

# Chapter 13

## Spectroscopy

### NMR, IR, MS, UV-Vis

#### Main points of the chapter

1. Hydrogen Nuclear Magnetic Resonance
  - a. Splitting or coupling (what's next to what)
  - b. Chemical shifts (what type is it)
  - c. Integration (how many are there)
2. <sup>13</sup>C NMR
3. InfraRed spectroscopy (identifying functional groups)
4. Mass spectroscopy (determining molecular weight, structural elements, molecular formula)

The various spectroscopies are the primary method for determining the structure of compounds. If the molecule is not too large or complex, the determination should be very accurate. These are simply done and rapid. They can be combined to give overlapping information.

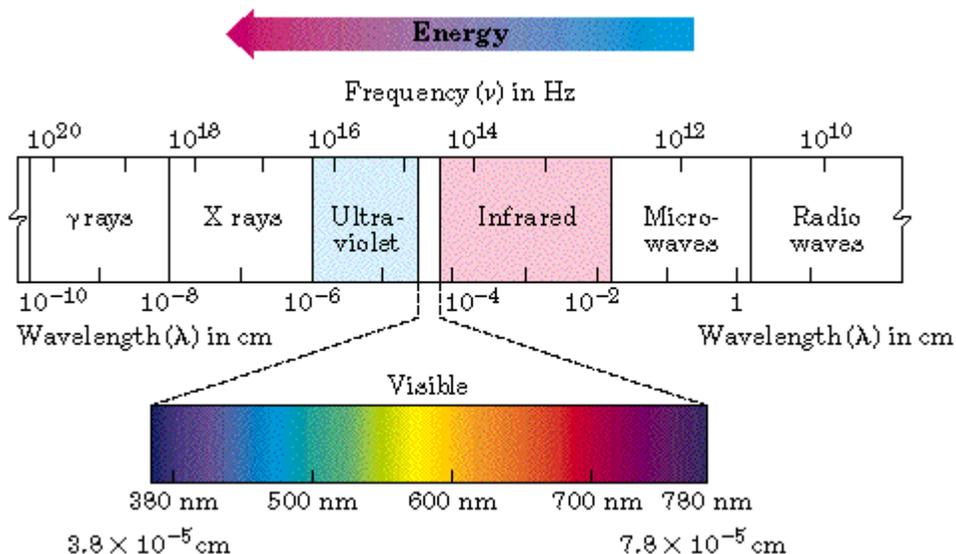
This is not chemistry in the sense of reactions but it is very interesting puzzle solving. Once you understand the rules, you will like it (except of course in exams).

The chapter begins with background information on how these techniques work which is interesting but not essential to using them to determine structures. In the NMR, the information sequence is the logical progression from the simple to the more complex. But do not think that the first item, chemical shift, or the second, integration, is the important component. The splitting or multiplicity is the key element in H-NMR. IR is much more straightforward; memorize a few absorption numbers to identify functional groups. MS is also straightforward. We will not do UV-Vis because it is not very useful for structure identification. It is an extremely important tool for quantitating substances and is used widely.

#### 1. Molecular interaction with electromagnetic radiation. (13.1-2)

Molecules have electromagnetic fields derived from their electrons and nuclei. We saw earlier that plane-polarized light interacts by being rotated by an enantiomer. As seen below, energy varies across the spectrum and matches that required for various interactions.

## The Electromagnetic Spectrum



Energy increases going to the left. The electromagnetic radiation interacts with the electromagnetic fields of the electrons to raise their energy levels from one state to the next. The nature of that interaction depends on the energy available. Ultraviolet and visible have sufficient energy to effect electronic transitions. Infrared has sufficient energy only to effect transitions between vibrational energy states. Microwave has only enough energy to effect transitions between rotationally energy states. Thus the radiation absorbed tells us different information. Radio waves have insufficient energy to effect molecules but affect nuclear spin energy states found in magnetic fields. This latter interaction is most important because it is used in Nuclear Magnetic Resonance spectroscopy.

## 2. NMR theory (13.3-13.5)

A. All nuclei with unpaired protons or neutrons are magnetically active- they have a magnetic field arising from the unpaired nuclear particle. Of greatest interest to an organic chemist is hydrogen (including deuterium) and carbon ( the  $^{13}\text{C}$  isotope not the  $^{12}\text{C}$  isotope which has paired neutrons and protons).

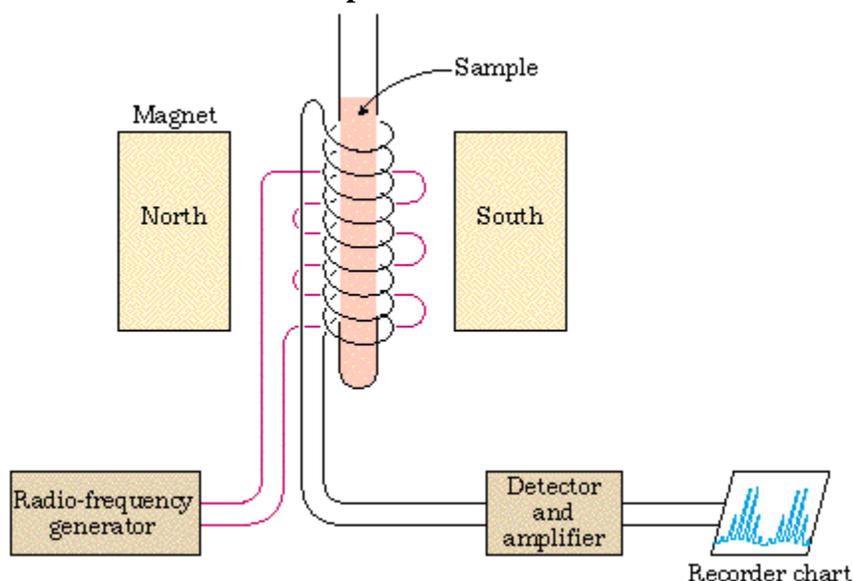
B. Placed in an external magnetic field this magnetic field of the nucleus has two stable states,

alignment with or against the applied field, which are of slightly different energies (aligned against is higher). The greater the applied field the greater this difference (this is a crucial fact).

a. Internal (in the molecule) factors which affect (add to or subtract from) the applied magnetic field so as to put the individual nucleus in a different magnetic environment from that felt by another nucleus create differences in the nuclei.

b. Higher applied magnetic fields will create larger absolute numerical values of the differences between energy states and allow easier distinction between two different nuclei (better resolution).

A schematic of an NMR spectrometer



C. Electromagnetic radiation of radio frequency wavelengths is of the right energy range to cause the nucleus to move (resonate) between these two energy states. This absorption allows detection of the hydrogen or carbon-13 nucleus. Different nuclei experiencing different magnetic fields and thus different energy differences between states will absorb different radio frequencies or at a particular constant frequency will absorb at different applied magnetic fields and allow us to distinguish between them.

This selectivity of energy required to match the energy differences between states is fundamental for all spectroscopies. The energy states are termed quantized. Transitions can occur only when the precise energy corresponding to the energy difference between the states is delivered to the system to excite it to the higher state. So the frequency (or wavelength) of radiation absorbed is specific to that energy transition. When the energy difference between

the states changes or is different, the frequency of light absorbed will change.

**D. What internal magnetic factors modify the applied magnetic field to create the effective field experienced by the individual nuclei, thus changing the energy (frequency) needed for the transition (resonance)?**

**Two:**

- a. The electrons in the bonds around those nuclei.**
- b. The magnetic fields of neighboring nuclei.**

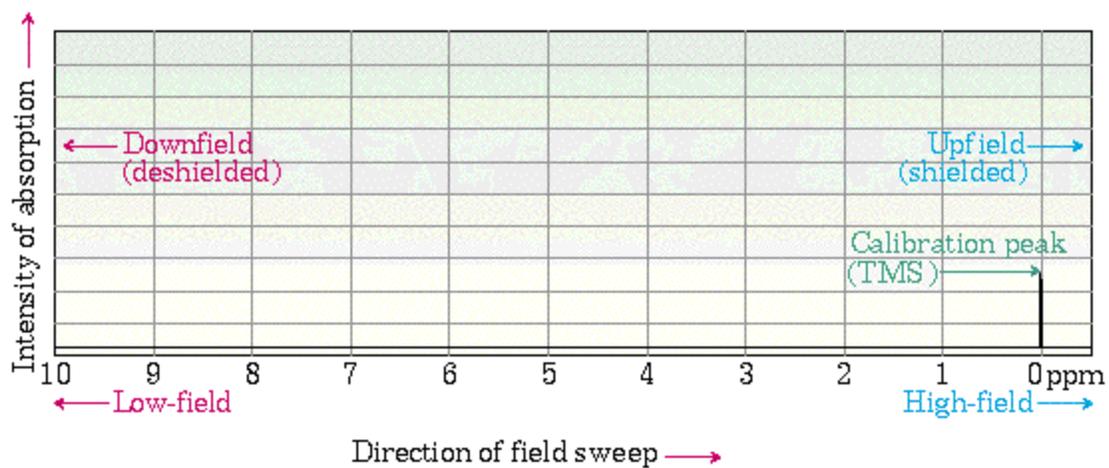
**Consider a. first.**

The electrons act to oppose the applied field shielding the nuclei from it. Since every different type of hydrogen is in a different electronic environment, each type will experience a different effective magnetic field and thus a different resonance frequency. We can tell one type of nucleus from another type. We term this value the chemical shift. Chemical shift is expressed as a delta value.

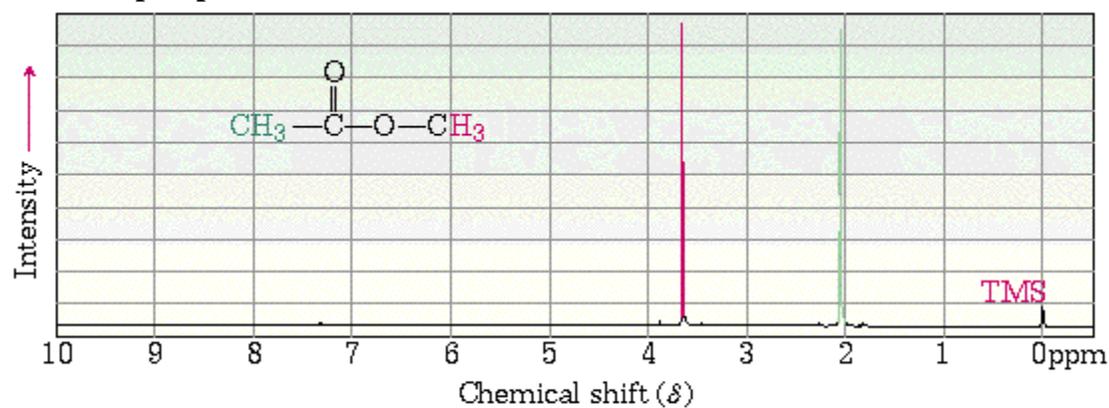
**delta = chemical shift (number of Hz away from standard TMS)/MHz of instrument**

**For example, delta = 60 Hz/ 60,000,000 Hz = 1 ppm**

The spectrum is presented as follows:

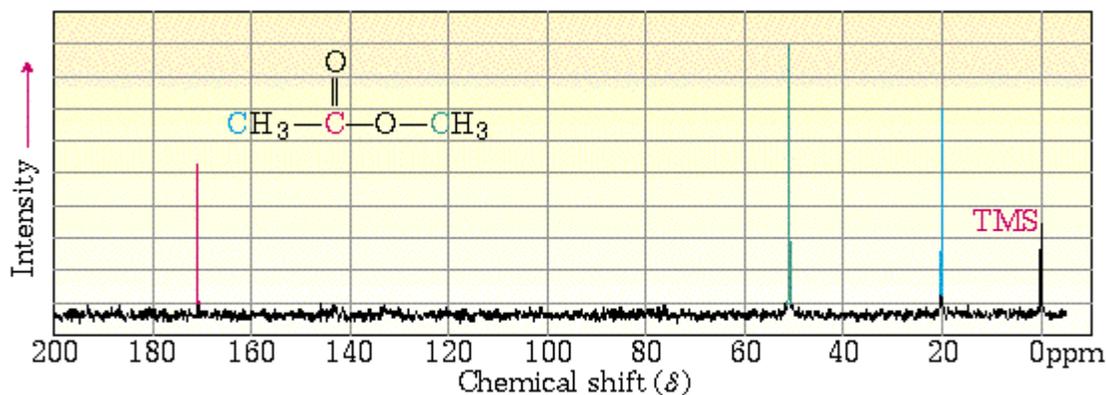


Some simple spectra:



(a)

**Figure 13.3** (a) The  $^1\text{H}$  NMR spectrum and (b) the  $^{13}\text{C}$  NMR spectrum of methyl acetate,  $\text{CH}_3\text{CO}_2\text{CH}_3$ .



(b)

**Note :**

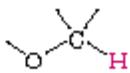
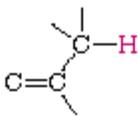
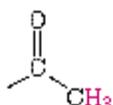
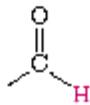
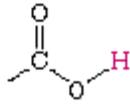
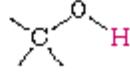
Two types of hydrogens, the hydrogens of a methyl are the same- they spin and experience the same average environment. The oxygen pulls electrons away from the right methyl and it is deshielded from the applied field, shifted downfield, a smaller field is needed to bring it into resonance. Three kinds of carbon. Note how deshielded the carbonyl carbon is.

Look at the chemical shift ranges. Very different for the different nuclei. TMS is tetramethylsilane and is chosen because all resonances are to the left of this peak so it's handy to use as a standard set to zero.

Identical nuclei have the same chemical shift. If you have a hard time deciding if they are identical, imagine substituting each with a halogen and ask if it would have the same name.

So chemical shifts are somewhat typical of particular types of hydrogen, predictable and useful for knowing what kind of group based on the chemical shift. See the table below. But beware. Due to deshielding substitutions, these values shift down quite a bit.

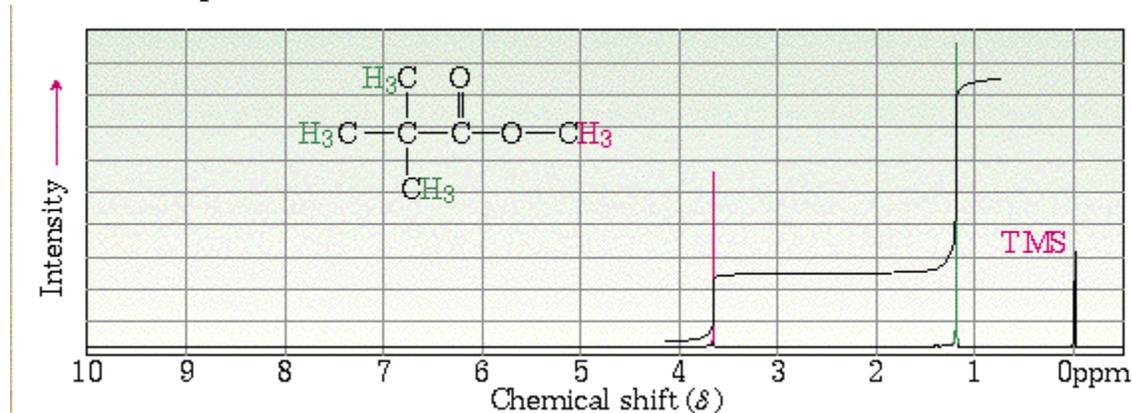
**Table 13.3 Correlation of  $^1\text{H}$  Chemical Shift with Environment**

Type of hydrogen	Chemical shift ( $\delta$ )	Type of hydrogen	Chemical shift ( $\delta$ )
Reference	$(\text{CH}_3)_4\text{Si}$ 0		
Saturated primary	$-\text{CH}_3$ 0.7 - 1.3	Alcohol, ether	 3.3 - 4.0
Saturated secondary	$-\text{CH}_2-$ 1.2 - 1.4	Alkynyl	$\text{C}\equiv\text{C}-\text{H}$ 2.5 - 2.7
Saturated tertiary	 1.4 - 1.7	Vinyllic	 5.0 - 6.5
Allylic	 1.6 - 2.2	Aromatic	$\text{Ar}-\text{H}$ 6.5 - 8.0
Methyl ketone	 2.1 - 2.4	Aldehyde	 9.7 - 10.0
Aromatic methyl	$\text{Ar}-\text{CH}_3$ 2.5 - 2.7	Carboxylic acid	 11.0 - 12.0
Alkyl halide X = Cl, Br, I	 2.5 - 4.0	Alcohol	 2.5 - 5.0 (Variable)

**E. Integration Section 13.6-** How many protons are producing this signal (integration does not work for carbon)

The area under the curve (correlates well with peak height) is proportional to the number of

protons producing the signal. So the area is integrated in the calculus sense and compared for the different resonances. The ratio of the areas equals the ratio of the protons producing the signal. This area is presented graphically by an integrating line in which the rise in the line as it passes through the peak is proportional to the area under the peak. Note that it is proportional. The absolute values mean nothing, only the relative areas under the peak. If the number of hydrogens in the molecule are known then the total rise divided by the number of hydrogens gives a rise/hydrogen and dividing that value into the rise in a peak will give the number of hydrogens in the peak. If the total is not known, then some peak must be guessed and the other peaks surmised from the relative areas.



### E. Spin - spin splitting: What's next door - the best information from NMR (sections 13.7-13.11)

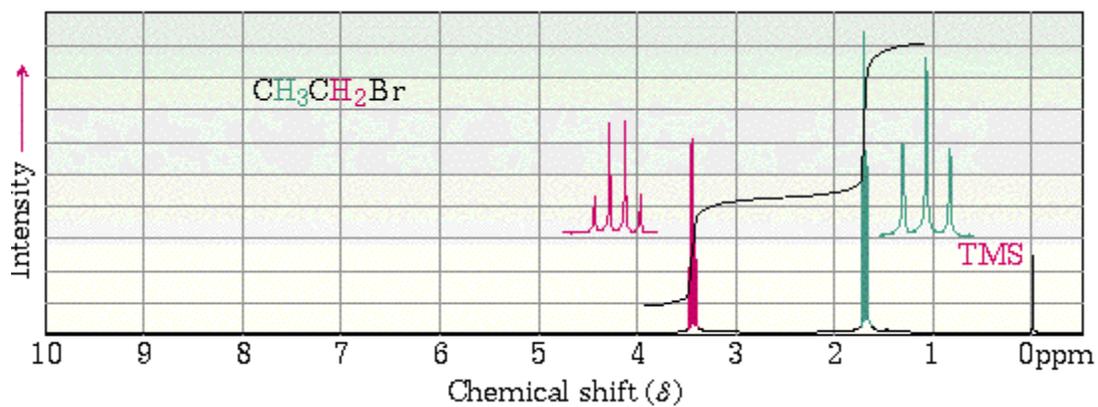
Since nuclei produce magnetic fields (the ones we've been talking about aligning with and against the field), those fields would affect the effective field felt by the hydrogen being measured. In the high energy state they would oppose (reduce) the field and in the low energy state reinforce (increase) the field.

Thus a neighboring hydrogen would cause another hydrogen to feel two fields

effective field = applied field - electron shielding + or - neighboring nuclei field

So instead of seeing one signal, if a single neighboring hydrogen splits the signal you would see two, called a doublet. At first this seems a painful complication but it tells you that if you see a doublet that nucleus has a single hydrogen adjacent. With such information you can put the pieces in order to make a structure.

Similarly, two neighboring nuclei yield three peaks, three yield four, etc. This is termed the n+1 rule stating that a signal will be split into n+1 peaks when n equivalent nuclei (hydrogens) are adjacent. The peak areas are also predictable based on an analysis of the possible states and can be readily remembered by Paschal's triangle.



**Note that the  $\text{CH}_3$  group is a triplet being split by the two neighboring hydrogens of the  $\text{CH}_2$ . The  $\text{CH}_2$  group is a quartet being split by the three hydrogens of the  $\text{CH}_3$ .**

Now let's see if you can predict the chemical shift and splitting pattern of isopropyl bromide.

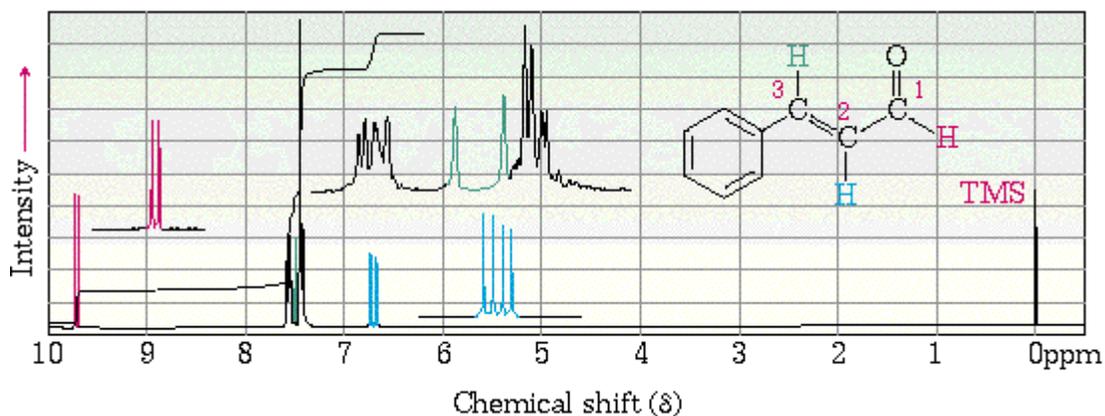
So, the rules for splitting are:

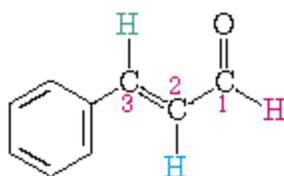
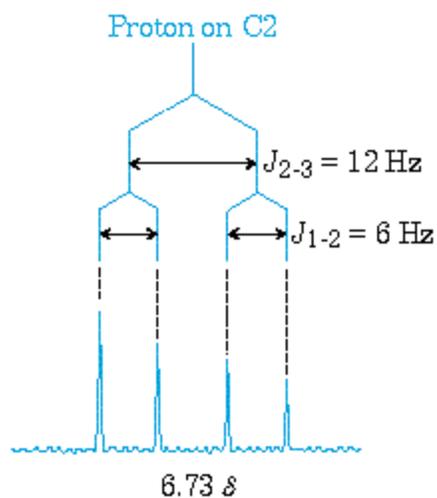
1. Equivalent hydrogens do not split one another.

2. a. The signal of a type of hydrogen is split into  $n+1$  peaks, where  $n$ =the number of equivalent neighboring hydrogens.

b. When two different types of hydrogen are adjacent, they split the signal independently to produce  $(n_a+1)(n_b+1)$  peaks.

Consider this more complicated example.





The amount by which the signal is split (the distance apart) is called  $J$ , the coupling constant but is not critical for our level of understanding. Hydrogens splitting each other have the same  $J$  value.

**Aromatic regions** are more complex because of the often very similar chemical shifts and small coupling constants and extensive overlaps of signals.

Two principal parameters - the electronic effects of the substituent and the substitution pattern.

### 3. $^{13}\text{C}$ NMR.

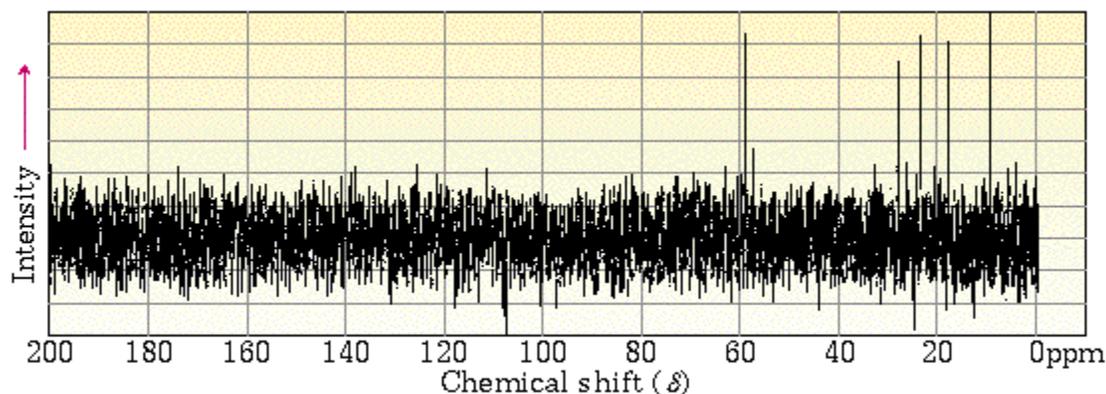
#### Similarities with H-NMR:

Chemical shift relative values. See earlier figures

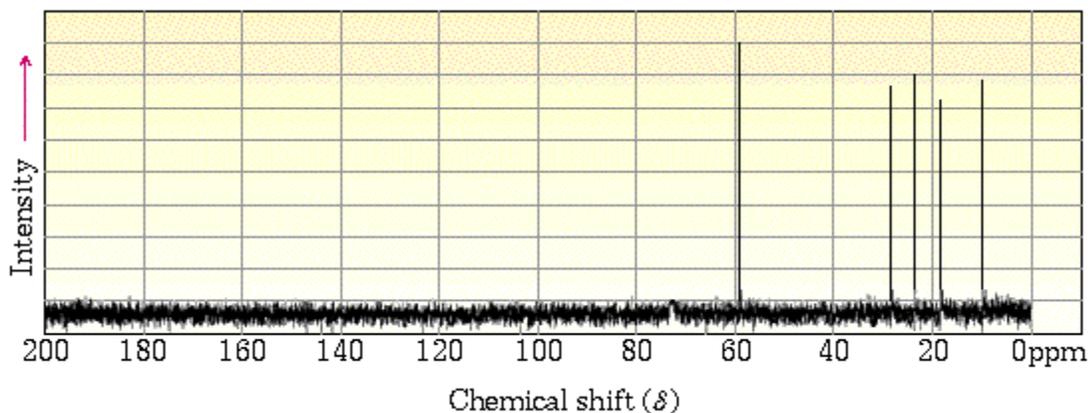
#### Differences:

a.  $^{13}\text{C}$  does not split adjacent carbon or hydrogen because it is present in only 1% abundance. Thus the splitting that would occur is not seen because it is only a small contribution to the whole which is dominated by the  $^{12}\text{C}$  effect (which is no splitting)

b. Because  $^{13}\text{C}$  is in such low abundance it is very hard to see its signal. This requires signal averaging over long times. Many spectra are taken and averaged. Since noise is random it does not increase with time, but the signal is additive over many spectra.

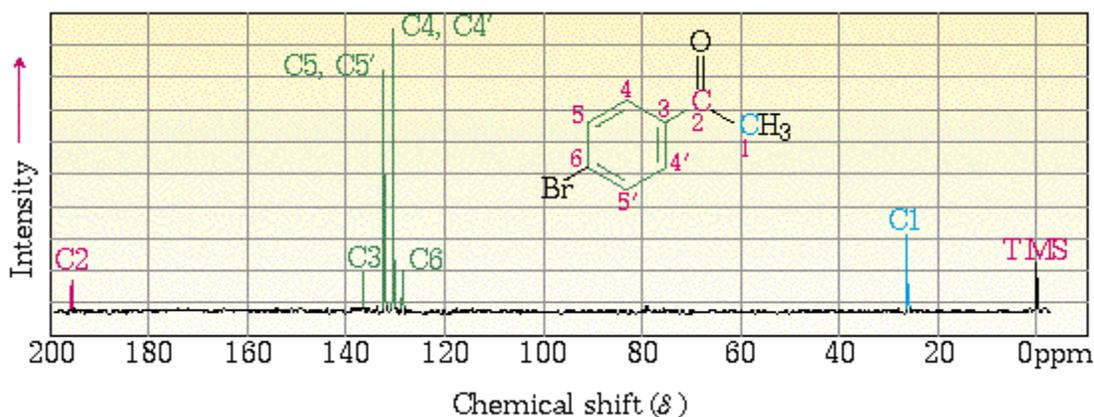
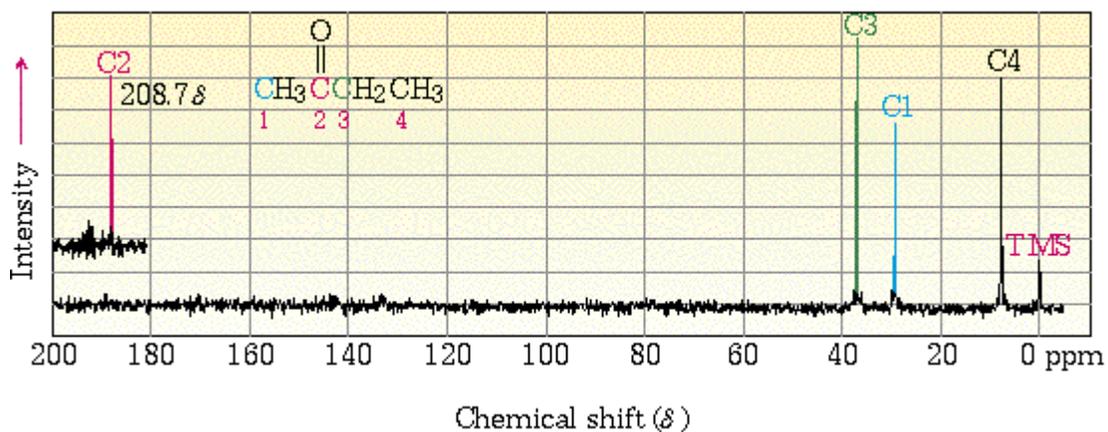


(a)



The above spectra is 1-pentanol,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ . Notice the five different signals for each carbon because each is different. With the much wider chemical shift range and single peaks there is little chance of overlap. Which resonance is associated with which carbon?

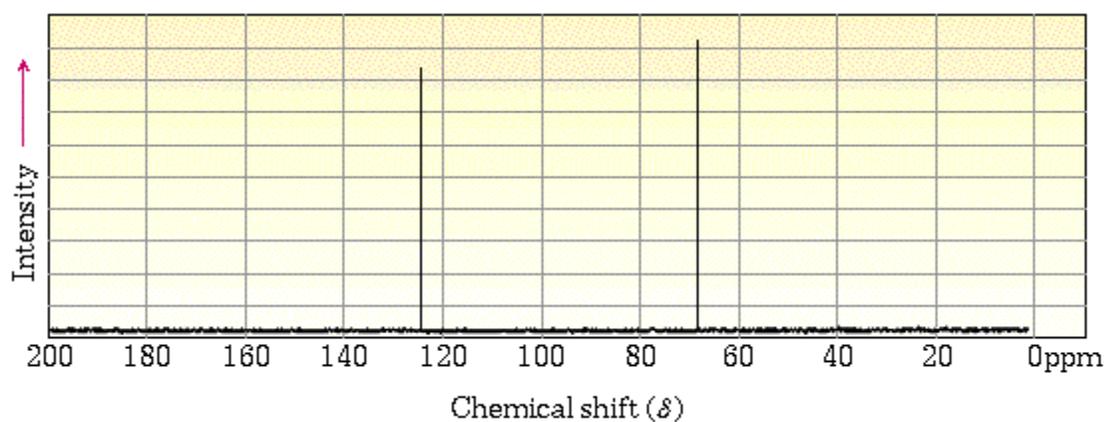
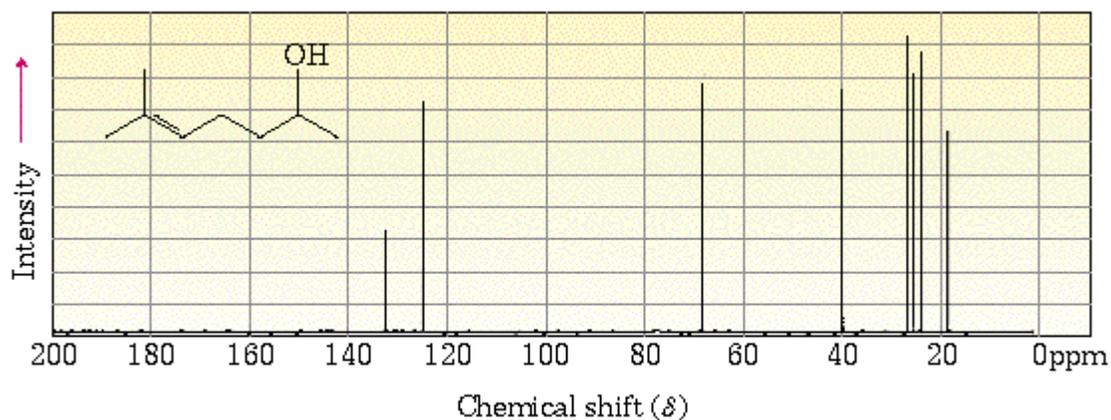
## Another Example



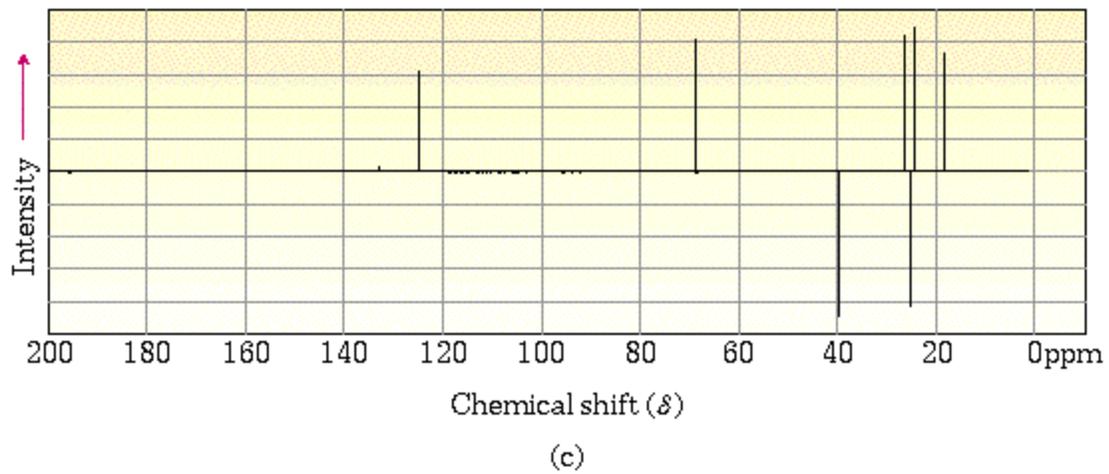
Notice that in these spectra that the peak heights for single carbons are not the same. And no attempt has been made to integrate them. This is because integration does not work for time averaged spectra.

Notice also that the hydrogens are not splitting the carbon signals as would be expected. This

is purposely done to simplify the spectrum by a broad band rf irradiation of the hydrogen region, which removes the splitting, the hydrogens no longer exist in one or the other energy state. Allowing such splitting causes  $\text{CH}_3$  carbon to appear as a quartet,  $\text{CH}_2$  as a triplet, and  $\text{CH}$  as a doublet thus allowing determination of what kind of carbon it is. Another technique for the same information is the Distortionless Enhancement by Polarization Transfer (DEPT).



In a) all carbons are seen, in b) only CH carbons show, in c) positive signals are seen for CH and  $\text{CH}_3$  and negative peaks are seen for  $\text{CH}_2$

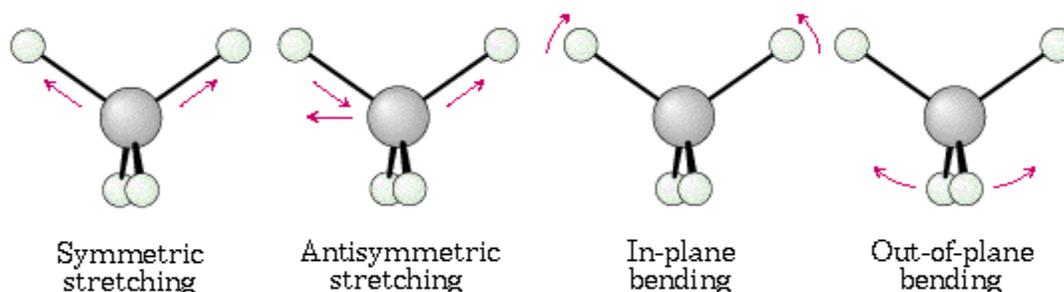


**Figure 13.19** DEPT-NMR spectra for 6-methyl-5-hepten-2-ol.

## 4. Infrared Spectroscopy (section 13.19)

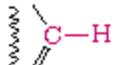
We mentioned in the chapter's beginning that infrared radiation was of the right energy level to cause increases in the vibrational energy states of organic molecules. The energy needed to change vibrational states depends on bond strength and the mass of the atoms bonded. Thus different bonds absorb different IR wavelengths and these are indicative of what functionality (bonds) are in the molecule. Each functionality can vibrate in several different ways and thus absorb several wavelengths but usually we use only one as diagnostic.

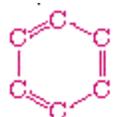
For example



In Table 12.1 (or 13.4 of our text) are collected more data than you need

Table 12.1 Characteristic IR Absorptions of Some Functional Groups

Functional group class	Band position ( $\text{cm}^{-1}$ )	Intensity of absorption
Alkanes, alkyl groups		
C—H	2850–2960	Medium to strong
Alkenes		
=C—H	3020–3100	Medium
C=C	1640–1680	Medium
Alkynes		
$\equiv\text{C—H}$	3300	Strong
—C $\equiv\text{C—}$	2100–2260	Medium
Alkyl halides		
C—Cl	600–800	Strong
C—Br	500–600	Strong
C—I	500	Strong
Alcohols		
O—H	3400–3650	Strong, broad
C—O	1050–1150	Strong
Aromatics		
 C—H	3030	Medium



Amines

N—H

C—N

Carbonyl compounds<sup>a</sup>

C=O

Carboxylic acids

O—H

Nitriles

C≡N

Nitro compounds

NO<sub>2</sub>

1600, 1500

Strong

3300–3500

Medium

1030, 1230

Medium

1680–1750

Strong

2500–3100

Strong, very broad

2210–2260

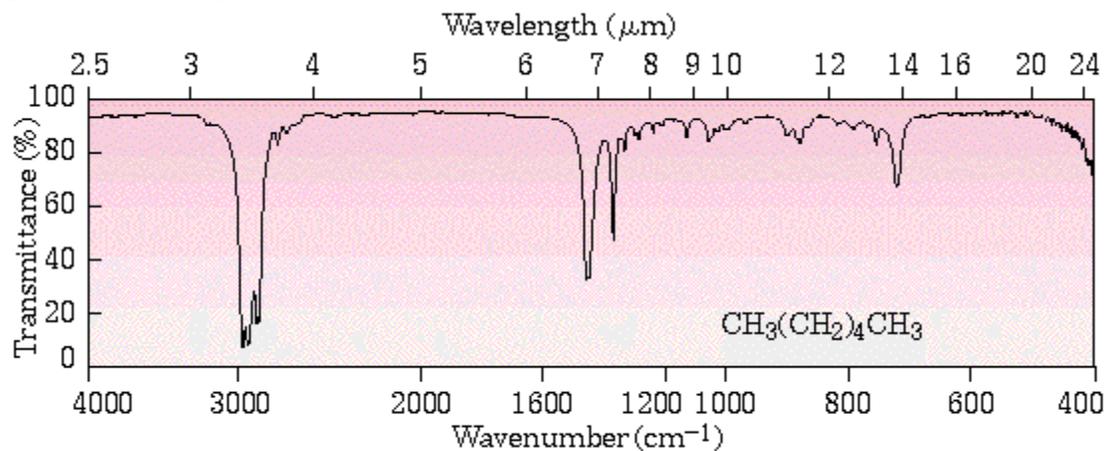
Medium

1540

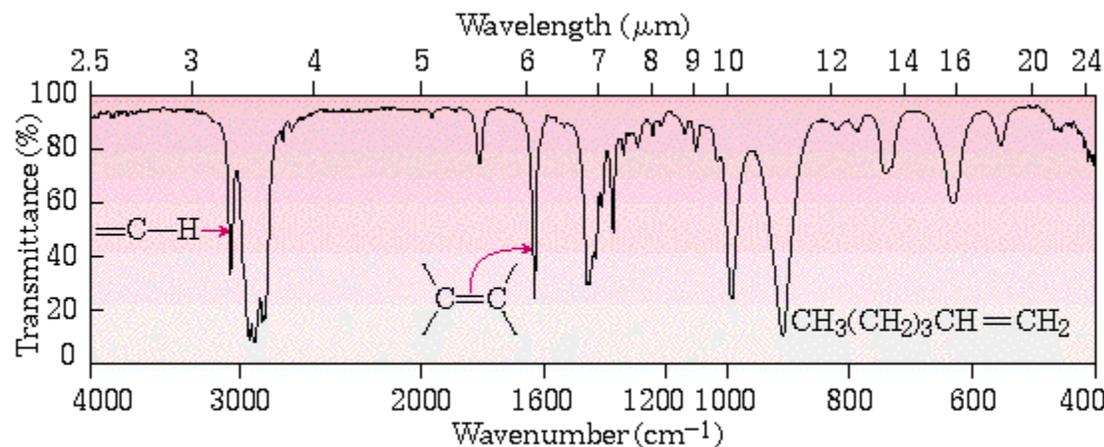
Strong

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

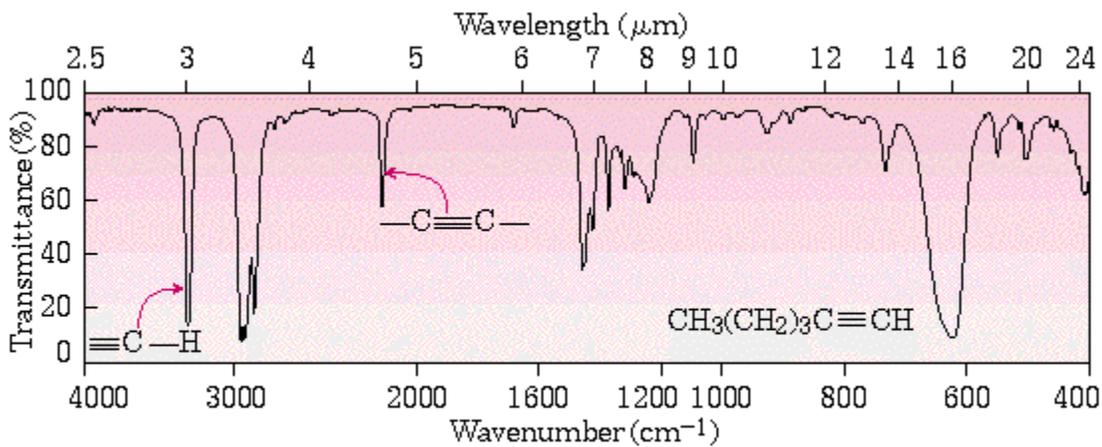
**So when we look at an IR spectrum we look for the absorptions that are indicative of particular groups. For example:**



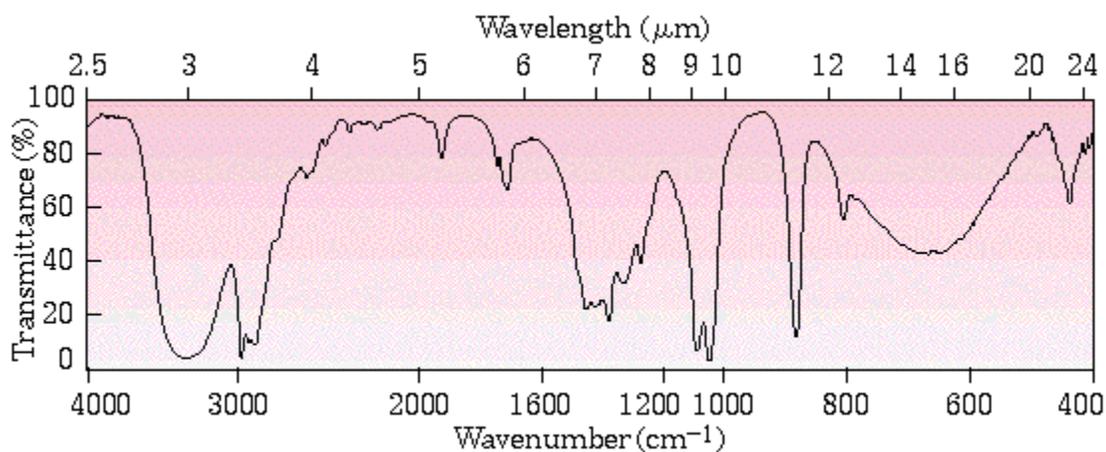
(a)



(b)



(c)



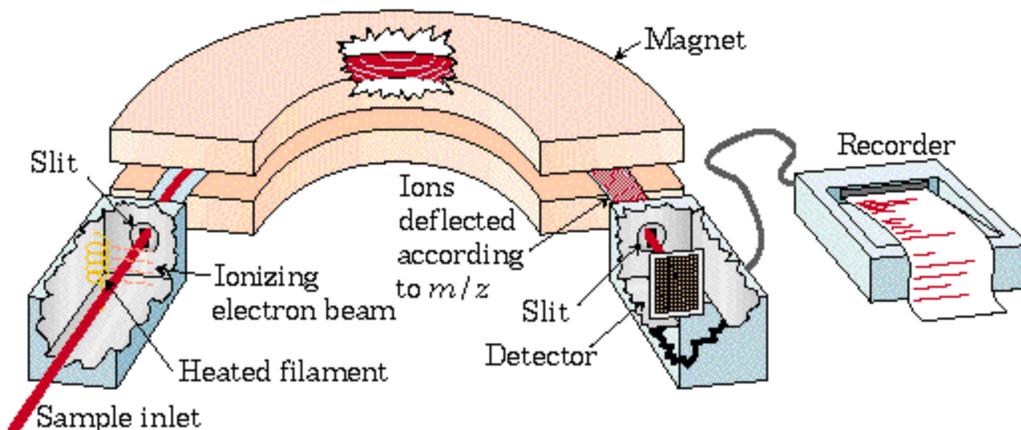
### Ethyl alcohol

The fingerprint region is that area below 1600 wavenumbers which is ordinarily too complex to be diagnostically useful. The fingerprint region can be interpreted but is principally used to compare individual compounds to one another for identification of the compound, hence the name fingerprint.

## 5. Mass spectrometry

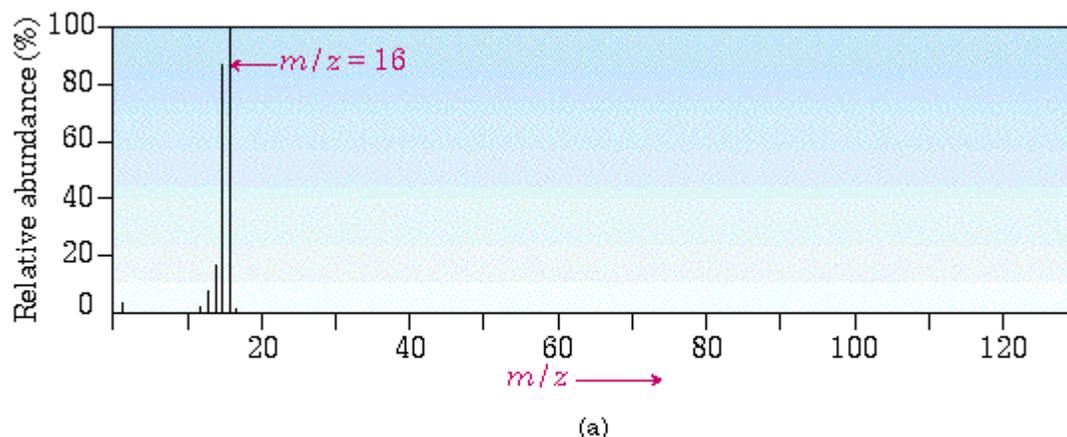
Mass spectra give us information on the molecular weight, the molecular formula (at high resolution), and what substructures are present.

How does it work?



An electron is ejected from the molecules by the ionizing electron beam and passed through an electrical field to accelerate them to a uniform velocity. These ions are then passed through a magnetic field. Moving charges are deflected by a magnetic field, with low mass ions being deflected more than heavy mass ions (the force is constant because they all have a single charge but momentum is greater for the heavier ions). These ion positions are recorded as they strike the detector and a spectrum with mass on the x-axis is recorded.

Two sample spectra:

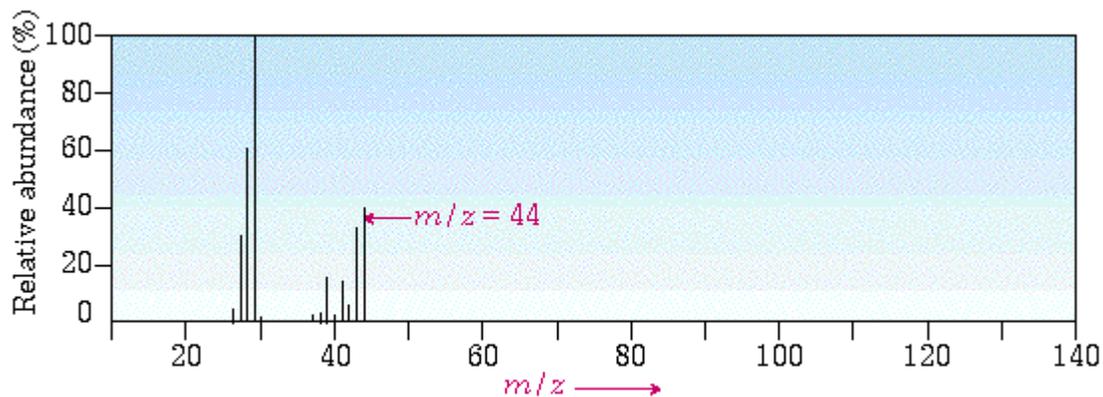


**Figure 12.2** Mass spectra of (a) methane ( $\text{CH}_4$ ; MW = 16) and (b) propane ( $\text{C}_3\text{H}_8$ ; MW = 44).

**Parent or molecular ion ( $M^+$ ) = The ion of the compound with only the loss of the electron. Usually the heaviest peak in the spectrum.**

**$M+1$ ,  $M+2$  = Small peaks higher than the molecular ion due the presence of isopes of hydrogen ( $D,T$ ) and carbon ( $^{13}\text{C}$ ) which give the molecule higher mass. Since the isotopes are low abundance, these mmolecules are not common and the peaks are small. Two exceptions to the low abundance isotope are Chlorine ( $^{35}\text{Cl} : ^{37}\text{Cl}$ , 3:1) and Bromine ( $^{79}\text{Br} : ^{81}\text{Br}$ , 1:1).**

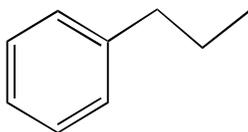
**Base peak = a book keeping device to record the intensity of the tallest peak in the spectrum as 100% and measure the other peaks in relation to it in percent. But also the most stable or readily formed cation.**



(b)

Propane

**Fragment or daughter ion.** A molecule with a missing electron is unstable and begins to break down. A typical example would be propyl benzene



Which will yield benxyl cations in good yield.

Other stable cations like t-butyl (57), phenyl (77), isopropyl (43) are common if they can be derived from the structure. Alkyl structures will peel off  $-CH_2-$  groups to give peaks differing by 14 mass units.

High resolution MS yields exact molecular formulas. If the mass resolution is to the fourth decimal eg. 196.3545 the formula can be determined uniquely, only one combination of elements can produce that value.

## **The presence of double bonds or rings indicated by molecular formula.**

One last item in this chapter is the use of a determination of the number of double bonds or rings from the molecular formula. This can be helpful in problem solving in spectroscopy.

The formula of an alkane is  $C_nH_{2n+2}$ ,  $C_4H_{10}$ . Alkenes or rings have the formula  $C_nH_{2n}$ ,  $C_4H_8$ . Increasing the number of double bonds increases that hydrogen deficiency by two for each double bond or ring. The benzene,  $C_6H_6$ , is eight hydrogens short of an alkane (saturated) formula which corresponds to 4 double bonds or ring, in this case one ring and three double bonds.

An oxygen in the formula has no effect on the C,H numbers. A halogen replaces an H so we can count H and X in determining the hydrogen deficiency. Nitrogen adds one hydrogen to the expected alkane formula, so  $C_8H_{19}N$  is a saturated alkane. Note the odd number of hydrogens resulting. This has an impact on molecular weight as well because it produces an odd numbered mass while organic molecules are invariably even-numbered. (This is due to the fact that O,C are even massed, H comes in twos, except when replaced by halogen which are odd-numbered). So only compounds with odd numbers of N are odd-number masses.