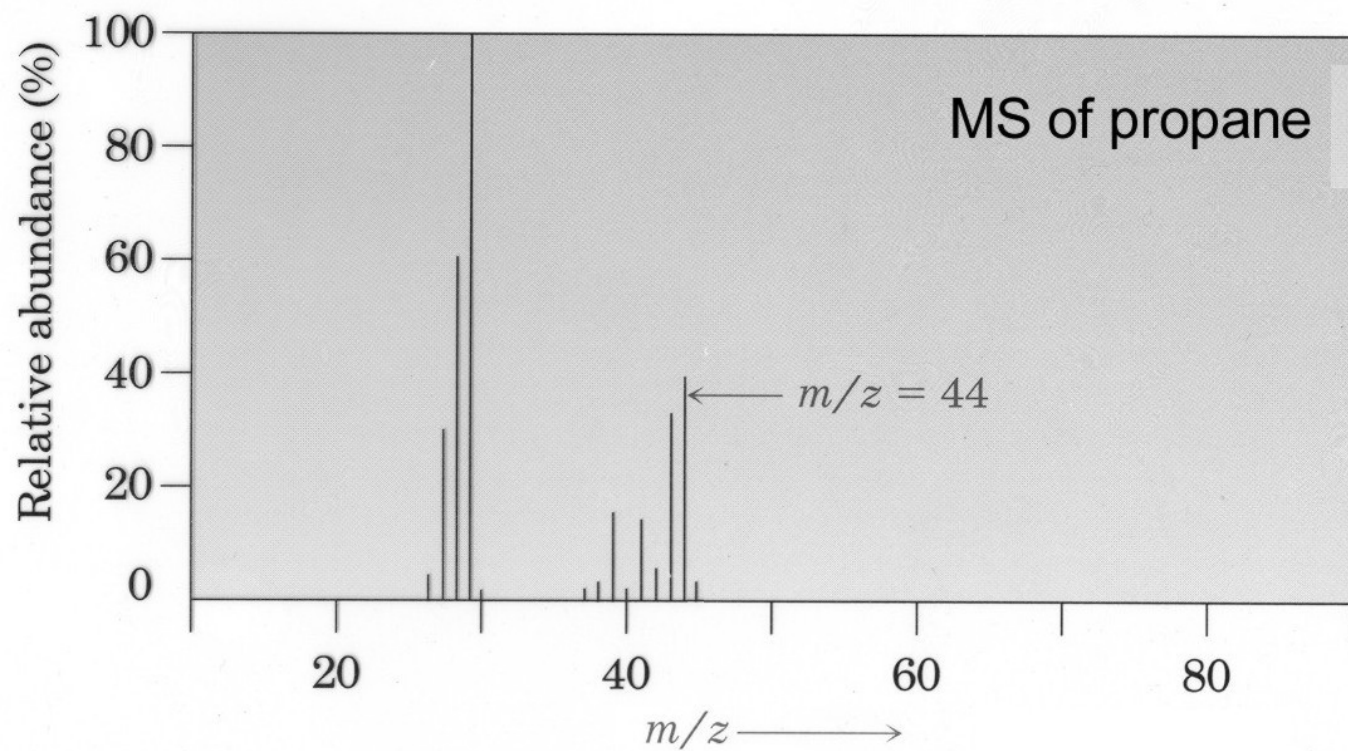
*e.g.*



Where does fragmentation occur?

$m/z$	Relative abundance	fragment
58		

↑  
Can't predict



Each line is from a different ion

## Isotope effects

Signals observed in MS reflect a

*e.g.* for butane,  $m/z = 58$  is for a molecule with  $^{12}\text{C}$  and  $^1\text{H}$  isotopes.

Replace one of the carbons by  $^{13}\text{C}$ : then  $m/z = 59$ ! i.e., Signal is at  $(M+1)^+$

*N.B.* You cannot use the average atomic mass from the periodic table in calculating  $m/z$  values! You *must* use the mass of the specific isotope:

$^1\text{H}=1$ ;  $^2\text{H}=2$ ;  $^{12}\text{C}=12$ ;  $^{13}\text{C}=13$ ;  $^{14}\text{N}=14$ ;  $^{16}\text{O}=16$ ;  $^{19}\text{F}=19$ , *etc* (whole numbers)

How big is butane's  $(M+1)^+$  peak?

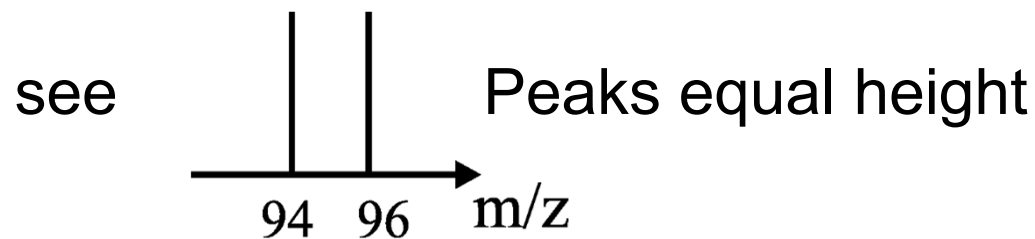
## Abundant isotopes

e.g. bromine:  $^{79}\text{Br}$   $\sim 50\%$  } natural abundance  
 $^{81}\text{Br}$   $\sim 50\%$  }

So  $\text{CH}_3\text{Br}$  will show two  $\text{M}^+$  peaks:

$\text{M}^+$  94 (for  $^{79}\text{Br}$ )

$\text{M}^+$  96 (for  $^{81}\text{Br}$ )

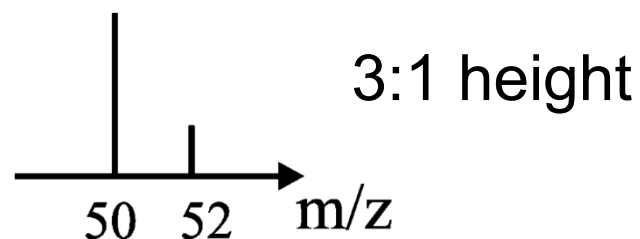


e.g. chlorine:  $^{35}\text{Cl}$   $\sim 75\%$  } natural abundance  
 $^{37}\text{Cl}$   $\sim 25\%$  }

So  $\text{CH}_3\text{Cl}$  will show two  $\text{M}^+$  peaks:

$\text{M}^+$  50 (FOR  $^{35}\text{Cl}$ )

$\text{M}^+$  52 (FOR  $^{37}\text{Cl}$ )



## Mass spec lecture example:

