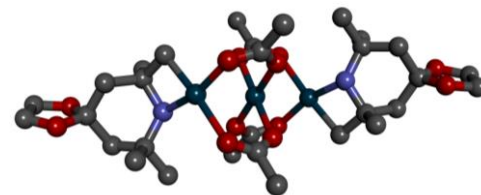
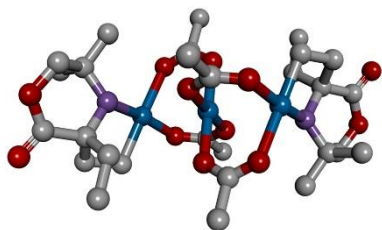


# Organic Chemistry

Dr. Chuan He (何川)



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Department of  
Chemistry



南方科技大学  
SOUTHERN UNIVERSITY OF SCIENCE AND TECHNOLOGY

## ***Chapter 3 Determining organic structures***

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- Introduction
- Mass Spectrometry
- Nuclear Magnetic Resonance
- Infrared Spectra (IR)
- Mass spectra, NMR, and IR combined make quick identification

## Introduction

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In the last chapter, to draw structures realistically, we now need to answer the question: what is realistic? How do we know what structures molecules actually have?

Organic structures can be determined accurately and quickly by *spectroscopy*.

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Organic structures can be determined accurately and quickly by **spectroscopy**.

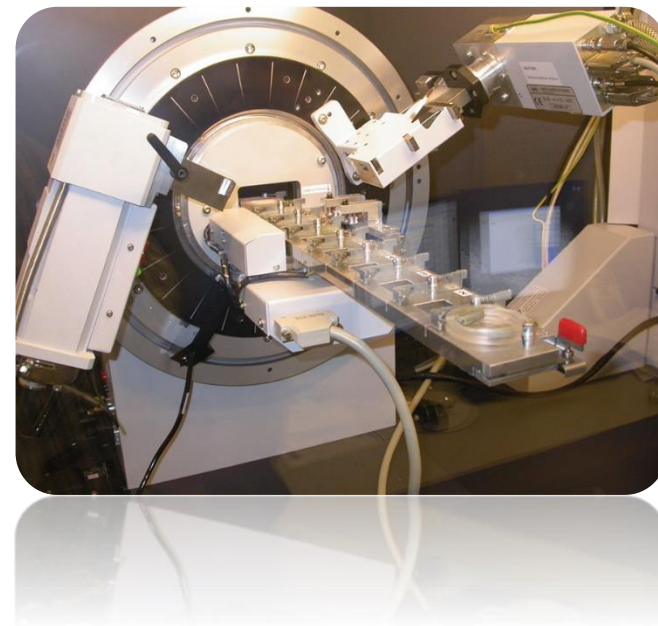
## ● What is spectroscopy?

Rays or waves interact with molecules	Spectroscopy	Tells us about
X-rays are scattered by atoms	Measures the scattering pattern	Bond lengths and angles
Radio waves make nuclei resonate	Plots charts of resonant frequencies	The symmetry and connectivity of the hydrocarbon skeleton
Infrared waves make bonds vibrate	Plots charts of absorption	The functional groups in the molecule

- **Mass Spectrometry** (to determine mass of the molecule and atomic composition)
- **Nuclear Magnetic Resonance** (NMR) spectroscopy (to determine symmetry, branching, and connectivity in the molecule)
- **Infrared Spectroscopy** (to determine the functional groups in the molecule).

## X-ray is the final appeal

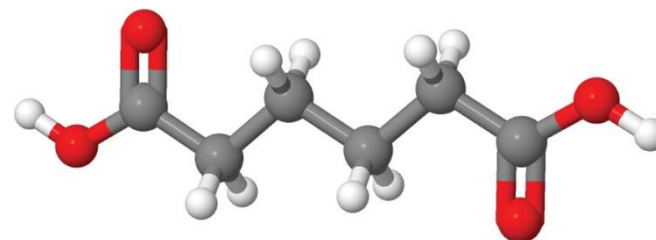
We suggested you draw saturated carbon chains as zig-zags. The X-ray crystal structure of the chain diacid is clearly the zig-zag, the planar carboxylic acid groups, and even the hydrogen atoms coming towards you and going away from you.



hexanedioic acid



shape of hexanedioic acid



# Introduction

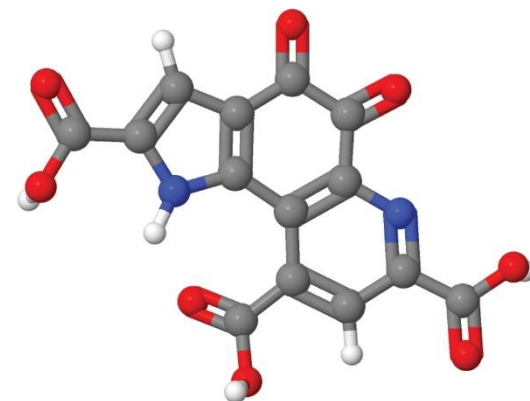
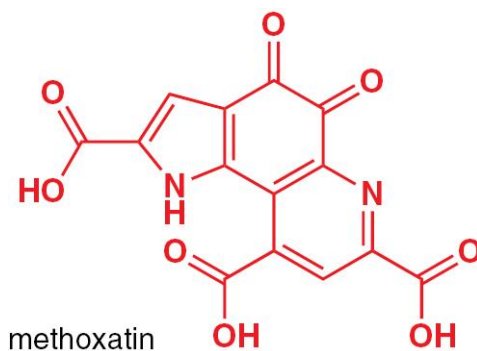
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## X-ray is the final appeal

X-ray crystal structures are determined by allowing a sample of a crystalline compound to diffract X-rays. From the resulting diffraction pattern, it is possible to deduce the precise spatial arrangement of the atoms in the molecule.

It can solve the structures of new *unknown compounds*.

In 1979 it was found that the bacteria use a coenzyme, given the trivial name 'methoxatin', to oxidize methane to methanol.



## X-ray crystallography has its limitations

If X-ray crystallography is so powerful, why do we bother with other methods?

- X-ray crystallography works by the scattering of X-rays from electrons and **requires crystalline solids**.
- X-ray crystallography is a science in its own right, requiring **specialized skills**, and a structure determination **can take a long time**. By contrast a modern NMR machine with a robot attachment can run more than 100 spectra overnight. We normally use NMR routinely and reserve X-rays for difficult unknown structures and for determining the detailed shape of important molecules.

## *Introduction*

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Put yourself in these situations, regularly encountered by professional chemists:

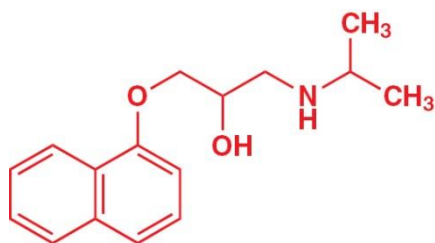
- You notice an unexpected product from a chemical reaction.
- You discover a previously unknown compound in a plant extract.
- You detect a suspected food contaminant and need to know what it is.
- You are routinely checking purity during the manufacture of a drug.



# Introduction

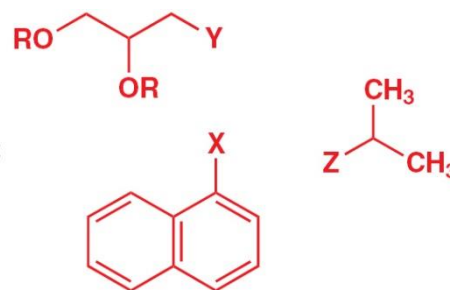
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propranolol  $\text{C}_{16}\text{H}_{21}\text{NO}_2$

fragments of propranolol  
from the NMR spectrum:

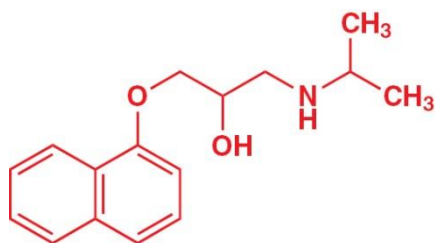


Suppose you are trying to identify the heart drug propranolol. You would first want to know the **molecular weight and atomic composition**, and these would come from a **mass spectrum**. Next you would need the **carbon skeleton**—this would come from **NMR**, which would reveal the three fragments shown above.

# Introduction

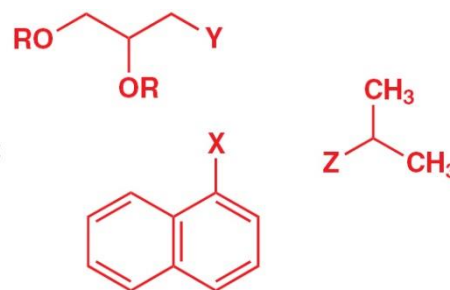
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propranolol  $C_{16}H_{21}NO_2$

fragments of propranolol  
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More information comes from the *infrared spectrum*, which highlights the **functional groups**, and which would show that there is an OH and an NH in the molecule but not other functional groups such as CN or NO<sub>2</sub>.

## Mass spectrometry weighs the molecule

It's not easy to weigh a neutral molecule, and a mass spectrometer works by measuring the mass of a charged ion instead: the charge makes the molecule controllable by an electric field. A mass spectrometer therefore has three basic components:

- something to volatilize and ionize the molecule into a beam of charged particles
- something to focus the beam so that particles of the same mass: charge ratio are separated from all others
- something to detect the particles



# Mass Spectrometry

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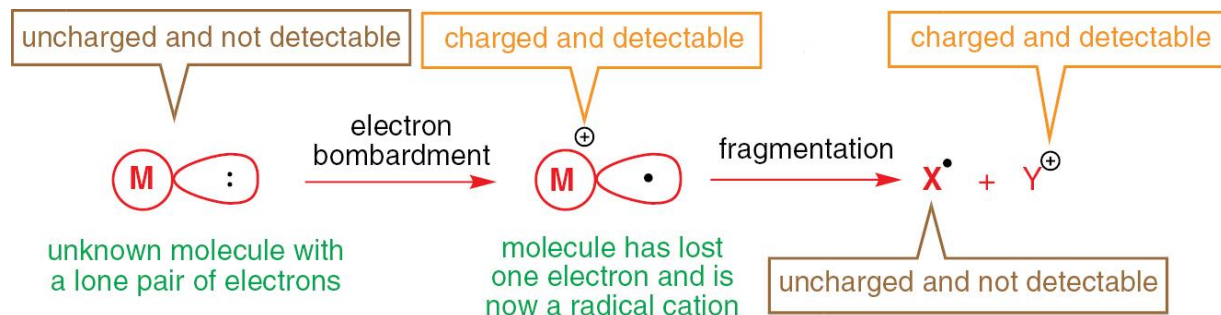


All spectrometers in common use operate in a high vacuum and use one of several methods to convert neutral molecules into cations, the most common being **electron impact**, **chemical ionization**, and **electrospray**.

# Mass Spectrometry

## Mass spectrometry by electron impact (EI)

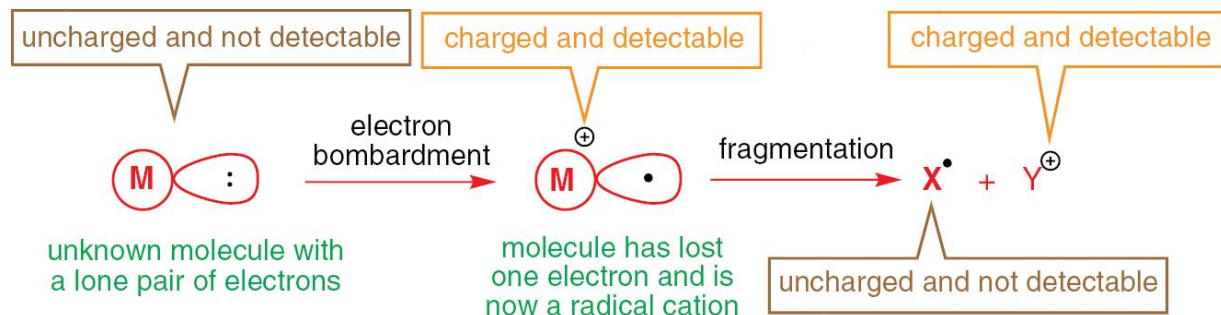
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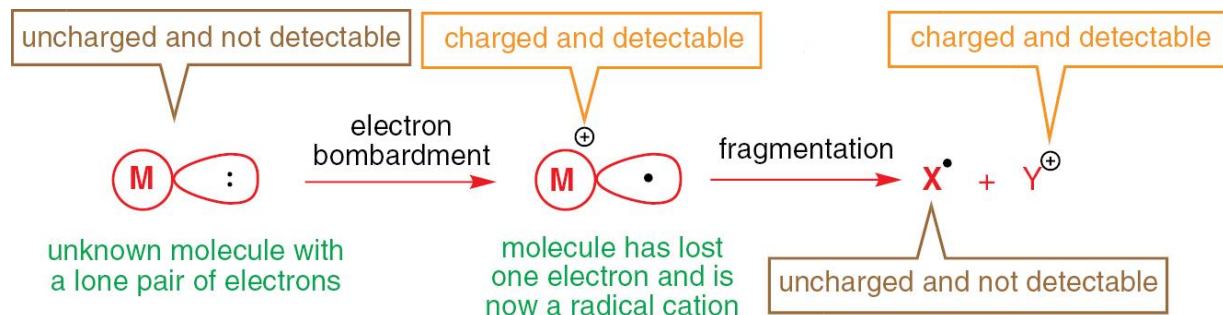


These unstable species are known as **radical cations**, and being charged they are accelerated by an electric field and focused onto the detector, which detects the mass of the ion by how far its path has been deflected by the electric field. Sometimes they fragment before they get there, in which case other ions will also be detected.

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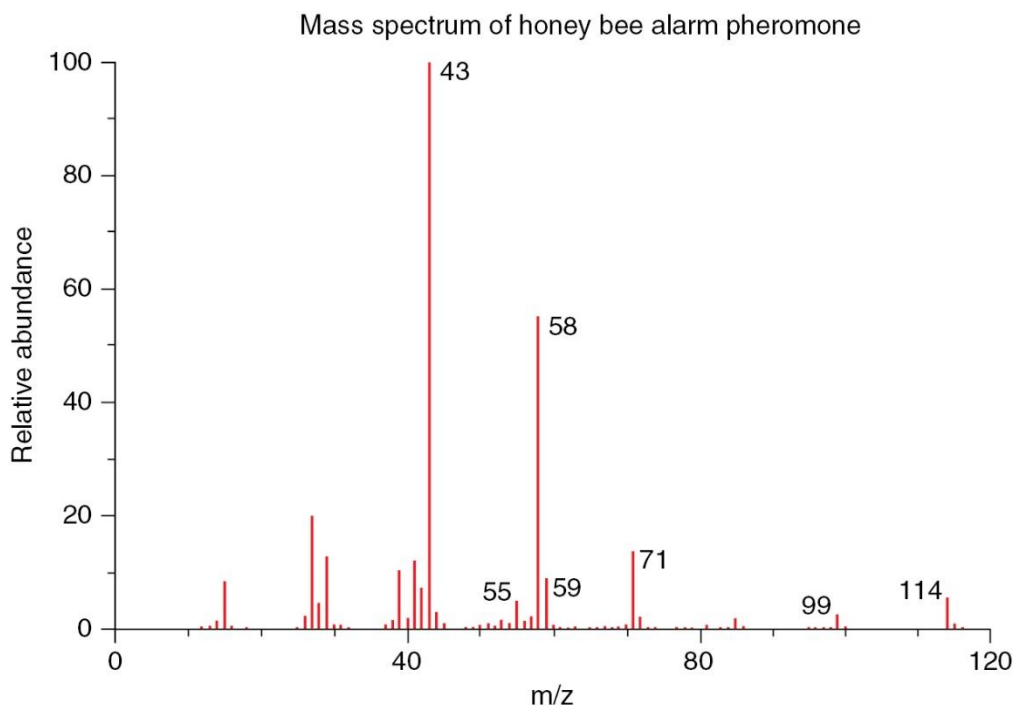
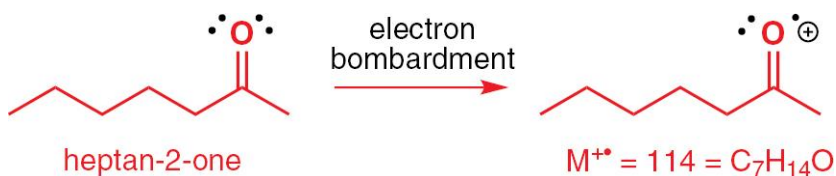


**Radicals** have unpaired electrons. Molecules that carry a negative charge are **anions**; with a positive charge are **cations**.

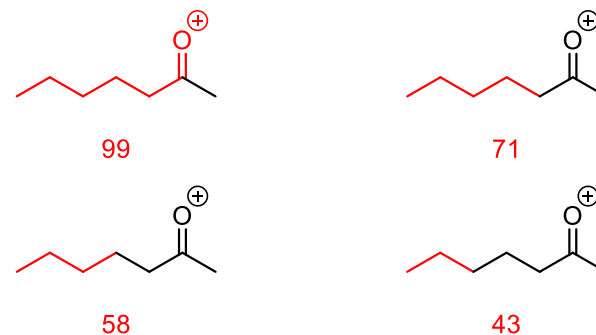
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# Mass Spectrometry

This compound was identified as a pheromone deposited by worker bees



Mass spectrometry is successful even on a microgram scale. The spectrum you see here indicates that the molecule has a mass of 114 because that is the highest mass observed in the spectrum.





## Mass spectrometry by chemical ionization

A problem with EI mass spectrometry is that, for fragile molecules, the energy of the bombarding electron can be sufficient to cause it to fragment completely, losing all trace of the molecular ion. This can be achieved using any of a number of other techniques, of which the most common are **chemical ionization (CI)** and **electrospray (ES)**.

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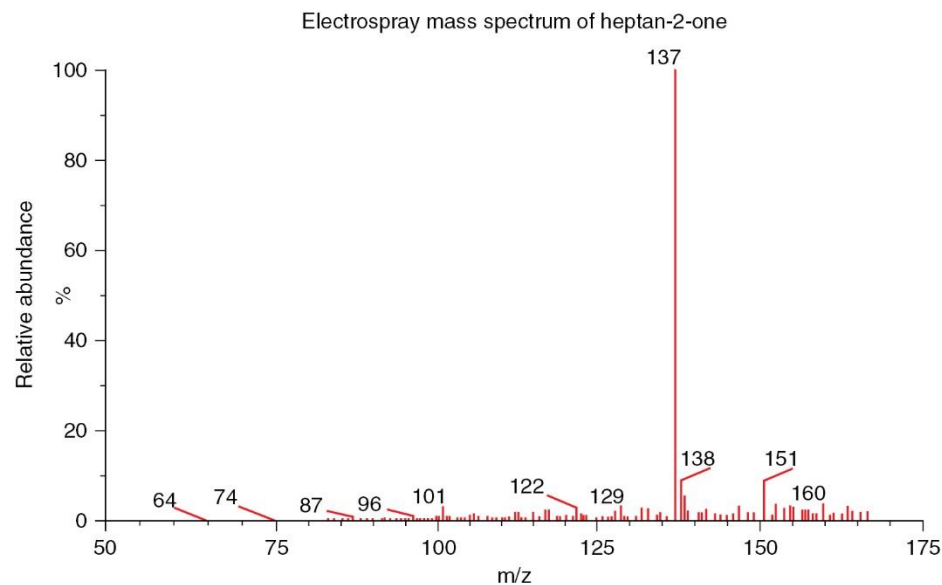
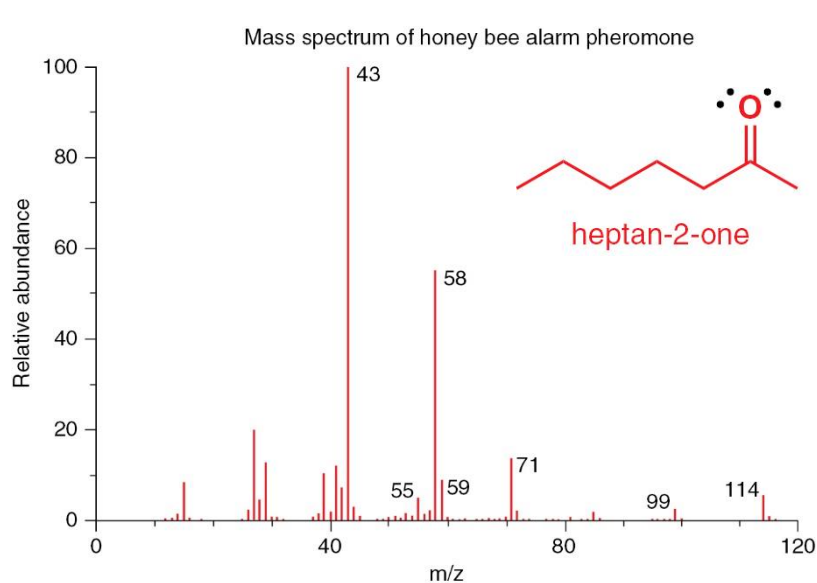
Chemical ionization is achieved by **mixing a gas such as ammonia with the substrate** in the spectrometer. Bombardment of  $\text{NH}_3$  with electrons leads to formation of some  **$\text{NH}_4^+$**  by proton transfer, and reaction of this ion with the substrate makes a charged complex.

The masses observed by chemical ionization spectroscopy carried out in this way are usually  $M + 1$  or  $M + 18$  (the mass of  $\text{NH}_4^+$ ) relative to the mass of the substrate.

# Mass Spectrometry

## Mass spectrometry by electrospray

With **electrospray** mass spectroscopy, an aerosol of the substrate is ionized, and ionization in the presence of **sodium ions** means that masses of  $M + 1$  and  $M + 23$  are often seen.



Notice how a single molecular ion is clearly visible this time, but that it has a mass of 137, which is 23 more than the mass of 114 (in other words, this is the mass of  $M + \text{Na}^+$ ).

# Mass Spectrometry

---

## Mass spectrometry detects isotopes

Most elements can exist as more than one isotope. Usually, one isotope accounts for the vast majority of the atoms of an element. But for some elements, atoms of several isotopes make up a significant proportion of the total in a sample.

**Chlorine** is normally a 3:1 mixture of  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  (the averaged relative atomic mass of 35.5 for chlorine), while **bromine** is an almost 1:1 mixture of  $^{79}\text{Br}$  and  $^{81}\text{Br}$  (the average mass of 80 for bromine).

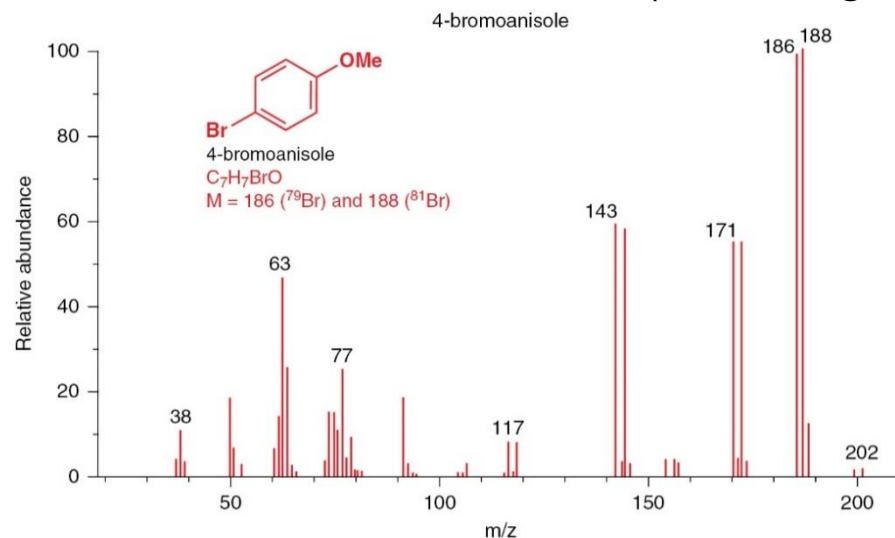
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Having two molecular ions of equal intensity separated by 2 mass units is indicative of **bromine** in a molecule.



Because mass spectrometry weighs individual molecules, there is no averaging: instead it detects the true weight of each molecule, whatever isotope it contains.

# Mass Spectrometry

---

## Mass spectrometry detects isotopes

The mass spectrum of a **chlorine**-containing molecule is likewise easy to identify from two peaks separated by two mass units, but this time in a ratio of 3:1, arising from the 3:1 isotopic ratio of  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ .

What happens with more than one Br or Cl? Here's an example: the painkiller diclofenac.

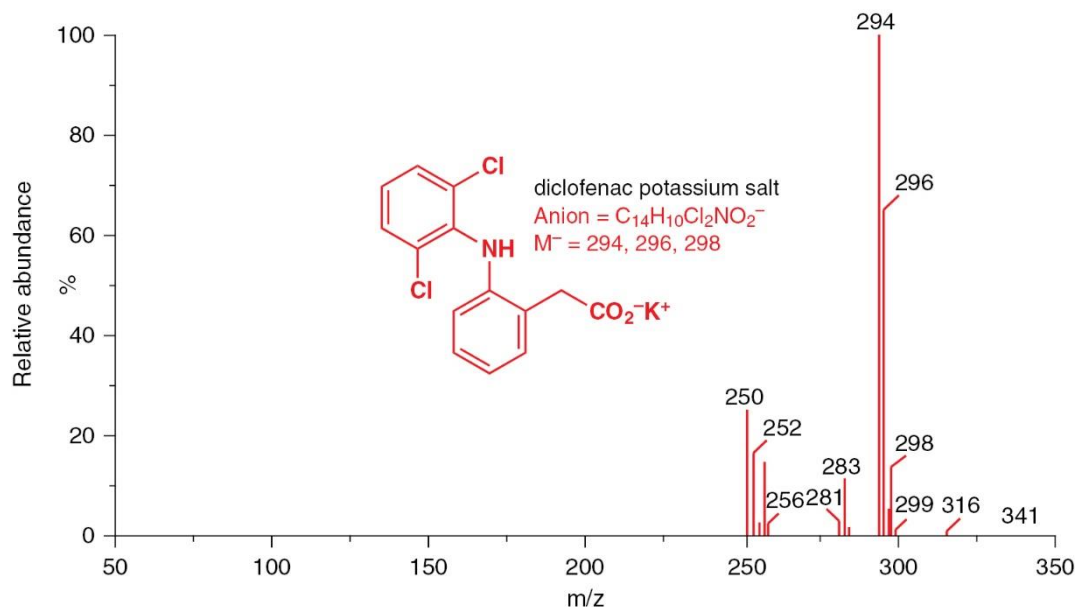
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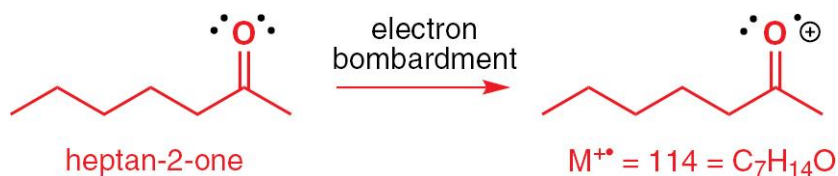
What happens with more than one Br or Cl? Here's an example: the painkiller diclofenac.

The ES spectrum shows the mass of the carboxylate anion as three peaks, at 294, 296, and 298. The relative size of the peaks can be worked out from the 75% probability that each Cl atom will be  $^{35}\text{Cl}$  and the 25% probability it will be  $^{37}\text{Cl}$ . The ratios are therefore  $(3/4 \times 3/4) : (3/4 \times 1/4 + 1/4 \times 3/4) : (1/4 \times 1/4)$  or 9 : 6 : 1.

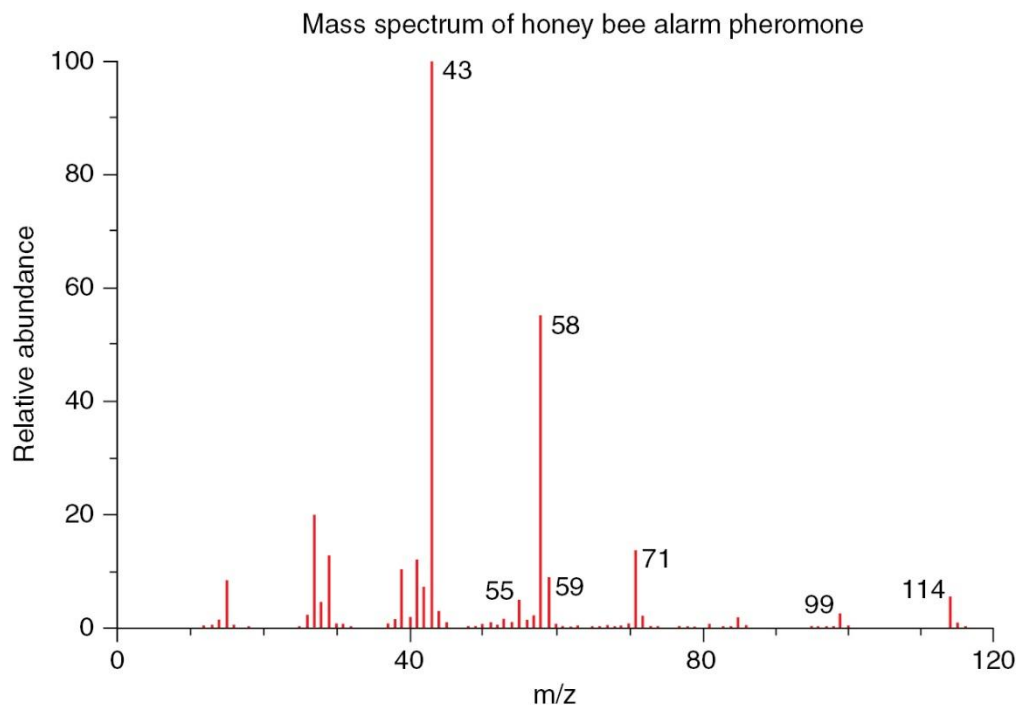


# Mass Spectrometry

## Atomic composition can be determined by high-resolution mass spectrometry



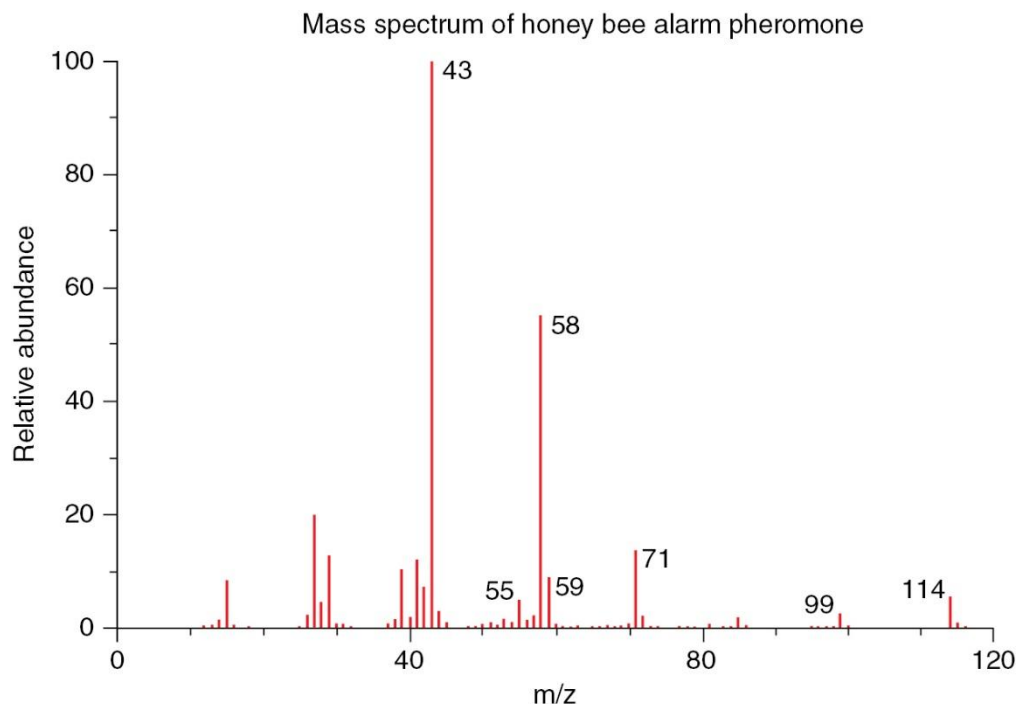
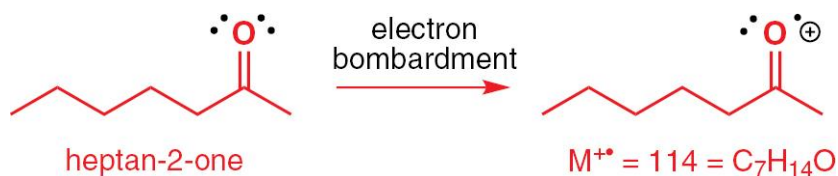
The bee pheromone ketone had MW 114. When we revealed it was  $C_7H_{14}O$ , we had to use other information to infer this, because 114 could also be many other things, such as  $C_8H_{18}$  or  $C_6H_{10}O_2$  or  $C_6H_{14}N_2$ .





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However, these different atomic compositions for the same molecular weight can be distinguished if we know the **exact molecular weight**, since individual isotopes have non-integral masses.

# Mass Spectrometry

## Atomic composition can be determined by high-resolution mass spectrometry

The table below gives these masses to five decimal places, which is the sort of accuracy you need for meaningful results. Such accurate mass measurements are obtained by a technique called *high-resolution mass spectrometry*.

Exact masses of common elements

Element	Isotope	Mass number	Exact mass
hydrogen	$^1\text{H}$	1	1.00783
carbon	$^{12}\text{C}$	12	12.00000
carbon	$^{13}\text{C}$	13	13.00335
nitrogen	$^{14}\text{N}$	14	14.00307
oxygen	$^{16}\text{O}$	16	15.99492
fluorine	$^{19}\text{F}$	19	18.99840
phosphorus	$^{31}\text{P}$	31	30.97376
sulfur	$^{32}\text{S}$	32	31.97207
chlorine	$^{35}\text{Cl}$	35	34.96886
chlorine	$^{37}\text{Cl}$	37	36.96590
bromine	$^{79}\text{Br}$	79	78.91835
bromine	$^{81}\text{Br}$	81	80.91635

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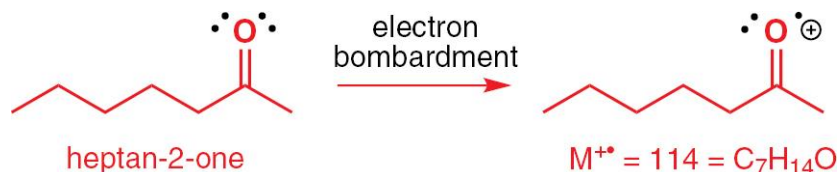
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chlorine	$^{37}\text{Cl}$	37	36.96590
bromine	$^{79}\text{Br}$	79	78.91835
bromine	$^{81}\text{Br}$	81	80.91635

The reason that exact masses are not integers lies in the slight mass difference between a **proton** ( $1.67262 \times 10^{-27}$  kg) and a **neutron** ( $1.67493 \times 10^{-27}$  kg), and in the fact that **electrons** have mass ( $9.10956 \times 10^{-31}$  kg).

# Mass Spectrometry

## Atomic composition can be determined by high-resolution mass spectrometry



The accurate mass turns out to be **114.1039**. The table below compares possible atomic compositions for an approximate MW 114, and the result is conclusive.

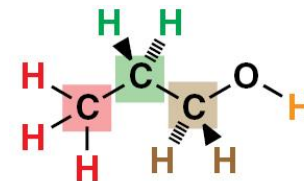
Exact mass determination for the bee alarm pheromone

Composition	Calculated $M^{+}$	Observed $M^{+}$	Error in ppm
$C_6H_{10}O_2$	114.068075	114.1039	358
$C_6H_{14}N_2$	114.115693	114.1039	118
$C_7H_{14}O$	<b>114.104457</b>	<b>114.1039</b>	5
$C_8H_{18}$	114.140844	114.1039	369

The exact masses to three places of decimals fit the observed exact mass only for the composition  $C_7H_{14}O$ .

# Nuclear Magnetic Resonance

NMR (actually  $^1\text{H}$ , or proton, NMR) can easily distinguish between these different sorts of hydrogens by detecting the environment the hydrogen's nucleus finds itself in. Likewise, carbon (more precisely  $^{13}\text{C}$  NMR) can easily distinguish between the three different carbon atoms.

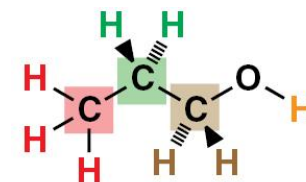


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NMR is extremely versatile: it can even scan living human brains but the principle is still the same: being able to detect nuclei in different environments.



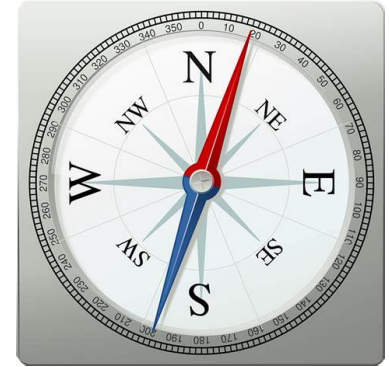
When NMR is used medically it is usually called **Magnetic Resonance Imaging** (MRI) for fear of alarming patients wary of all things nuclear.



# Nuclear Magnetic Resonance

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Some atomic nuclei act like tiny compass needles when placed in a magnetic field and have different energy levels. Just as a compass needle has to be made of a **magnetic material** to feel the effect of the earth's magnetism.

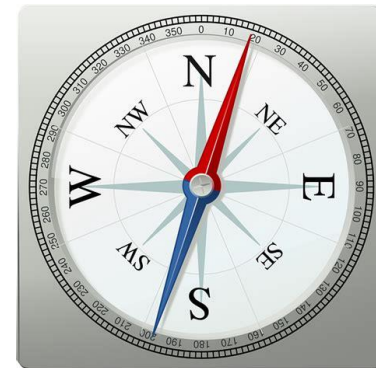


Many (including 'normal' carbon-12,  $^{12}\text{C}$ ) do not interact with a magnetic field at all and cannot be observed in an NMR machine. But, importantly, the minor carbon isotope  $^{13}\text{C}$  does display magnetic properties, as does  $^1\text{H}$ , the most abundant atomic nucleus on earth.

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When a  $^{13}\text{C}$  or  $^1\text{H}$  atom finds itself in a magnetic field, it has two available energy states: it can either align itself **with the field**, which would be the lowest energy state, or **against the field**, which is higher in energy.



# Nuclear Magnetic Resonance

---

The property of a nucleus that allows magnetic interactions is **spin**. the nucleus can point in one direction—it is the axis of the spin that is **aligned with** or **against** the field.

For a nucleus in a magnetic field, the difference in energy between the nuclear spin aligned with and against the applied field depends on:

- **how strong the magnetic field is**
- **the magnetic properties of the nucleus itself**

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The energy difference between the nuclear spin being aligned with the magnetic field and against it is really **very small**—so small that we need a very, very strong magnetic field to see any difference at all.

## ***NMR uses a strong magnetic field***

NMR machines contain very strong electromagnets. The earth's magnetic field has a field strength of between 30 and 60 microtesla. A typical magnet used in an NMR machine has a field strength of between 2 and 10 tesla, some  $10^5$  times stronger than the earth's field.

# Nuclear Magnetic Resonance

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## ***NMR also uses radio waves***

Since the amount of energy needed is so small, it can be provided by **low-energy electromagnetic radiation of radio-wave frequency**. Radio waves flip the nucleus from the lower energy state to the higher state. Turn off the radio pulse and the nucleus returns to the lower energy state. When it does so, the energy comes out again, and this (a tiny pulse of radio frequency electromagnetic radiation) is what we detect.

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**Radio waves are very, very low in energy**. You may know that the energy associated with electromagnetic radiation is related to its wavelength  $\lambda$  by the formula:  $E = hc/\lambda$ . Radio waves, whose **wavelengths are measured in metres**, are millions of times less energetic than rays of visible light (from 380 nm (violet) to 750 nm (red)).

# Nuclear Magnetic Resonance

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***We can now sum up how an NMR machine works:***

1. The sample of the unknown compound is dissolved in a suitable solvent, placed in a narrow tube, and put inside a very strong electromagnet. The tube is spun very fast by a stream of air. Inside the magnetic field, any atomic nuclei with a nuclear spin now possess different energy levels, the exact number of different energy levels depending on the value of the nuclear spin.

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2. The sample is irradiated with a short pulse of radiofrequency energy. This disturbs the equilibrium balance between the two energy levels: some nuclei absorb the energy and are promoted to a higher energy level.

# Nuclear Magnetic Resonance

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***We can now sum up how an NMR machine works:***

1. The sample of the unknown compound is dissolved in a suitable solvent, placed in a narrow tube, and put inside a very strong electromagnet. The tube is spun very fast by a stream of air. Inside the magnetic field, any atomic nuclei with a nuclear spin now possess different energy levels, the exact number of different energy levels depending on the value of the nuclear spin.
2. The sample is irradiated with a short pulse of radiofrequency energy. This disturbs the equilibrium balance between the two energy levels: some nuclei absorb the energy and are promoted to a higher energy level.
3. When the pulse finishes, the radiation given out as the nuclei fall back down to the lower energy level is detected.

# Nuclear Magnetic Resonance

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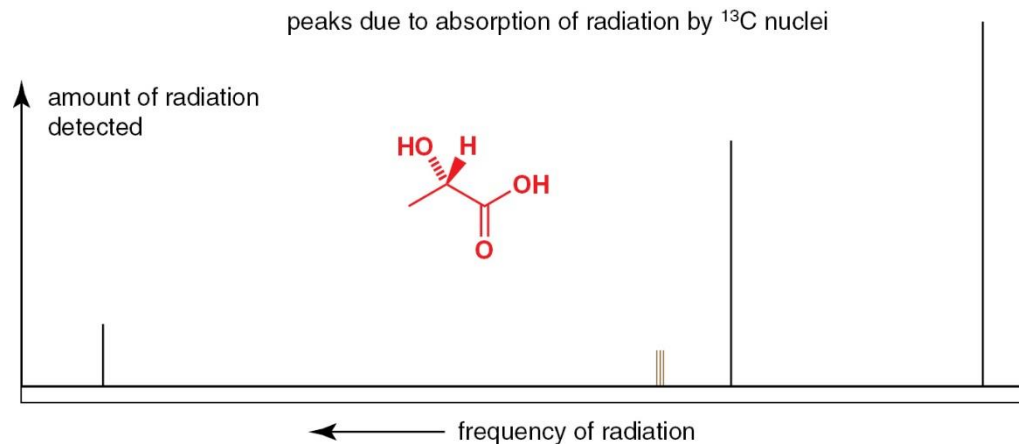
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3. When the pulse finishes, the radiation given out as the nuclei fall back down to the lower energy level is detected.
4. After lots of computation, the results are displayed in the form of intensity (i.e. number of absorptions) against frequency.



# Nuclear Magnetic Resonance

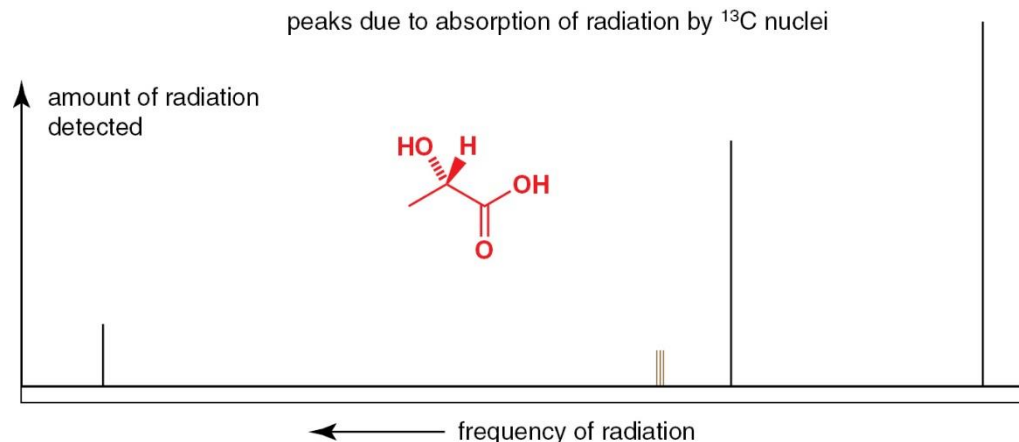
Why do chemically distinct nuclei absorb energy at different frequencies?



Each peak represents a different kind of carbon atom: each one absorbs energy at a different frequency. **But why should carbon atoms be 'different'?**

# Nuclear Magnetic Resonance

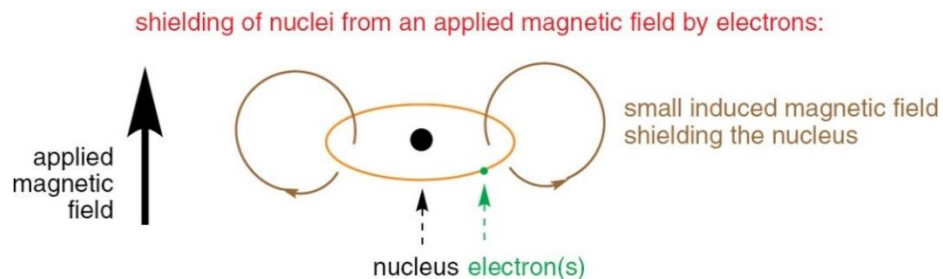
## Why do chemically distinct nuclei absorb energy at different frequencies?



Each peak represents a different kind of carbon atom: each one absorbs energy at a different frequency. **But why should carbon atoms be 'different'?**

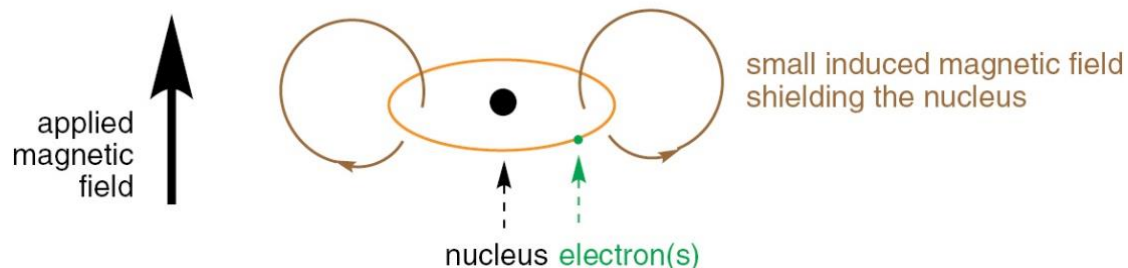
This means that the energy jump from 'nucleus-aligned-with' to 'nucleus-aligned-against' the applied magnetic field must be **different** for each type of carbon atom.

Each nucleus is surrounded by **electrons**, and in a magnetic field these will set up a tiny electric current. This current will set up its own magnetic, which will **oppose the magnetic field** that we apply.



# Nuclear Magnetic Resonance

shielding of nuclei from an applied magnetic field by electrons:



The electrons are said to **shield** the nucleus from the external magnetic field.

Changes in the distribution of electrons around a nucleus affect:

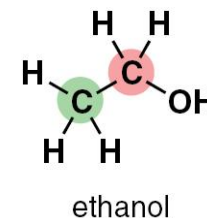
- the local magnetic field that the nucleus experiences
- the frequency at which the nucleus resonates
- the chemistry of the molecule at that atom

This variation in frequency is known as the **chemical shift**. Its symbol is  $\delta$ .

# Nuclear Magnetic Resonance

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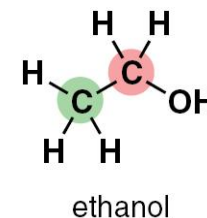
Ethanol, its **red carbon** attached to the OH group will have a smaller share of the electrons around it compared to the green carbon since the oxygen atom is **more electronegative** and pulls electrons towards it, away from the **red carbon** atom.



The magnetic field that the red carbon nucleus feels will therefore be slightly greater than that felt by the green carbon, since the **red carbon** is **less shielded**—in other words it is **deshielded**, or it is more ‘exposed’ to the field as it has lost some of its electronic shielding.

# Nuclear Magnetic Resonance

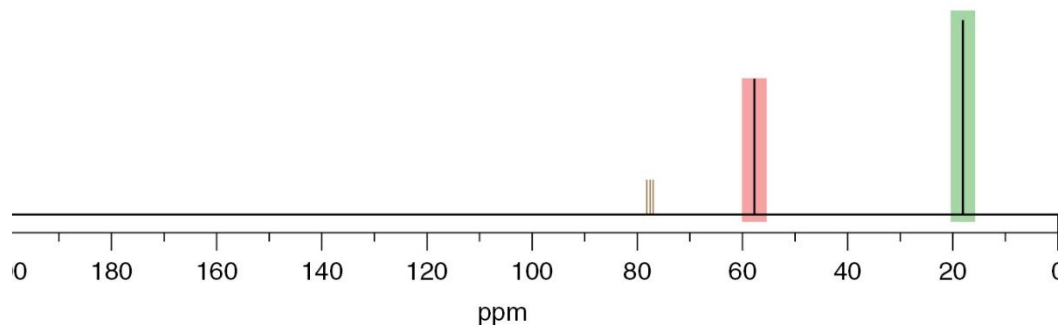
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So there will be a greater energy difference between the two alignments of its nucleus. The greater the energy difference, the higher the resonant frequency.

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



# ***Nuclear Magnetic Resonance***

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## **The chemical shift scale**

The scale of a real NMR spectrum does not appear to be in magnetic field units, nor in frequency, nor yet even energy, units, but in 'parts per million' (ppm).

The exact frequency at which the nucleus resonates depends on the external applied magnetic field.

# Nuclear Magnetic Resonance

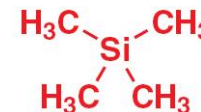
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## The reference sample—tetramethylsilane, TMS



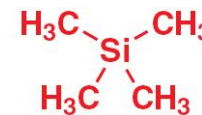
tetramethylsilane, TMS

The four carbon atoms attached to silicon are all equivalent and, because silicon is more electropositive than carbon, they are **fairly electron-rich** (or **shielded**), which means they resonate at a frequency a little less than that of most organic compounds. This is useful because it means our reference sample is not bang in the middle of our spectrum!

# Nuclear Magnetic Resonance

---

## The reference sample—tetramethylsilane, TMS



tetramethylsilane, TMS

Silicon and oxygen have opposite effects on an adjacent carbon atom: electropositive silicon shields; electronegative oxygen deshields.

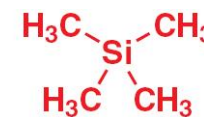
Electronegativities: Si: 1.8; C: 2.5;  
O: 3.5.



# Nuclear Magnetic Resonance

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## The reference sample—tetramethylsilane, TMS



tetramethylsilane, TMS

The chemical shift,  $\delta$ , in parts per million (ppm) of a given nucleus in our sample is defined in terms of the resonance frequency as:

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

Silicon and oxygen have opposite effects on an adjacent carbon atom: electropositive silicon shields; electronegative oxygen deshields.

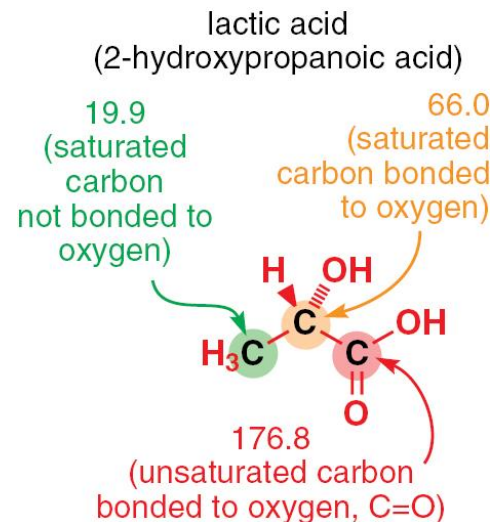
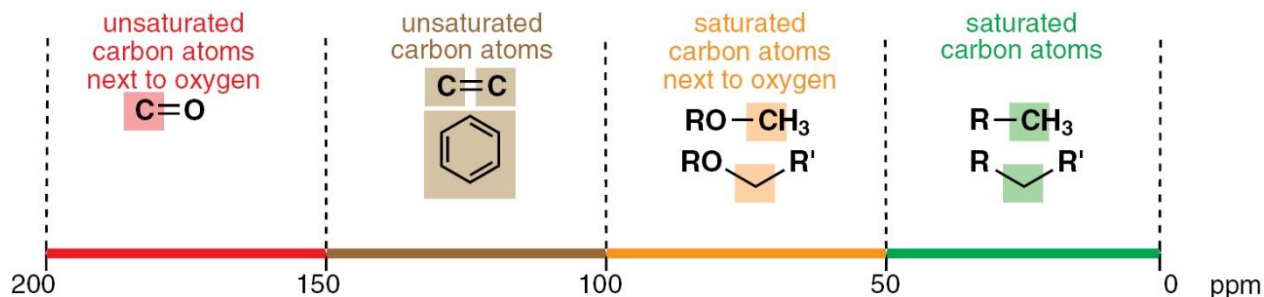
Electronegativities: Si: 1.8; C: 2.5; O: 3.5.

No matter what the operating frequency (i.e. strength of the magnet) of the NMR machine, the signals in a given sample will always occur at the same chemical shifts. Notice that by definition TMS itself resonates at 0 ppm.

# Nuclear Magnetic Resonance

## Regions of the $^{13}\text{C}$ NMR spectrum

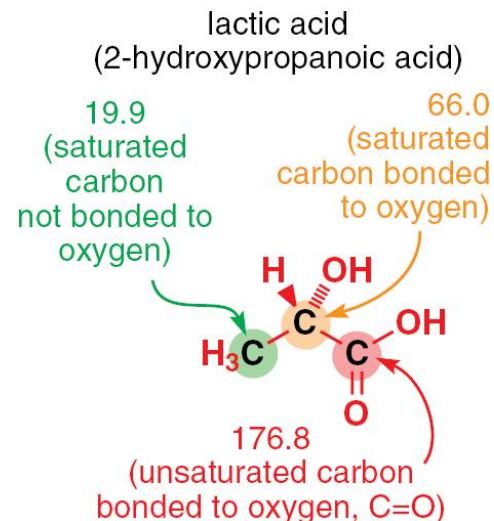
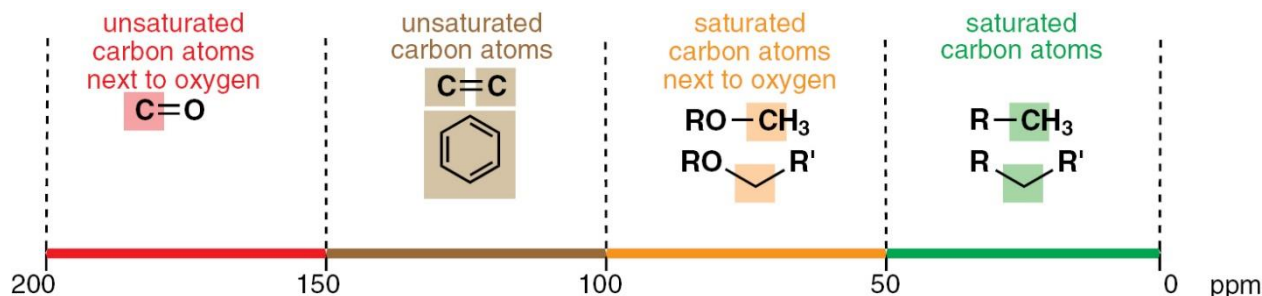
All  $^{13}\text{C}$  spectra can be divided into **four major regions**:



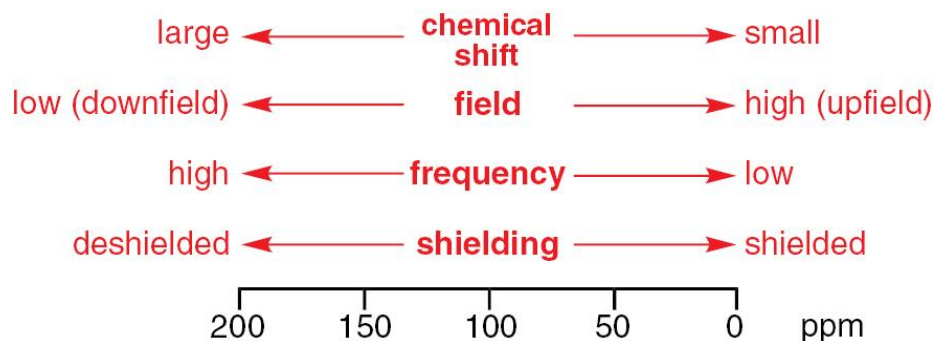
# Nuclear Magnetic Resonance

## Regions of the $^{13}\text{C}$ NMR spectrum

All  $^{13}\text{C}$  spectra can be divided into **four major regions**:



## Different ways of describing chemical shift

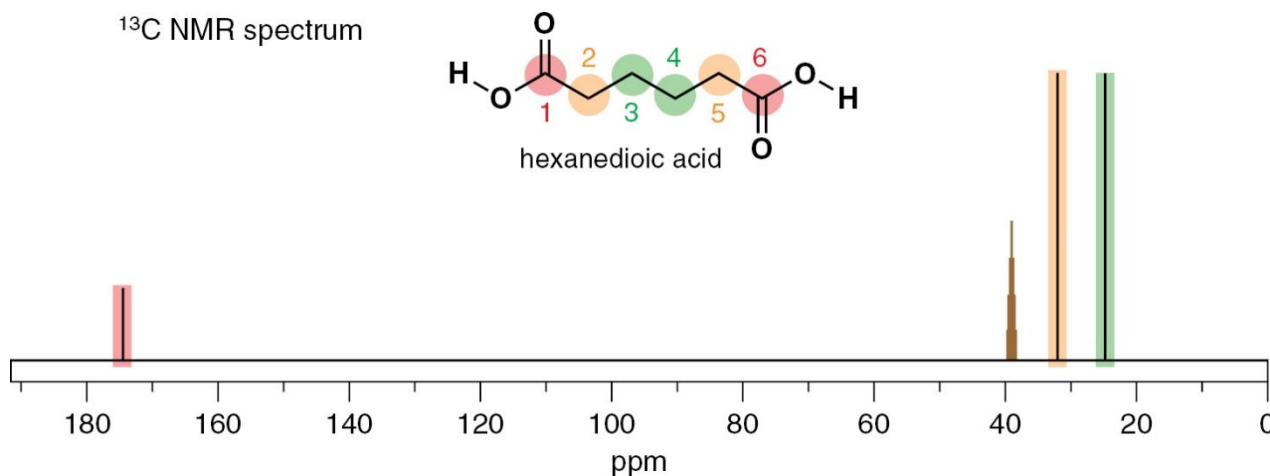


Unsaturated carbon atoms are more deshielded than saturated ones because a  $\pi$  bond has a nodal plane, i.e. a plane with no electron density in it. Electrons in  $\pi$  bonds are less efficient at shielding the nucleus than electrons in  $\sigma$  bonds.

# Nuclear Magnetic Resonance

## A guided tour of the $^{13}\text{C}$ NMR spectra of some simple molecules

The NMR spectrum of hexanedioic acid. Because of the **symmetry** of the molecule, the two carboxylic acids are identical and give one peak at 174.2 ppm. By the same token C2 and C5 are identical, and C3 and C4 are identical.

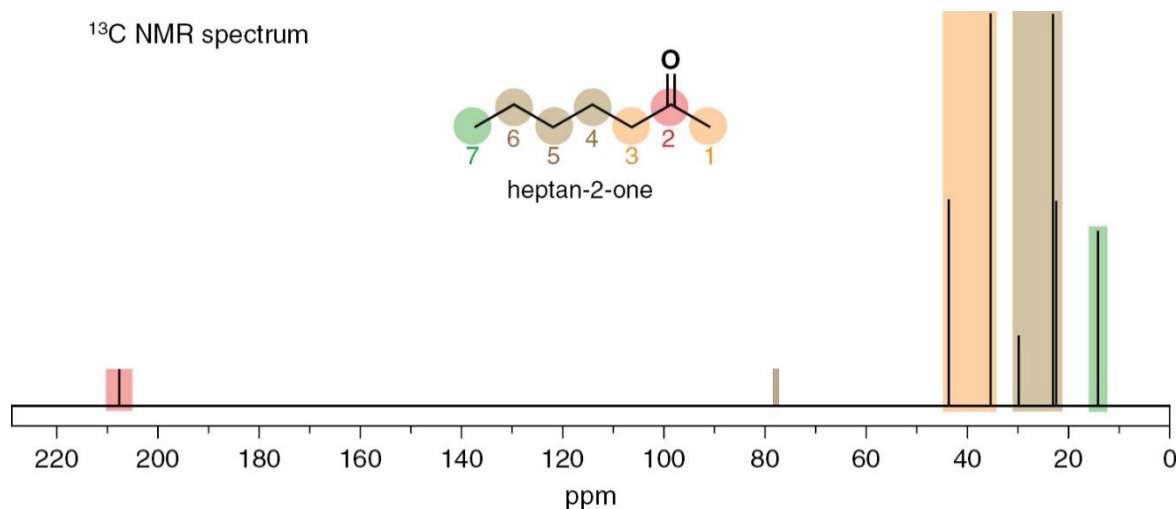


The carbons next to the electron-withdrawing  $\text{CO}_2\text{H}$  group will be more deshielded than the others. So we assign C2/C5 to the peak at 33.2 ppm and C3/C4 to 24.0 ppm.

# Nuclear Magnetic Resonance

## A guided tour of the $^{13}\text{C}$ NMR spectra of some simple molecules

Heptan-2-one has no symmetry so all its seven carbon atoms are different. The carbonyl group is easy to identify (208.8 ppm) but the rest are more difficult.



The two carbon atoms next to the carbonyl group come at lowest field, while C7 is at highest field (13.9 ppm). It is important that there is the right number of signals at about the right chemical shift.

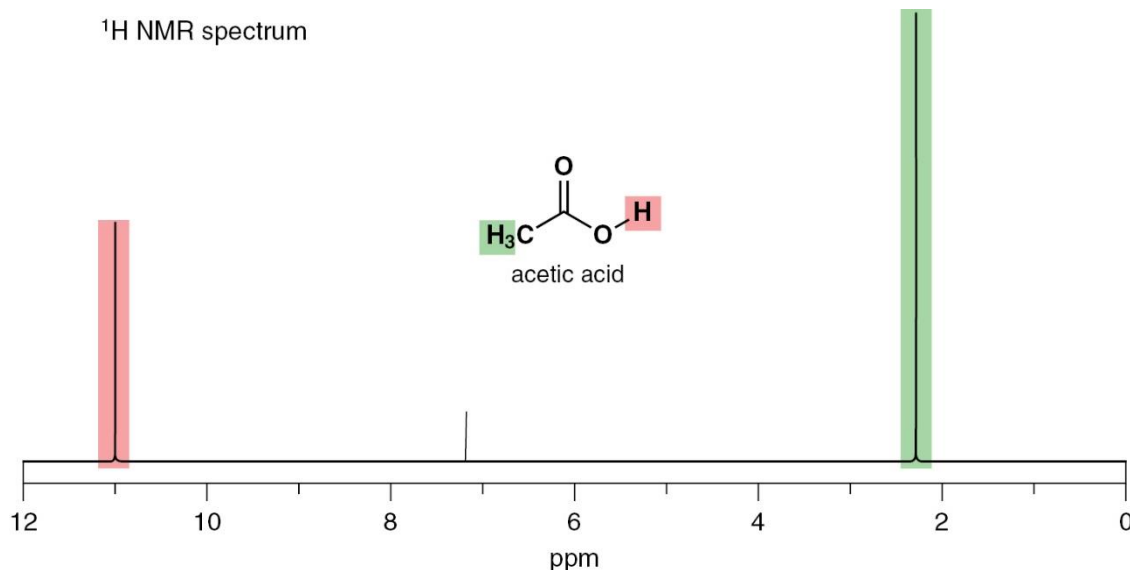
# Nuclear Magnetic Resonance

## The $^1\text{H}$ NMR spectrum

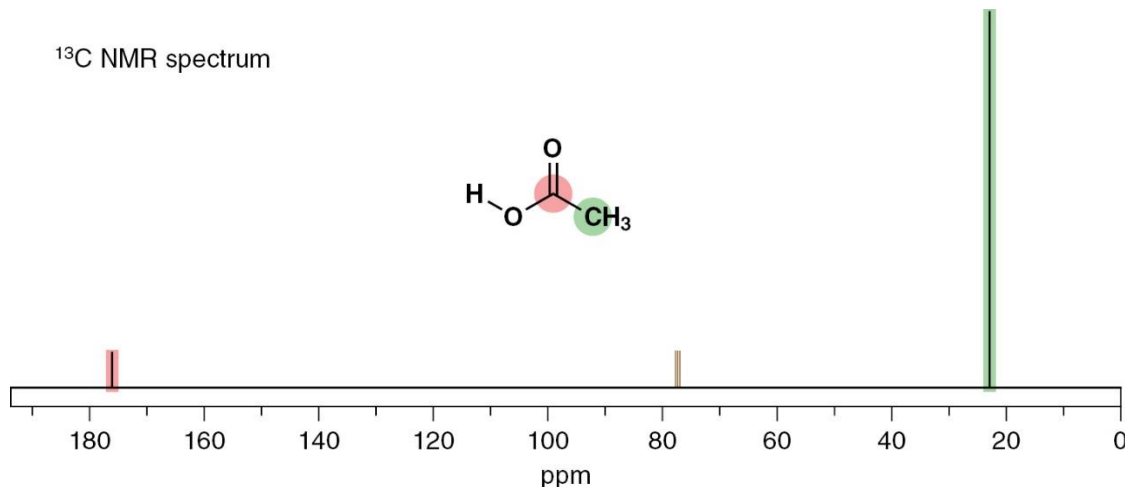
$^1\text{H}$  NMR spectra have many similarities with  $^{13}\text{C}$  NMR spectra: the scale runs from right to left and the zero point is given by the same reference compound  $\text{Me}_4\text{Si}$ .

However, as you immediately see in the spectrum above, the scale is much smaller, ranging over only about 10 ppm instead of the 200 ppm needed for carbon.

$^1\text{H}$  NMR spectrum



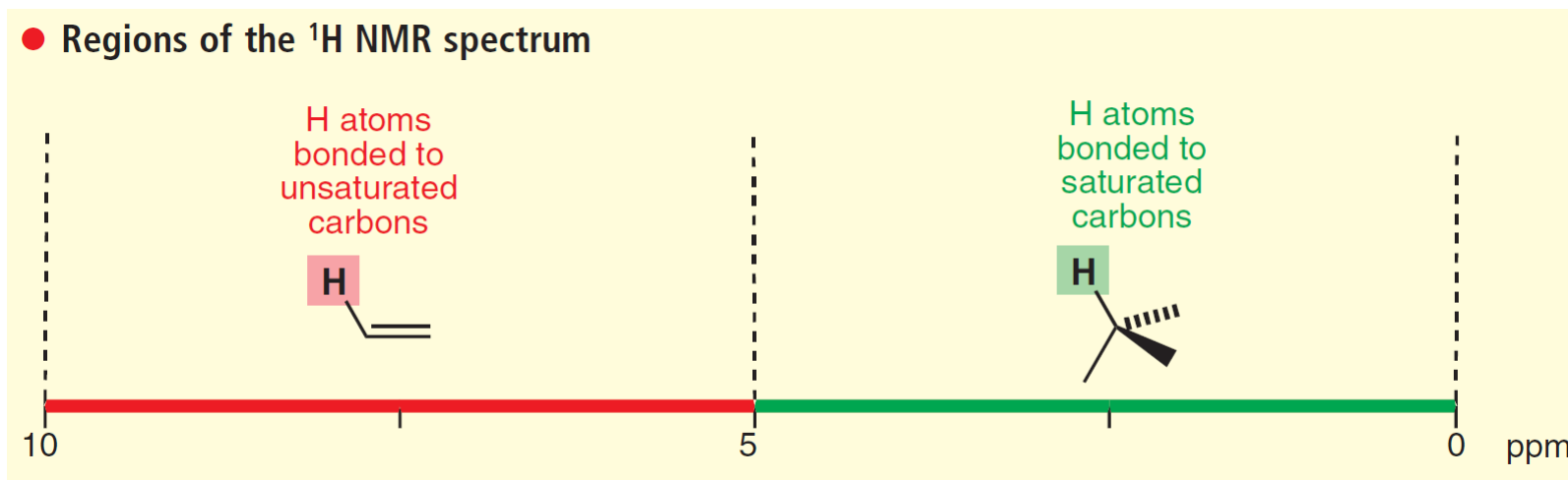
$^{13}\text{C}$  NMR spectrum



# Nuclear Magnetic Resonance

## The $^1\text{H}$ NMR spectrum

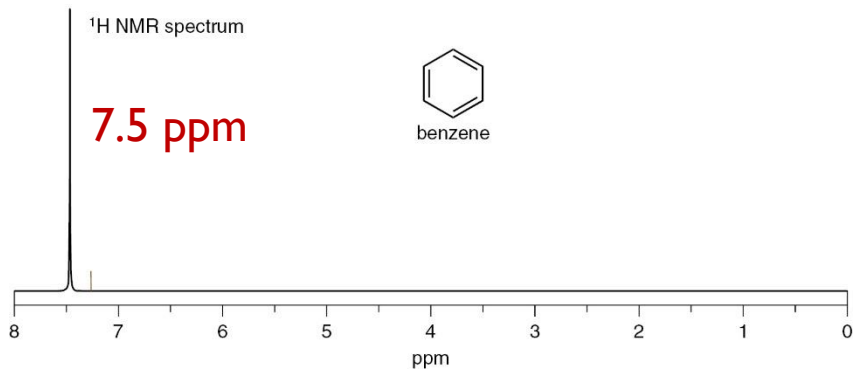
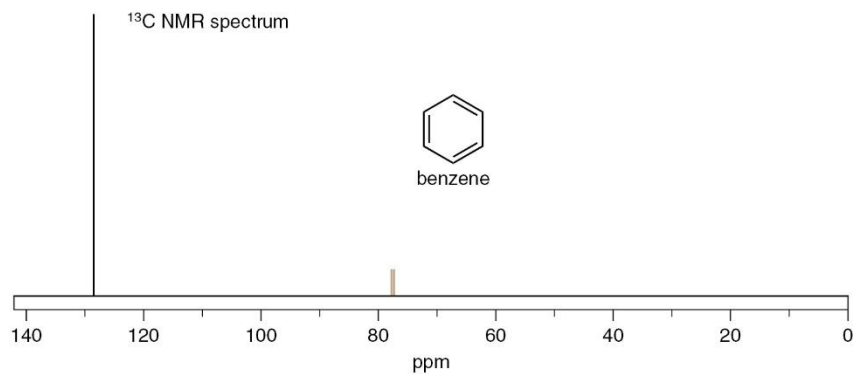
We can also divide up the  $^1\text{H}$  NMR spectrum into regions that parallel the regions of the  $^{13}\text{C}$  NMR spectrum. Hydrogen atoms bonded to saturated carbon atoms appear in the right-hand, more shielded (between 5 and 0 ppm) region of the spectrum, while those bonded to unsaturated carbon atoms (alkenes, arenes, or carbonyl groups primarily) appear in the left-hand, less shielded region between 10 and 5 ppm.



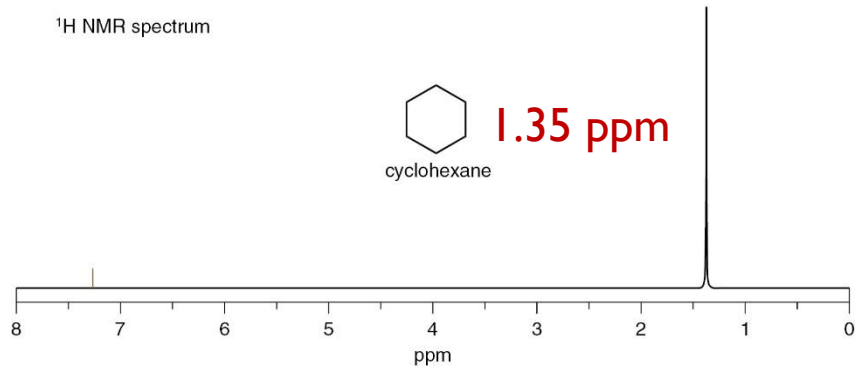
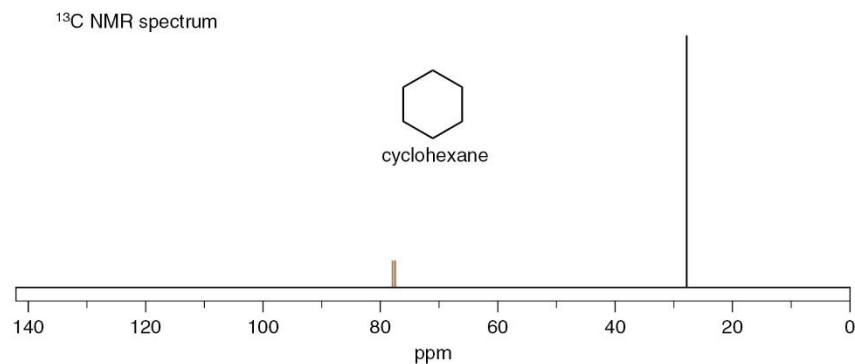
# Nuclear Magnetic Resonance

## Some examples of $^1\text{H}$ NMR spectra

129 ppm



27 ppm



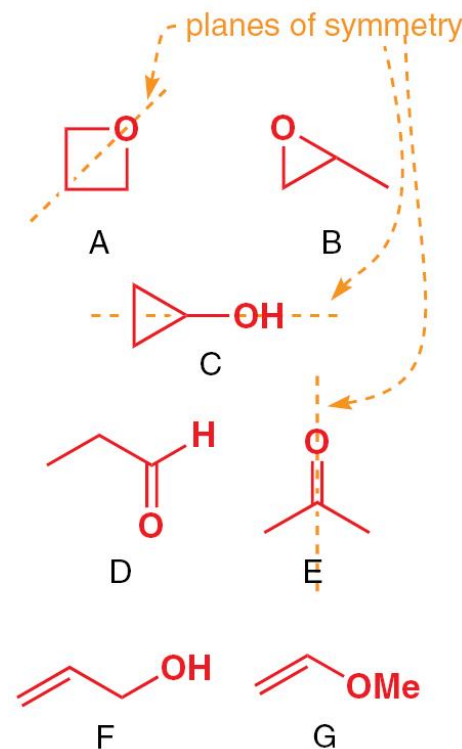


# Nuclear Magnetic Resonance

## NMR is a powerful tool for solving unknown structures

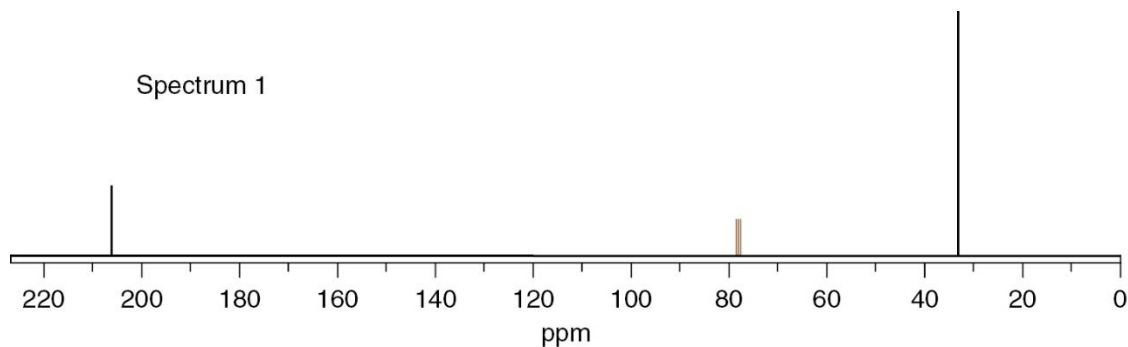
NMR has many more features, and it is no exaggeration to say it is more important for the routine determination of structure than all the other methods put together.

Here's an example: the formula  $C_3H_6O$  is represented by seven reasonable structures, as shown in the margin. The three  $^{13}C$  NMR spectra below represent three of these compounds.

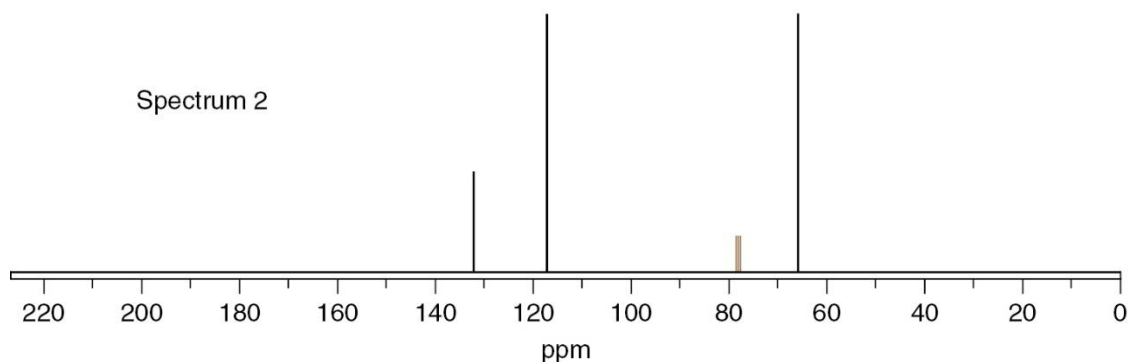


# Nuclear Magnetic Resonance

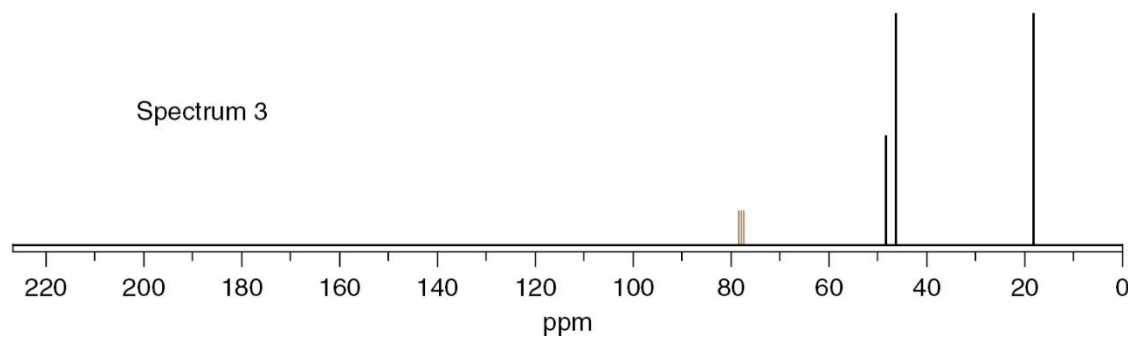
Spectrum 1



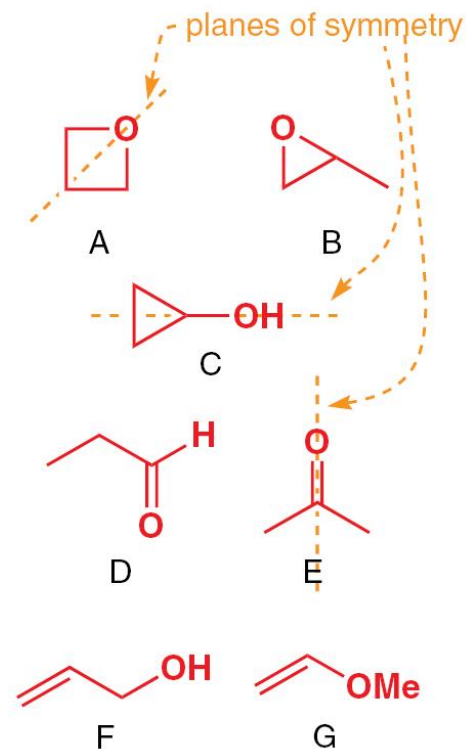
Spectrum 2



Spectrum 3

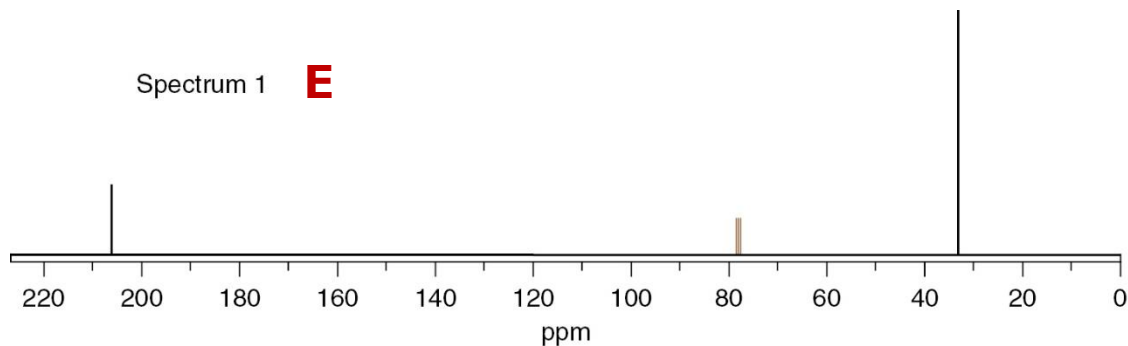


Which one is which one?

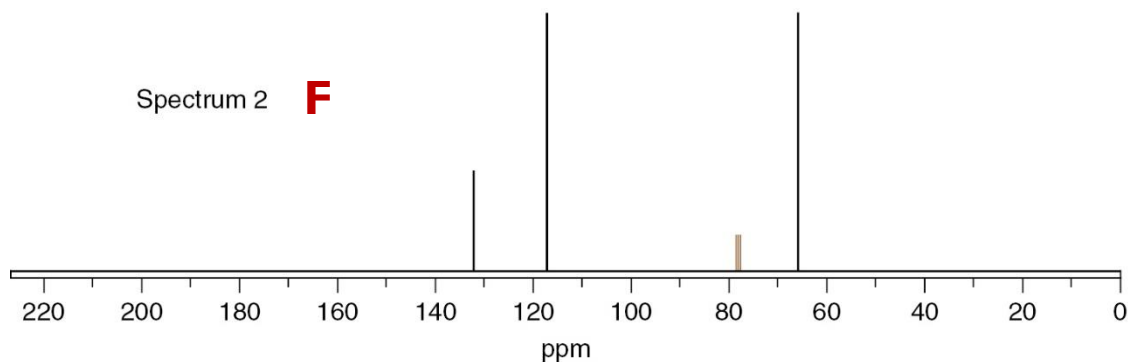


# Nuclear Magnetic Resonance

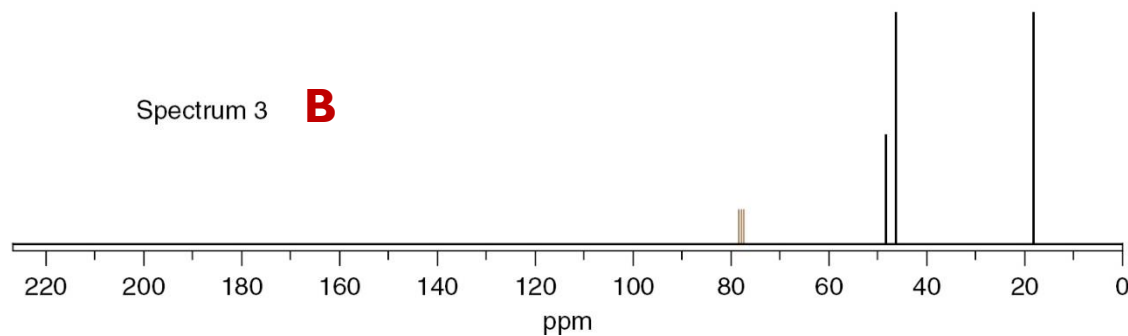
Spectrum 1 **E**



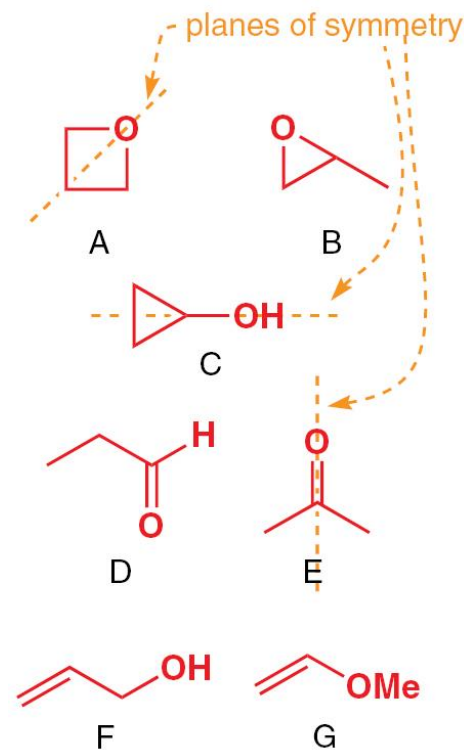
Spectrum 2 **F**



Spectrum 3 **B**



Which one is which one?



# Infrared Spectra (IR)

---

Functional groups are identified by infrared spectra

$^{13}\text{C}$  and  $^1\text{H}$  NMR spectra tell us a lot about the hydrocarbon skeleton of a molecule, and mass spectroscopy weighs the molecule as a whole. But none of these techniques reveal much about **functional groups**.

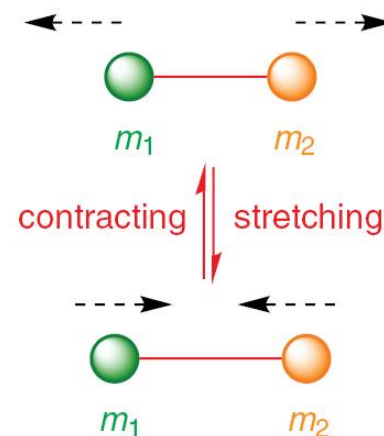
# Infrared Spectra (IR)

## Functional groups are identified by infrared spectra

$^{13}\text{C}$  and  $^1\text{H}$  NMR spectra tell us a lot about the **hydrocarbon skeleton** of a molecule, and **mass spectroscopy weighs** the molecule as a whole. But none of these techniques reveal much about **functional groups**.

**Infrared (IR) spectroscopy**, however, provides a direct way of observing these functional groups because it detects the **stretching and bending of bonds**. It is particularly good at detecting the **stretching of unsymmetrical bonds** of the kind found in functional groups such as OH, CO,  $\text{NH}_2$ , and  $\text{NO}_2$ , and for this reason IR spectroscopy complements NMR beautifully as a method for structural analysis.

bond vibration in the infrared



## *Infrared Spectra (IR)*

---

NMR requires electromagnetic waves in the radio-wave region of the spectrum to make nuclei flip from one state to another. The amount of energy needed for stretching and bending individual bonds, while still very small, is rather greater. These wavelengths lie in the *infrared* (wavelengths between 10 and 100  $\mu\text{m}$ ).

## Infrared Spectra (IR)

NMR requires electromagnetic waves in the radio-wave region of the spectrum to make nuclei flip from one state to another. The amount of energy needed for stretching and bending individual bonds, while still very small, is rather greater. These wavelengths lie in the **infrared** (wavelengths between 10 and 100  $\mu\text{m}$ ).

When the carbon skeleton of a molecule vibrates, some bonds stretch essentially independently of the rest of the molecule, and we can use these to identify functional groups.

**Stronger bonds vibrate faster and so do lighter atoms.**

---

Values chiefly affected by mass of atoms (lighter atom, higher frequency)

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C—H	C—D	C—O	C—Cl
3000 $\text{cm}^{-1}$	2200 $\text{cm}^{-1}$	1100 $\text{cm}^{-1}$	700 $\text{cm}^{-1}$

---

Values chiefly affected by bond strength (stronger bond, higher frequency)

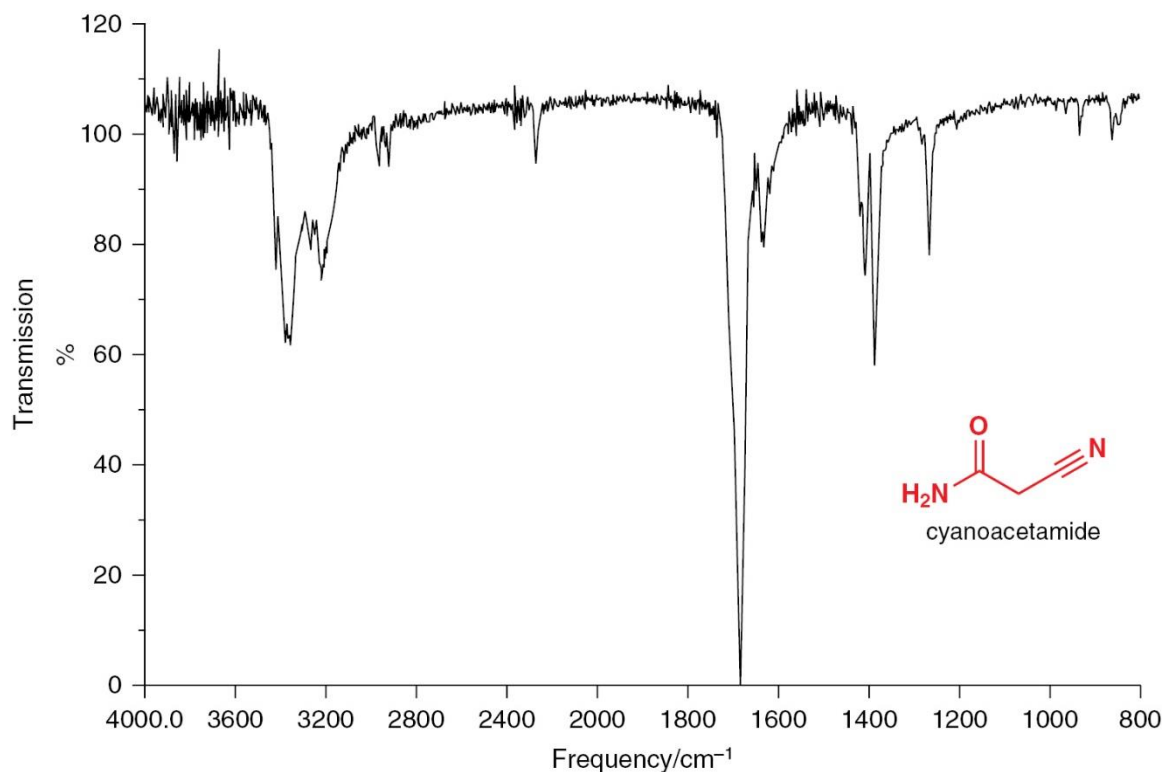
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$\text{C}\equiv\text{O}$	$\text{C}=\text{O}$	$\text{C}-\text{O}$
2143 $\text{cm}^{-1}$	1715 $\text{cm}^{-1}$	1100 $\text{cm}^{-1}$

---

## Infrared Spectra (IR)

Here's what a typical IR spectrum actually looks like: notice that the wavenumber scale runs from high to low but also that absorption maxima are shown upside down.



The overall shape of the spectrum is characteristic of this compound, but we need to be able to interpret the spectrum, and we can do this by dividing it up into regions.

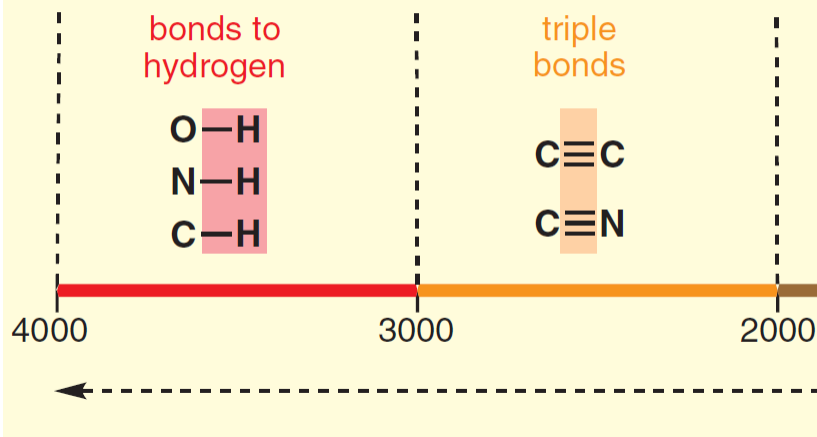


# Infrared Spectra (IR)

## There are four important regions of the infrared spectrum

From **4000 to 2500  $\text{cm}^{-1}$**  is the region for **C-H, N-H, and O-H** bond stretching. Most of the atoms in an organic molecule (C, N, O, for example) are about the same weight (12, 14, 16. . .). **Hydrogen is an order of magnitude lighter than any of these**, so any bond to H comes right at the left-hand end of the spectrum.

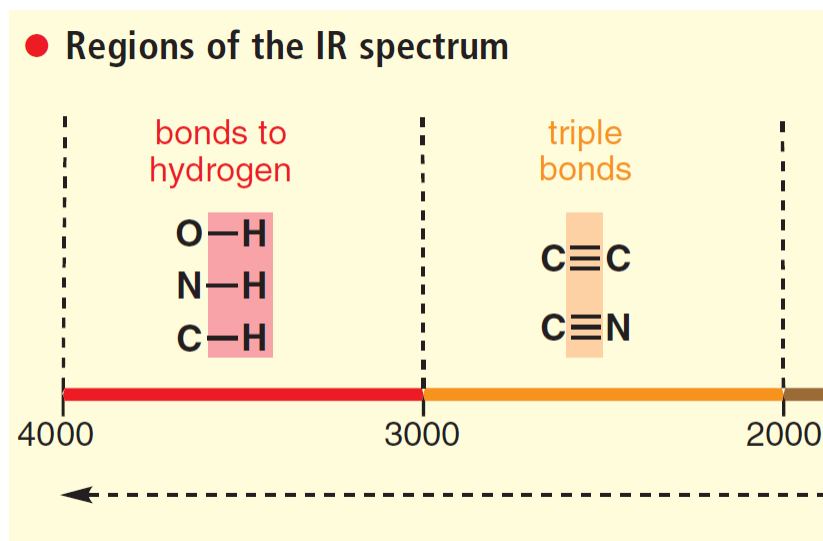
### ● Regions of the IR spectrum



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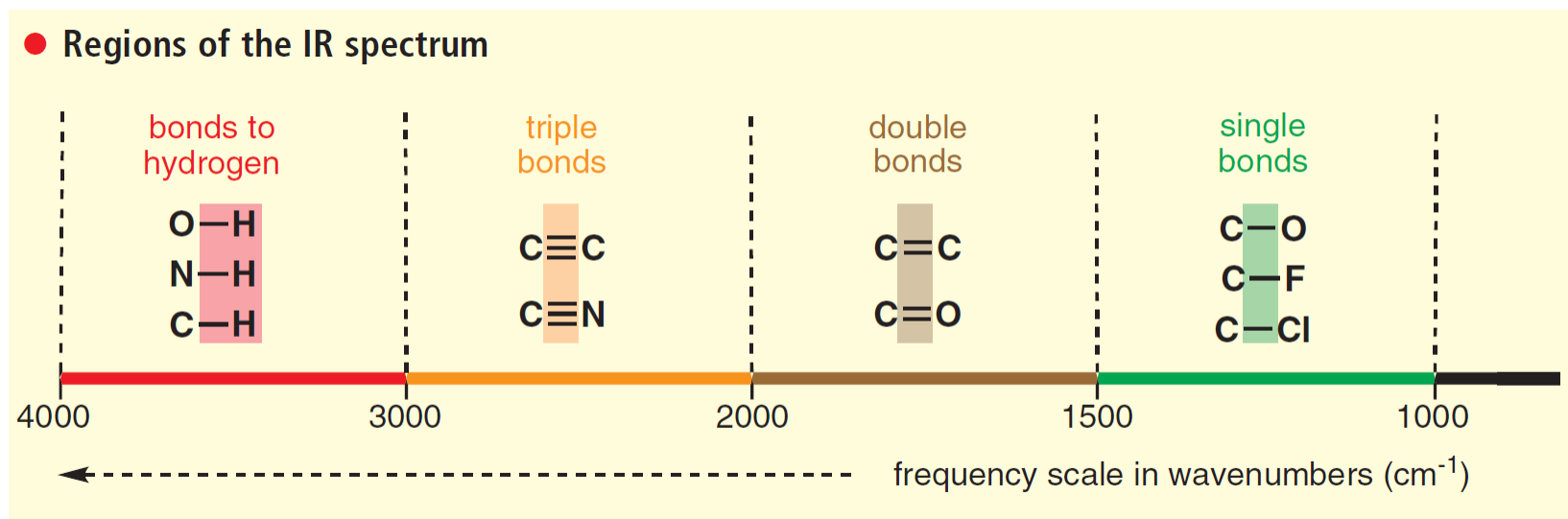


Even the strongest bonds between non-H atoms—**triple bonds such as  $\text{C}\equiv\text{C}$  or  $\text{C}\equiv\text{N}$** —absorb at slightly lower frequencies than bonds to hydrogen: these are in the next region, **the triple bond region from about 2500 to 2000  $\text{cm}^{-1}$** .

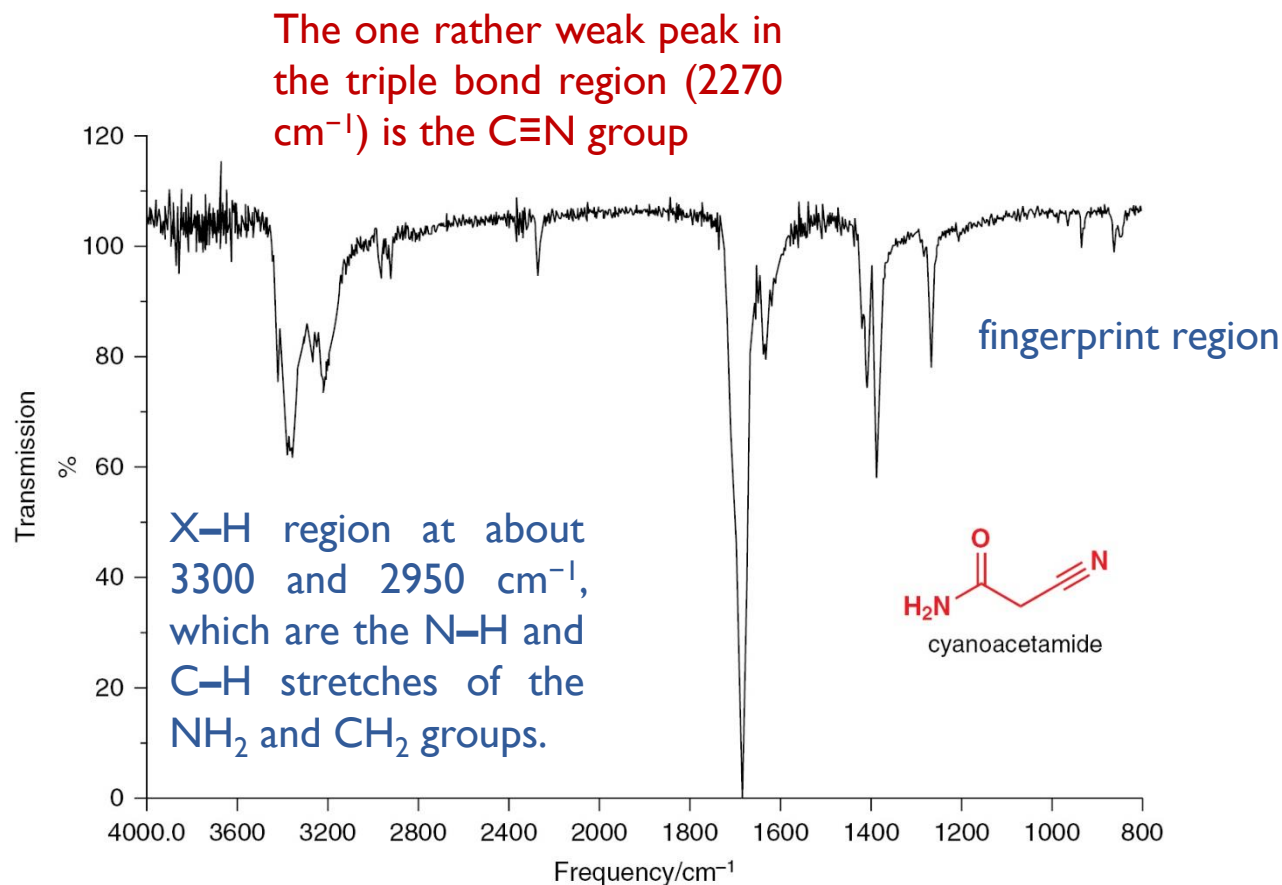
# Infrared Spectra (IR)

There are four important regions of the infrared spectrum

***C=C and C=O double bonds appear about 2000–1500  $\text{cm}^{-1}$  and at the right-hand end of the spectrum come single bonds, below 1500  $\text{cm}^{-1}$ .***



# Infrared Spectra (IR)



Absorptions in the IR are frequently referred to as '**peaks**'.

the strong peak at about  $1670\text{ cm}^{-1}$  belongs to the CO group.

## Infrared Spectra (IR)

The **X–H** region (**4000–3000 cm<sup>-1</sup>**) distinguishes **C–H**, **N–H**, and **O–H** bonds

In practice, **C–H stretches** occur at around **3000 cm<sup>-1</sup>**, **N–H stretches** occur at about **3300 cm<sup>-1</sup>**, and **O–H stretches** higher still at around **3500 cm<sup>-1</sup>**. We can immediately deduce that the O–H bond is stronger than N–H, which is stronger than C–H. *IR is a good way to measure such bond strengths.*

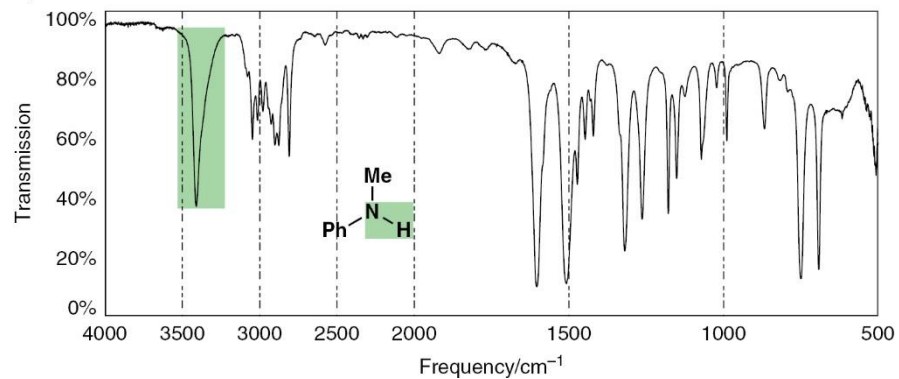
IR bands for bonds to hydrogen

Bond	Reduced mass, $\mu$	IR frequency, cm <sup>-1</sup>	Typical bond strength, kJ mol <sup>-1</sup>
C–H	12/13 = 0.92	2900–3200	CH <sub>4</sub> : 440
N–H	14/15 = 0.93	3300–3400	NH <sub>3</sub> : 450
O–H	16/17 = 0.94	3500–3600 <sup>a</sup>	H <sub>2</sub> O: 500

<sup>a</sup>When not hydrogen-bonded: see below.

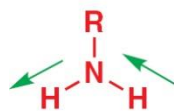
# Infrared Spectra (IR)

Spectrum 1

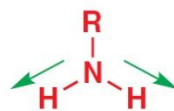


antisymmetric  
NH<sub>2</sub> stretch

symmetric  
NH<sub>2</sub> stretch

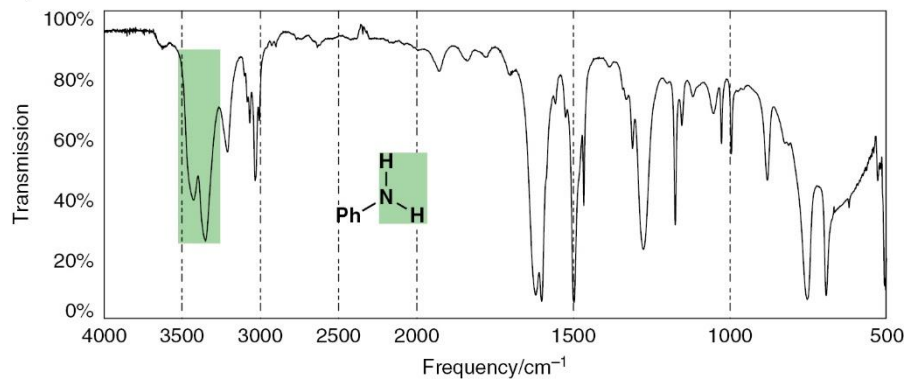


about  
3400 cm<sup>-1</sup>



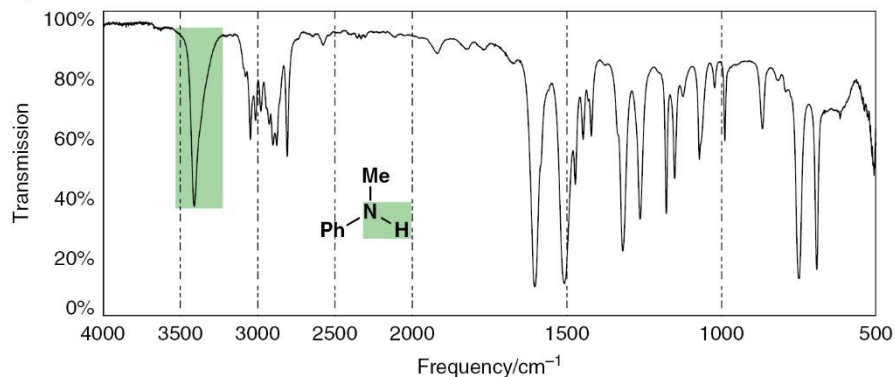
about  
3300 cm<sup>-1</sup>

Spectrum 2



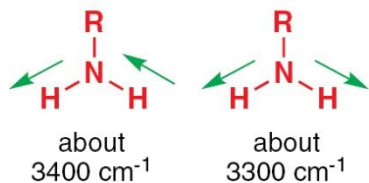
# Infrared Spectra (IR)

Spectrum 1

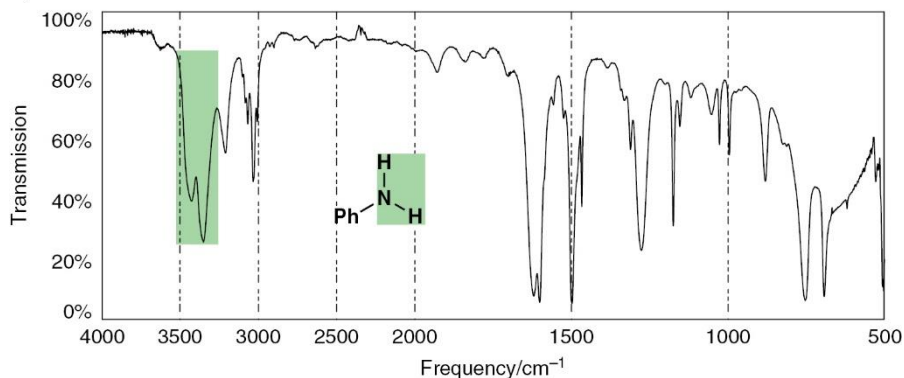


antisymmetric  
NH<sub>2</sub> stretch

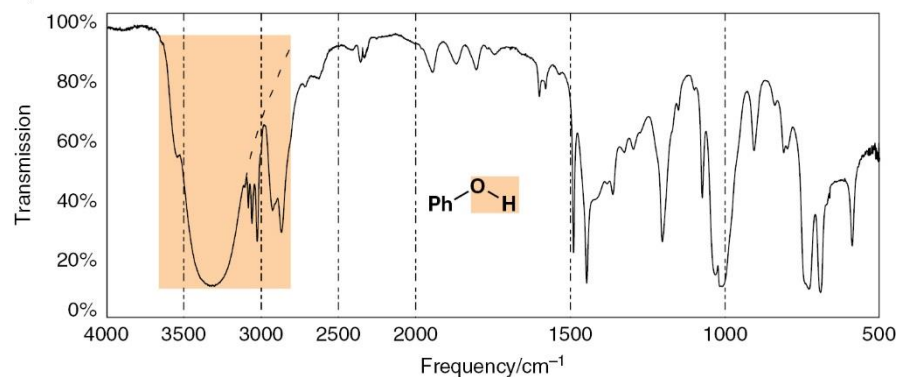
symmetric  
NH<sub>2</sub> stretch



Spectrum 2

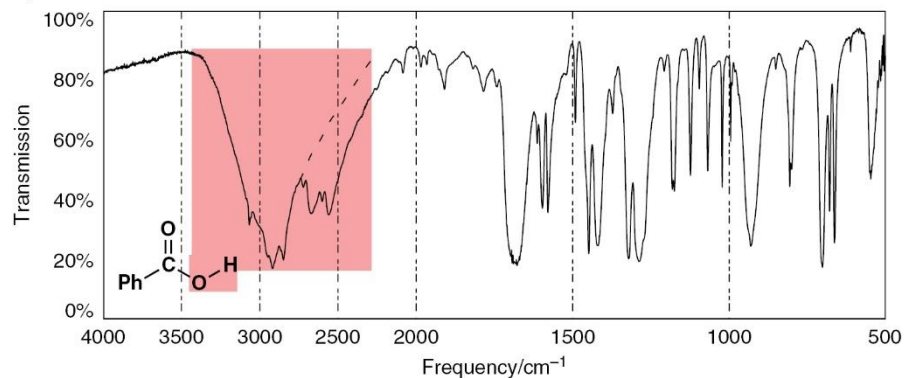


Spectrum 3

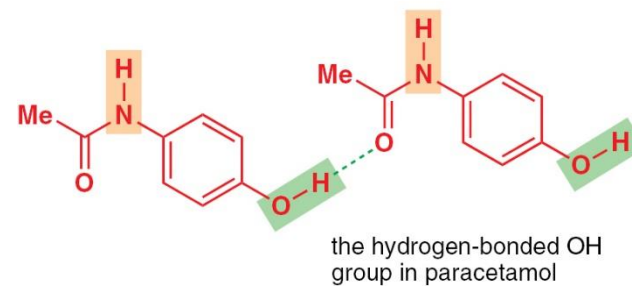
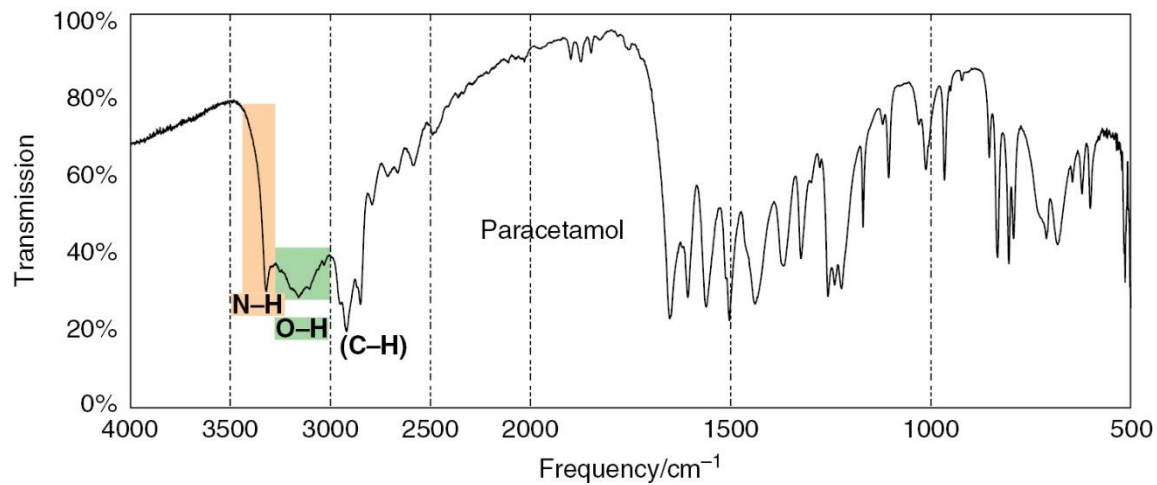


A broad absorption at anywhere from 3500 to 2900 cm<sup>-1</sup>. This is because OH groups form strong **hydrogen bonds** that vary in length and strength.

Spectrum 4

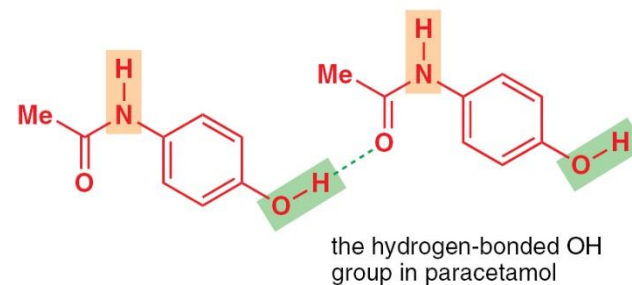
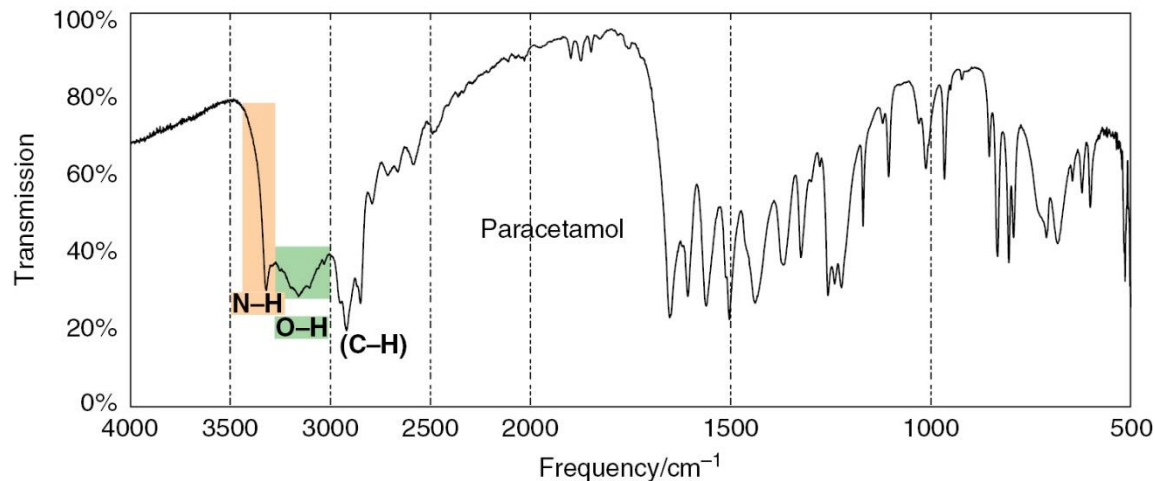


# Infrared Spectra (IR)

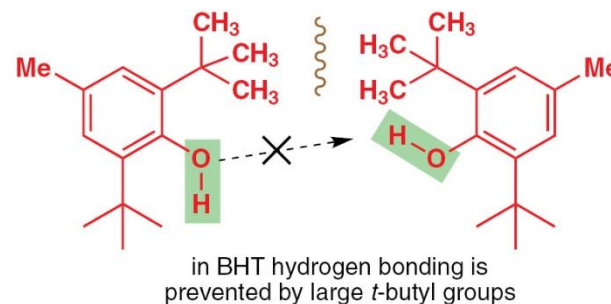
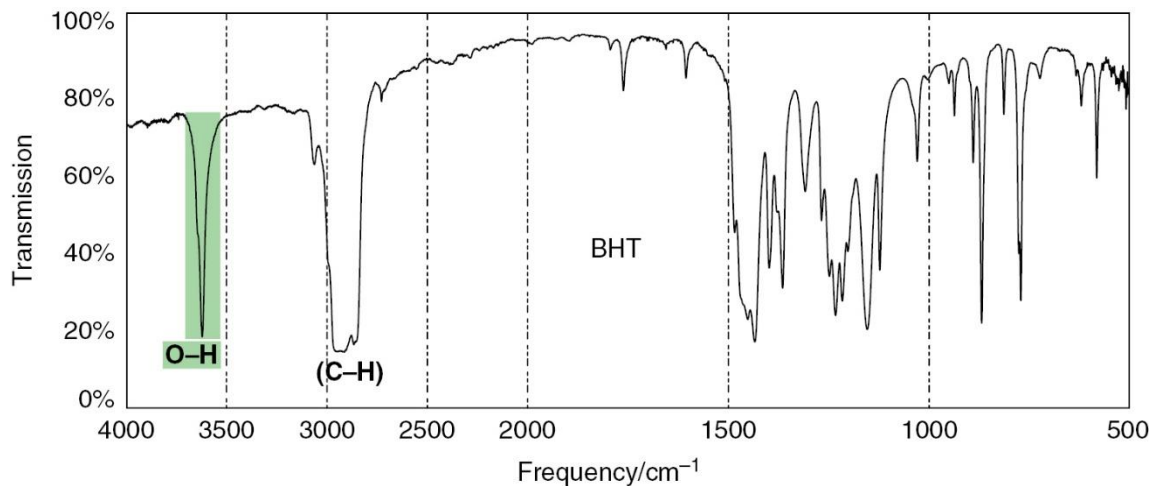




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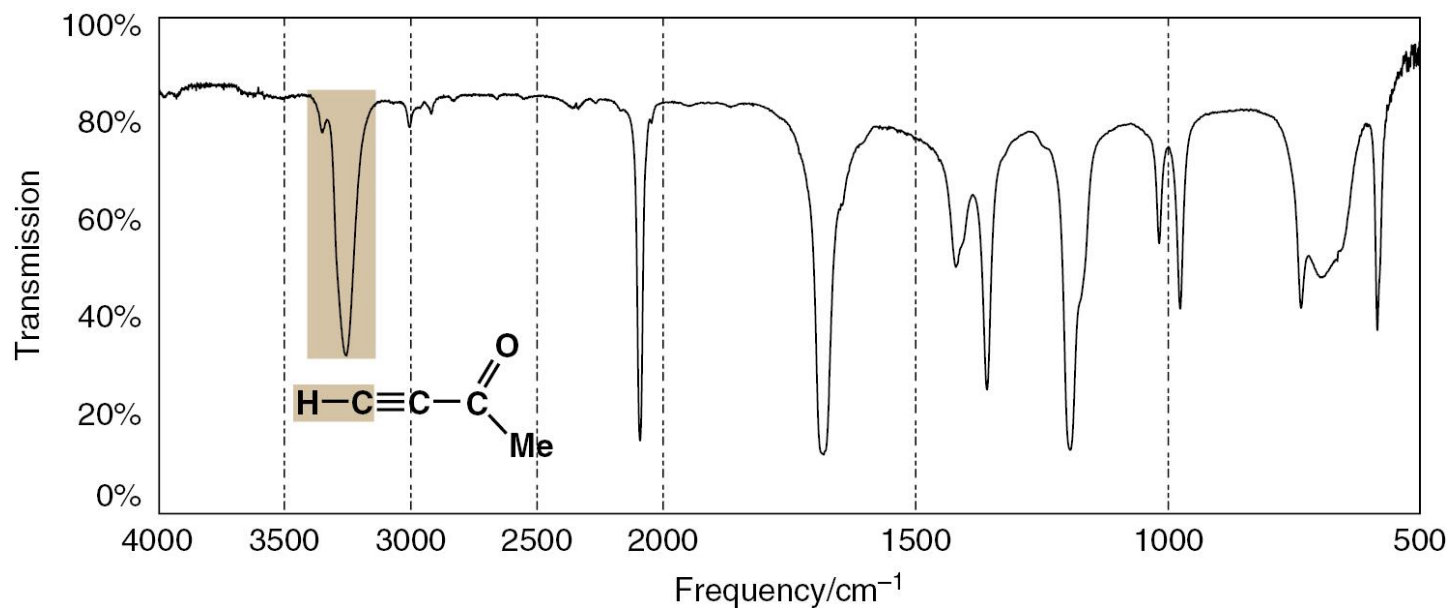


A sharp absorption at  $3600\text{ cm}^{-1}$  indicates a non-hydrogen-bonded OH group.



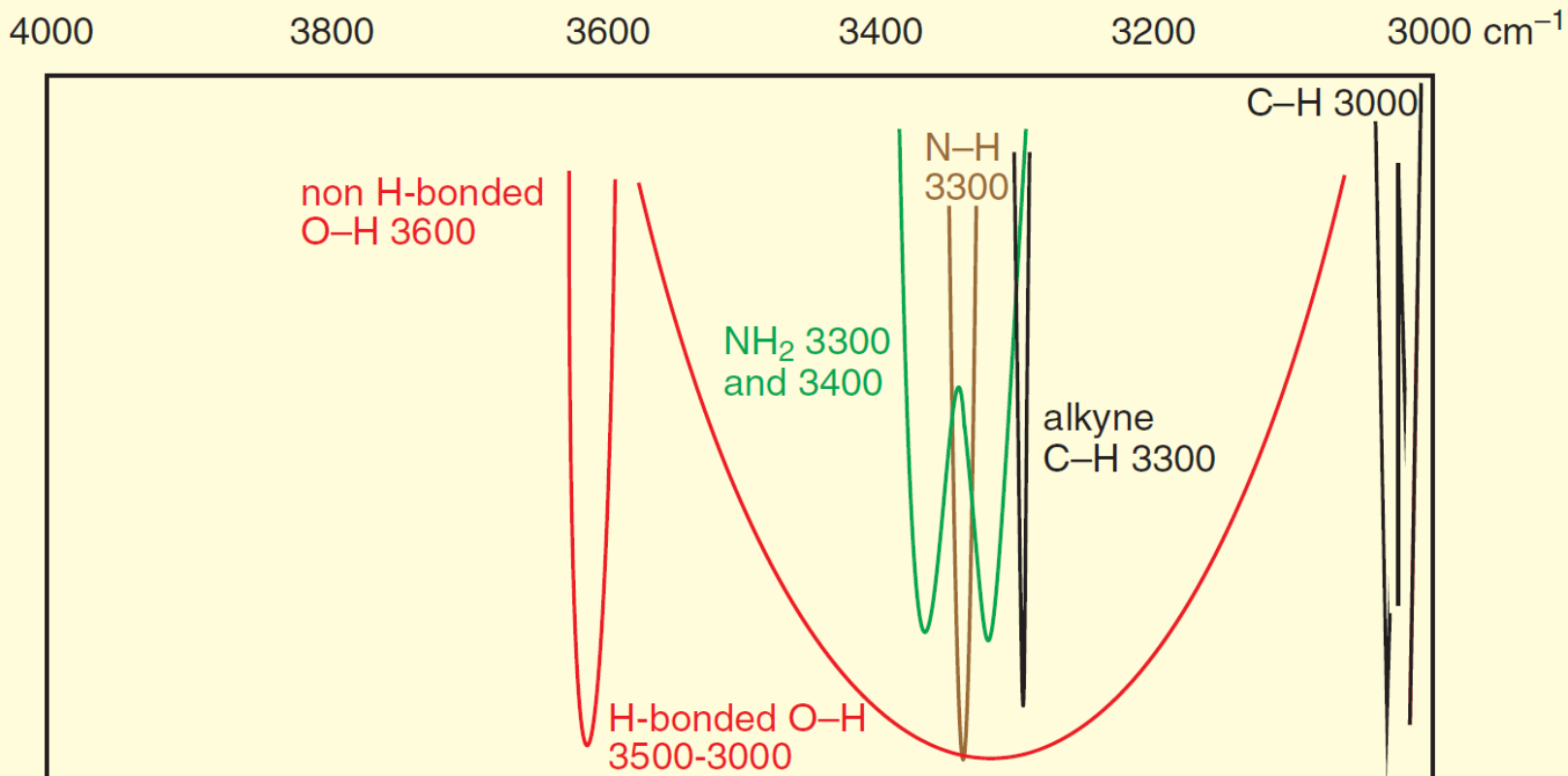
# Infrared Spectra (IR)

The alkyne C–H bond is shorter and stronger than alkane C–H bonds



# Infrared Spectra (IR)

- Typical peak shapes and frequencies for X–H bonds in the region 4000–3000  $\text{cm}^{-1}$ .

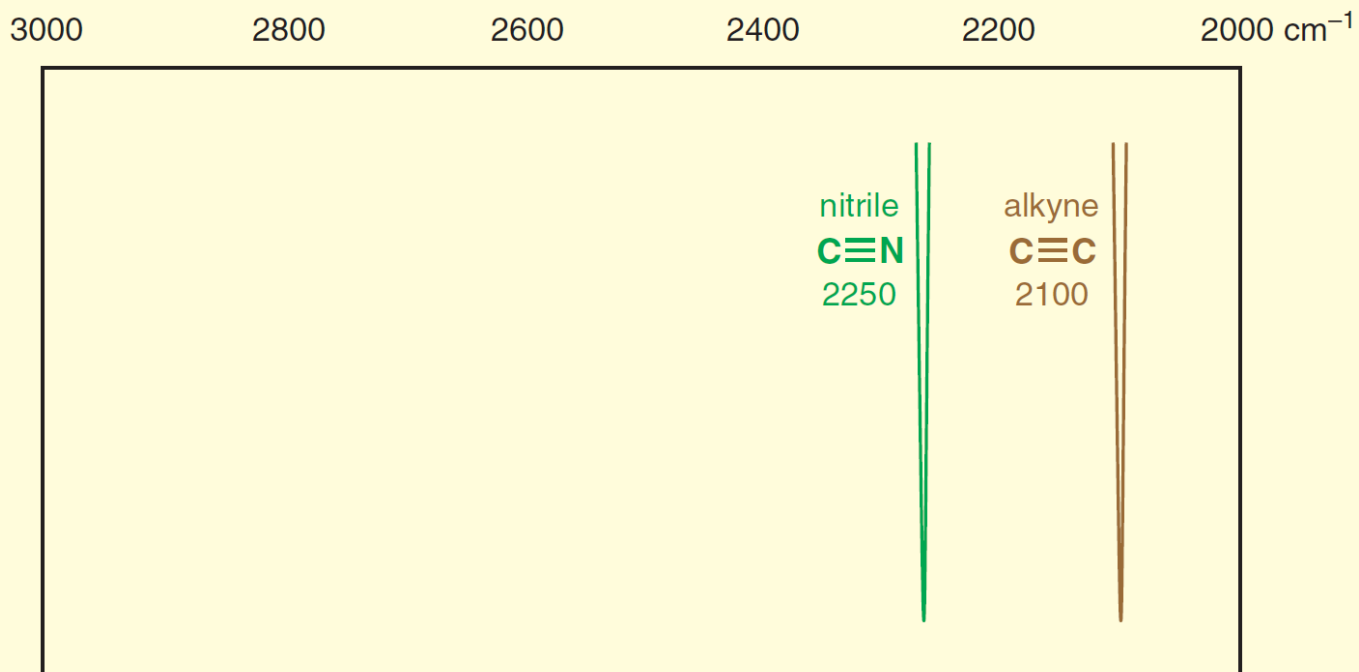


# Infrared Spectra (IR)

## The triple bond region (3000–2000 $\text{cm}^{-1}$ )

This region is often empty, meaning that when you do see a peak between **2000 and 2500  $\text{cm}^{-1}$**  you can be absolutely certain that the compound is an **alkyne** (usually at around **2100  $\text{cm}^{-1}$** ) or a **nitrile** (at **2250  $\text{cm}^{-1}$** ).

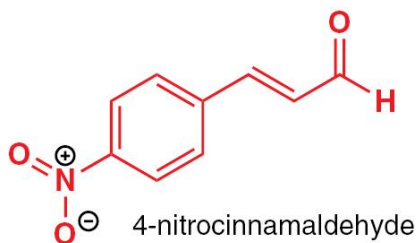
- The only two peaks in the triple bond region



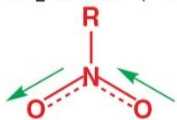
# Infrared Spectra (IR)

## The double bond region is the most important in IR spectra

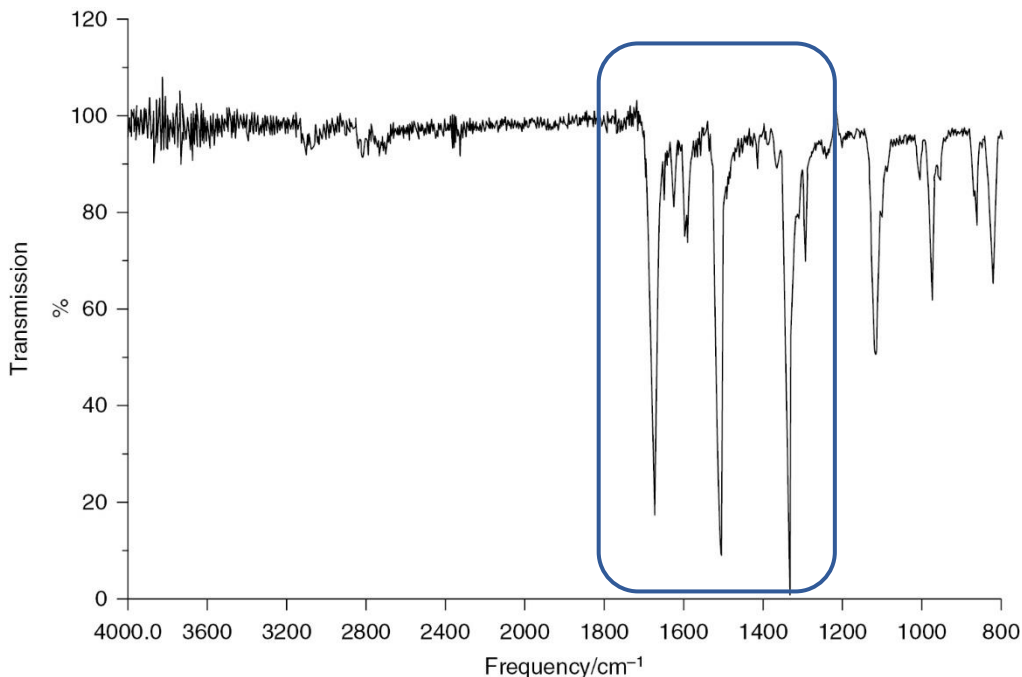
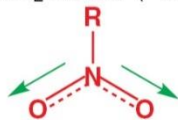
The most important absorptions in the double bond region are those of the **carbonyl (C=O)**, **alkene or arene (C=C)**, and **nitro (NO<sub>2</sub>)** groups. All give rise to sharp bands, **C=O** gives one strong (i.e. intense) band anywhere between **1900 and 1500 cm<sup>-1</sup>**; alkene **C=C** gives one weak band at about **1640 cm<sup>-1</sup>**, and **NO<sub>2</sub>** gives two strong (intense) bands in the **mid-1500s** and **mid-1300s cm<sup>-1</sup>**.



antisymmetric  
NO<sub>2</sub> stretch (~1550)



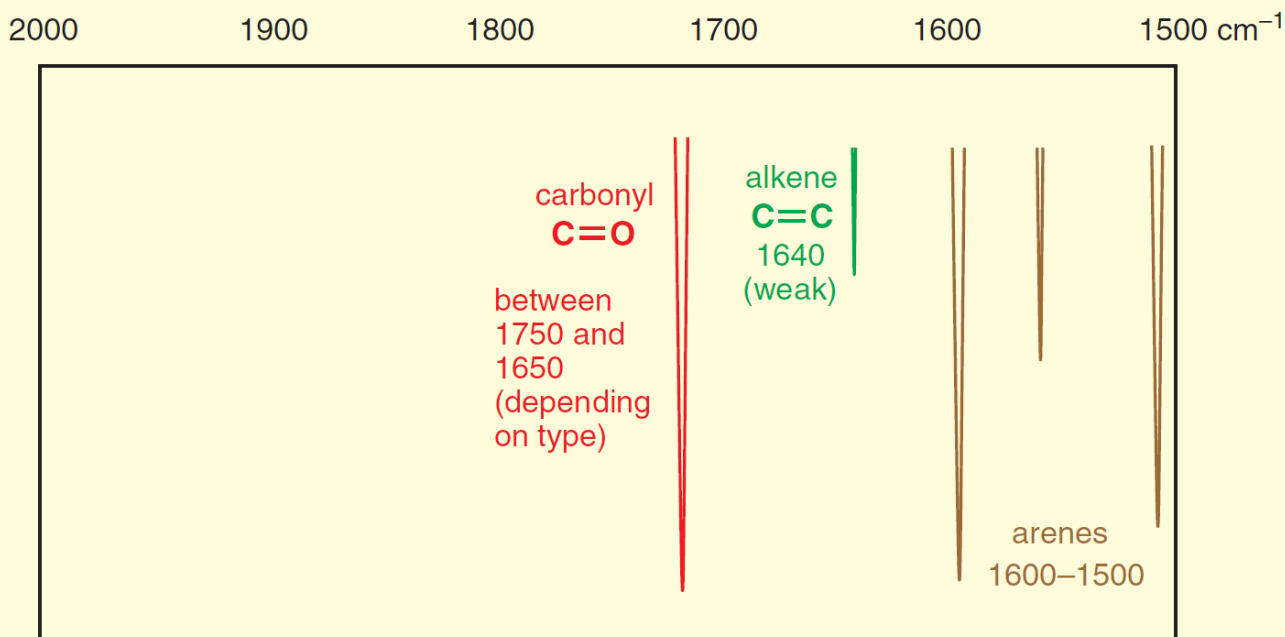
symmetric  
NO<sub>2</sub> stretch (~1350)



## Infrared Spectra (IR)

Arenes have a much more complex pattern of vibration that cannot be analysed simply. However, it's worth noting that arene C=C bonds come at lower frequency ( $<1600\text{ cm}^{-1}$ ) than alkene C=C bonds ( $>1600\text{ cm}^{-1}$ ).

### ● Important absorptions in the double bond region



## Infrared Spectra (IR)

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### The strength of an IR absorption depends on dipole moment

The **strength** of an IR absorption varies with the change of **dipole moment** when the bond is stretched. If the bond is **perfectly symmetrical**, there is no change in dipole moment and there is **no IR absorption**.

Obviously, the C=C bond is less polar than either C=O or N=O and its absorption is less intense in the IR. By contrast **the carbonyl group is very polarized**, with oxygen attracting the electrons away from carbon, and stretching it causes a large change in dipole moment. O–H and N–H stretches are stronger than C–H stretches because C–H bonds are only weakly polarized.

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**Dipole moment** depends on the variation in distribution of electrons along the bond and also its length, which is why stretching a bond can change its dipole moment. For bonds between unlike atoms, **the larger the difference in electronegativity, the greater the dipole moment** and the more it changes when stretched.

Stretching frequencies for symmetrical molecules can be measured using an alternative method known as **Raman spectroscopy**.



## Infrared Spectra (IR)

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### The single bond region is used as a molecular fingerprint

The region **below  $1500\text{ cm}^{-1}$**  is where the single bond vibrations occur. The atoms C, N, and O all have about the same atomic weight and C–C, C–N, and C–O single bonds all have about the same strength.

The only one of these single bonds of any value is **C–O**, which is polar enough to show up as a strong absorption at about  **$1100\text{ cm}^{-1}$** . Some other single bonds, such as **C–Cl**, are quite useful at about  **$700\text{ cm}^{-1}$** .

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Stretching is not the only bond movement that leads to IR absorption. **Bending of bonds**, particularly C–H and N–H bonds, also leads to quite strong peaks. These are called **deformations**. Bending a bond is easier than stretching it. Consequently, bending absorptions need less energy and come at lower frequencies than stretching absorptions for the same bonds.

#### Deformation frequencies

Group	Frequency, $\text{cm}^{-1}$
$\text{CH}_2$	1440–1470
$\text{CH}_3$	~1380
$\text{NH}_2$	1550–1650