7 Spectroscopy of Organic Compounds

7.1 Introduction

Modern spectroscopy methods have revolutionized the study of organic chemistry. Nearly all compounds that one encounters in an introductory organic chemistry course can be quickly identified using readily available spectroscopic techniques. This contrasts with traditional chemical characterization methods used before modern spectroscopy was available. It generally requires several hours, in some cases days, of laboratory work to fully characterize a compound using chemical methods, whereas the same degree of characterization can often be achieved in minutes using spectroscopy.

Particularly useful to the practicing organic chemist are Infrared (IR) and Nuclear Magnetic Resonance (NMR) Spectroscopy. These two techniques alone are often sufficient to determine the structure and purity of a compound once the molecular formula is determined by other means. This chapter will specifically focus on the use of IR and NMR spectroscopy to determine the structure and purity of organic compounds synthesized in the laboratory.

Interaction of Light and Matter: The Physical Basis of Spectroscopy

As simple as it sounds, spectroscopy consists of shining light on matter and monitoring which wavelengths are absorbed and which wavelengths are reflected or transmitted. Although the concept is very simple, it wasn't until the 20th century that scientists began to understand the amazing analytical power of probing the stucture of matter by using a wide range of wavelengths of light within and outside the visible range. The major breakthrough that led to this was understanding of the quantum nature of light and matter and the quantum mechanical nature of their interaction. Once these relationships were understood, it was realized that photons of light can serve as quantum probes, giving back precise information about energy levels within molecules.

Properties of Light: Wavelength, Frequency and Energy

Although the term "light" is routinely used to refer to visible light, the portion of the electromagnetic radiation spectrum that the human eye is sensitive to, the term light in its broader definition includes the entire electromagnetic radiation spectrum, as represented in

Figure 7.1. The spectrum is continuous and covers a very wide range of wavelengths from radio waves with greater than a 10 meter wavelength to gamma rays with wavelenths shorter than 10^{-17} meters.

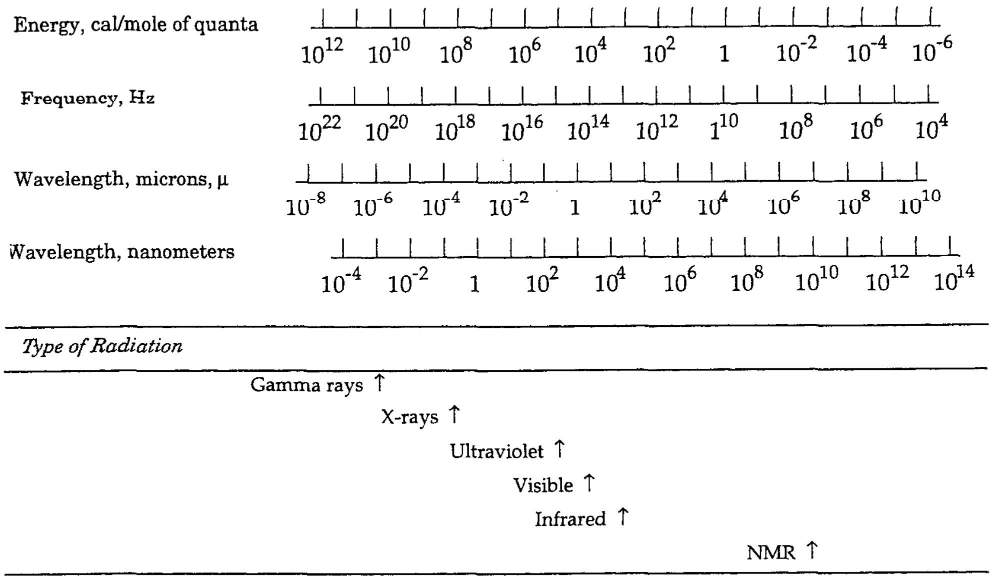


Figure 7.1: The electromagnetic spectrum: energy, frequency, and wavelength.

Since the speed of light is the same for all wavelenghts, then for any specific wavelength, the relationship between frequency (ν = number of waves per second) and wavelength (λ = meters) is given by:

$$\nu = c/\lambda$$

where c is the speed of light. According to this equation, wavelength and frequency are inversely proportional. The shorter the wavelength, the higher the frequency.

In addition to its wave properties, all light is known to exist as small indivisible units, or particles called photons. For any specific wavelength of light, the enrgy of each photon is exactly the same. The photon energy can be readily calculated using the relationship:

$$E = h\nu = hc/\lambda$$

Where h = Plank's constant. Therefore, the photon energy is inversely proportional to the **wavelength** and directly proportional to the **frequency**.

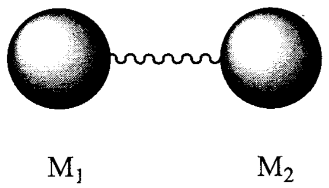
Energy States of Matter

When matter is observed at the atomic or molecular level, all energy changes are discontinuous; they take place in quantized steps or jumps. This is true, for all types of energy changes, whether they involve, for example, changes in the rotation of molecules, the vibration of atoms connected by chemical bonds, or the energy states of electrons in molecular orbitals. This quantum nature of matter taken together with the quantum nature of light provides interesting consequences when light interacts with matter. When the energy of a photon of light exactly matches the difference between two energy levels within a molecule, the photon can be absorbed by the molecule and the photon's energy completely transferred to the molecule resulting in the disappearance of the photon. This absorption of light photons with a change in energy of molecules is the common basis for all forms of spectroscopy.

7.2 Infrared Absorption Spectroscopy

Infrared Light Absorption and Molecular Structure

The photon energy of light in the infrared range corresponds to differences in vibrational energy levels of molecules. Absorption of infrared light results in an increase in the amplitude of various molecular vibrations. To interpret infrared spectra, bonds between atoms in molecules can be thought of as springs, and the atoms as point masses at the ends of the springs. According to this model, parts of the molecule can stretch and bend independently of the rest of the molecule. The frequency of stretching and bending can be related to the atomic masses and the force constants of the springs as shown below:



$$\nu \propto \sqrt{\frac{k}{\mu}} \qquad\qquad \mu = \frac{M_1 M_2}{M_1 + M_2}$$

where, ν is the frequency of stretching or bending, **k** is the force constant (a measure of the stiffness of the spring), and **μ** is the reduced mass (incorporating the masses at the two ends of the spring). The reduced mass is defined as:

where **M_1**, and **M_2** are the total masses at the two ends of the spring.

Uses of Infrared Spectra

Infrared spectra are used for identification and for structural determination. The simplest use of infrared spectra is to determine whether two samples are identical. The infrared spectrum of an organic compound provides such a detailed and unique patten of vibrational absorption bands that it serves as a "fingerprint" of the compound. If two samples are the same, their IR spectra, obtained under the same conditions, must be the same. If the samples are different, their spectra will be different.

When synthesizing a known compound in the laboratory, comparison of the IR spectrum of the newly synthsized sample with a sample of known structure and purity is a convenient and sensitive way to establish the identity and purity of the laboratory sample. Comparison of the IR spectra of different fractions obtained in a fractional distillation or of material before and after recrystallization is one way to follow the progress of a purification.

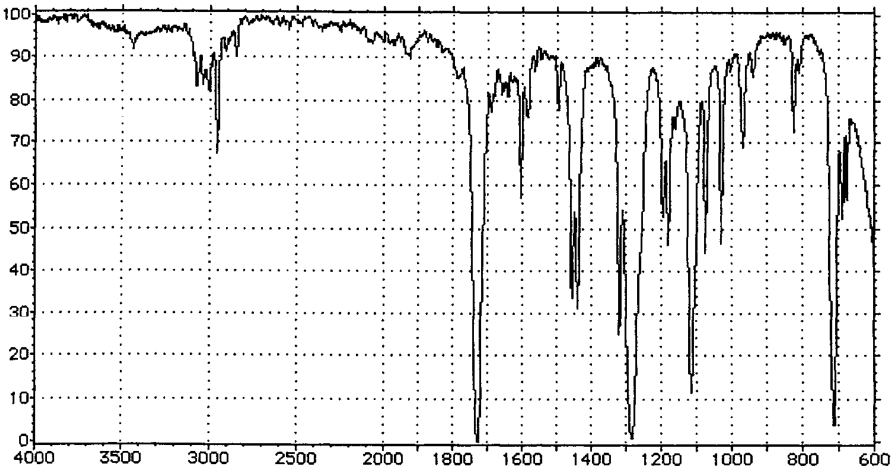


Figure 7.2 : IR spectrum of the aromatic compound methyl benzoate; thin film.

Determination of Molecular Structure

A more sophisticated level of interpretation of an IR spectrum is to use it to establish the structure of an unknown material. Comparison of IR spectra of substances of known structure has led to the establishment of many correlations between wavelength (or frequency) of IR absorption and features of molecular structure. The presence or absence of absorption at certain wavelengths indicates the presence or absence of certain functional groups or structural features. Table 7.1 presents many of the most useful correlations for structure determination. Establishing the presence or absence of carbonyl groups and alcohol groups is among the easiest and most definitive of functional group assignments that can be made using IR. The C=O stretching absorption of any carbonyl group typically shows a distinctive strong band in the region of 1730-1670 cm^{-1}. Figure 7.2 shows the IR spectrum of methyl benzoate (an ester).

The cabonyl stretching band is the strong peak slightly above 1700 cm^{-1}.
The O-H stretching absorption of an alcohol group shows up as a medium to strong band in the region 3700-3300 cm^{-1}. Figure 7.3 shows the IR spectrum of isopropanol as a pure liquid. The very stong, broad absorption band in the range of 3300 to 3500 cm^{-1} is the O-H stretching band. The broad appearance of this band is due to extensive hydrogen bonding.

Sample Preparation

For infrared absorption spectrometry the sample must be placed in a beam of infrared radiation. The container or support for the sample must be transparent to infrared radiation and must therefore be made of one of a small number of materials which cannot include glass. The most commonly used material is sodium chloride, which is transparent between 5000 and 600 cm^{-1}.

Liquid Samples

The spectrum of a pure liquid is most easily determined as a liquid film between a pair of sodium chloride plates. A drop of the liquid is placed in the center of one of the salt plates, and the second plate is put on top. The pair of plates with the thin liquid film in between is then carefully placed in a sample holder and the top of the holder is gently pressed in place tohold the plates together. The sample holder is then placed in the sample beam of the instrument, after a background scan has been obtained. If the strongest peak in the spectrum absorbs more than about 98% of the light, then the amount of sample is reduced by separating the plates and wiping one of the plates clean with a chem-wipe tissue. After removing the sample from one side of the plates, the plates may be placed together again in the holder and another scan taken. The spectra shown in Figures 7.2 and 7.3 were obtained using thin films of liquid.

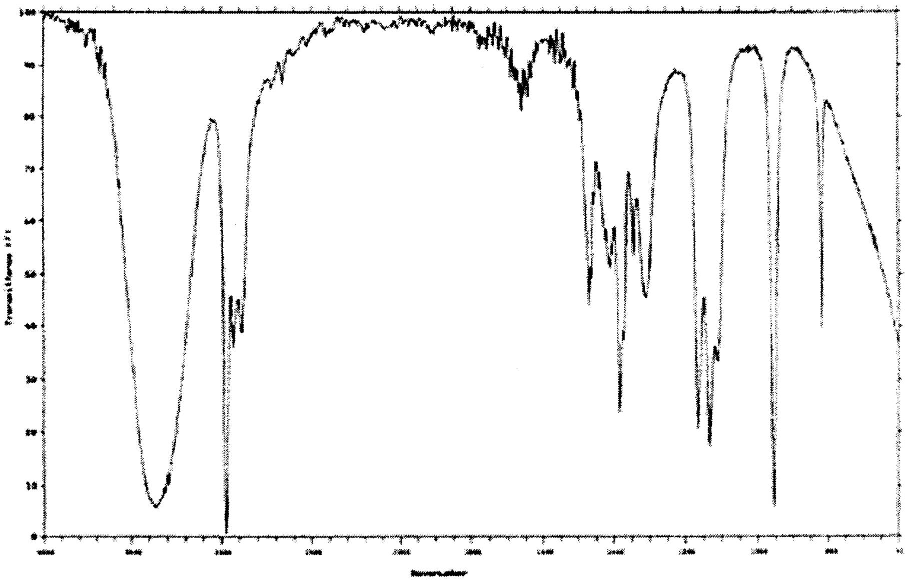


Figure 7.3: IR spectrum of compound isopropanol.

Solid Samples: The Thin Film Method

With modern, high resolution FTIR instruments, good IR spectra can be obtained on solid samples as thin films on sodium chloride plates. This is the simplest and easiest way to obtain the IR spectrum of a solid sample. A small amount of sample (< 20 mg) is dissolved in a minimum amount (< 5 ml) of a dry, volatile solvent (e.g. dichloromethane). A few drops of the solution are placed on the face of a sodium chloride plate and allowed to evaporate leaving a thin film of solid on the face of the plate. A second clean salt plate is positioned over the film, the plates are placed in a sample holder and the spectrum is obtained as with liquid thin films. If the IR absorption bands in the spectrum are too weak, the salt plates are separated and a few more drops of solution are evaporated onto the plate containing the film. If a NMR spectrum has been obtained on a solid sample dissolved in a typical NMR solvent (e.g. $CDCl_3$) a few drops of this solution evaporated onto a salt plate is normally sufficient to obtain the IR spectrum.

Solid Samples: The Solution Method

The IR spectra of solids are very often determined in solution. The concentration should be adjusted, if necessary, so that the strongest peak will absorb between 90 and 98% of the light. The absorbance of a sample is proportional to both its concentration and its thickness.

The ideal solvent would be transparent over the entire infrared range of wavelengths, but no such liquids are known. For this reason, the spectrum of the solvent must be subtracted from that of the sample dissolved in this solvent. This is done in a double beam instrument by placing a second cell that contains pure solvent in the reference beam, or in a single beam instrument by recording the spectrum of the pure solvent as background and then subtracting this background spectrum. Carbon tetrachloride, and chloroform are the solvents most often used for infrared spectroscopy.

Solid Samples: The KBr Method

Another method commonly employed to obtain the infrared spectrum of a solid is to prepare a potassium bromide salt pellet containing the solid sample evenly dispersed throughout the pellet. This method incorporates the solid sample right into the salt window. KBr pellets can be prepared by grinding 1-2 mg of sample with about 100-400 mg of anhydrous potassium bromide in a clean mortar and to press the resulting mixture into a translucent wafer, using a die press. The wafer is then mounted in the sample beam.

Absorption in the -OH region in a spectrum obtained by the KBr pellet method must be interpreted with great caution, since it is hard to make sure that no water gets into the sample during preparation.

Table 7.1: Infrared absorption-structure correlations

		Range (microns)	*Intensity*	*Range (cm^{-1})*
C-H stretching vibrations				
Alkane		3.38-3.51	m-s	2962-2853
Alkene		3.23-3.32	m	3095-3010
Alkyne		3.03	s	3300
Aromatic		3.30	v	3030
Aldehyde		3.45-3.55	w	2900-2820
	and	3.60-3.70	v	2775-2700
C-H bending vibrations				
Alkane		6.74-7.33	v	1485-1365
Alkene				
monosubstituted (vinyl)		7.04-7.09	s	1420-1410
		7.69-7.75	w-s	1300-1290
		10.05-10.15	s	995-985
	and	10.93-11.05	s	915-905
disubstituted cis		14.5	s	690
disubstituted trans		7.64-7.72	m	1310-1295
	and	10.31-10.42	s	970-960
disubstituted gem		7.04-7.09	s	1420-1410
	and	11.17-11.30	s	895-885
trisubstituted		11.90-12.66	s	840-790
Aromatic				
5 adjacent H atoms		13.3	v,s	750
	and	14.3	v,s	700
4 adjacent H atoms		13.3	v,s	750
3 adjacent H atoms		12.8	v,m	780
2 adjacent H atoms		12.0	v,m	830
1 isolated H atom		11.3	v,w	880
N-H stretching vibrations				
Amine not hydrogen bonded		2.86-3.03	m	3500-3300
Amide		2.86-3.2	m	3500-3140
O-H stretching vibrations				
Alcohols and phenols				
not hydrogen bonded		2.74-2.79	v,sh	3650-3590
hydrogen bonded		2.80-3.13	v,b	3750-3200
Carboxylic acids				
hydrogen bonded		3.70-4.00	w	2700-2500
C-O stretching vibrations				
Esters				
formates		8.33-8.48	s	1200-1180
acetates		8.00-8.13	s	1250-1230
propionates etc.		8.33-8.70	s	1200-1150
benzoates; phthalates		7.63-8.00	s	1310-1250
	and	8.69-9.09	s	1150-1100

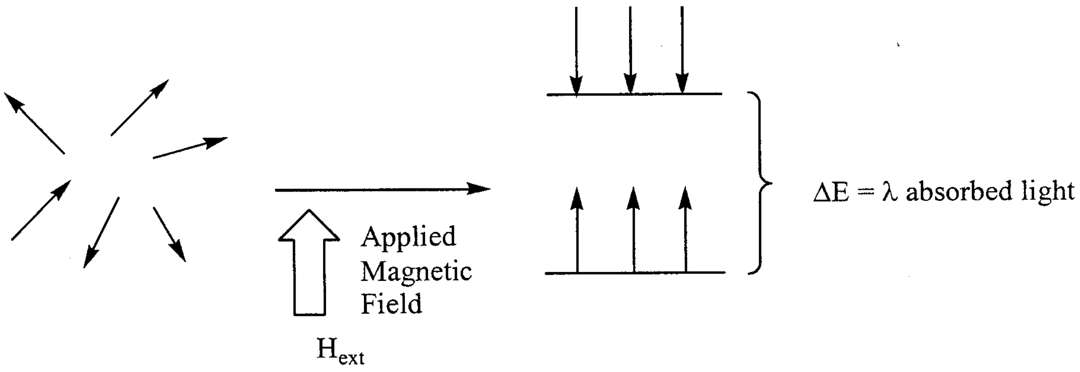
Table 7.1: Infrared absorption-structure correlations

Carbon-halogen stretching vibrations				
C-F		7.1-10.00	s	1400-1000
C-Cl		12.5-16.6	s	800-600
C-Br		16.6-20.0	s	600-500
C-I		approx. 20	s	approx. 500
C=C stretching vibrations				
Isolated alkene		5.99-6.08	v	1669-1645
Conjugated alkene				
C=C conjugated		6.25	m-s	1600
C=O conjugated		6.07-6.17	m-s	1647-1621
phenyl conjugated		6.15	m-s	1625
Aromatic		6.25	v	1600
		6.33	m	1580
		6.67	v	1500
	and	6.90	m	450
C=0 stretching vibrations				
Aldehydes				
saturated aliphatic		5.75-5.81	s	1740-1720
α,ß-unsaturated aliphatic		5.87-5.95	s	1705-1680
Ketones				
saturated acyclic		5.80-5.87	s	1725-1705
saturated 6-ring and larger		5.80-5.87	s	1725-1705
saturated 5-membered ring		5.71-5.75	s	1750-1740
α,ß-unsaturated acyclic		5.94-6.01	s	1685-1665
aryl alkyl		5.88-5.95	s	1700-1680
diaryl		5.99-6.02	s	1670-1660
Carboxylic acids				
saturated aliphatic		5.80-5.88	s	725-1700
aromatic		5.88-5.95	s	1700-1680
Carboxylic acid anhydrides				
saturated acyclic		5.41-5.56	s	1850-1800
	and	5.59-5.75	s	1790-1740
Acyl halides				
chlorides		5.57	s	1795
bromides		5.53	s	*1810*
Esters and lactones (cyclic esters)				
saturated acyclic		571-5.76	s	1750-1735
saturated 6-ring and larger		5.71-5.76	s	1750-1735
α,β-unsaturated and aryl		5.78-5.82	s	1730-1717
vinyl esters		5.56-5.65	s	1800-1770
Amides and lactams (cyclic amides)		5.88-6.14	s	1700-1630
Triple bond stretching vibrations				
C≡N		4.42-4.51	m	2260-2215
C≡C		4.42-4.76	v,m	2260-2100

w = weak absorption m = medium absorption s = strong absorption
v = variable intensity of absorption sh = sharp absorption b = broad absorption.

7.3 Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectrometry (NMR) measures the absorption of "light" energy in the radio-frequency portion of the electromagnetic spectrum (Figure 7.1). The mechanism of energy absorption involves reorientation of magnetic nuclei with respect to an applied magnetic field (Figure 7.4). NMR spectrometry is based on the fact that the energy of the photon of absorbed radio-frequency (rf) radiation goes into changing the orientation of the magnetic nucleus from being "with" the magnetic field to being "against" the field.



Spin

Only atoms with spin can be viewed by NMR. Spin is defined by the mass number (the number of protons and neutrons) and the atomic number (the number of protons).

Spin 1/2 atoms: mass number is odd. examples: ^{1}H and ^{13}C.

Spin 1 atoms: mass number is even. examples: ^{2}H and ^{14}N.

Spin 0 atoms: mass number is even. examples: ^{12}C and ^{16}O.

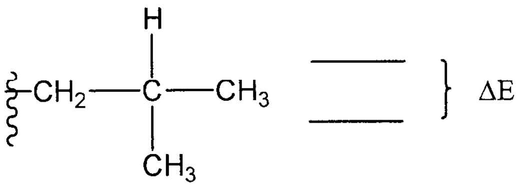
For the purposes of this course, proton NMR (in which hydrogen nuclei are observed) will be discussed. However, any nuclei with spin can be observed (carbon-13 and fluorine-19 are also common).

Shielding

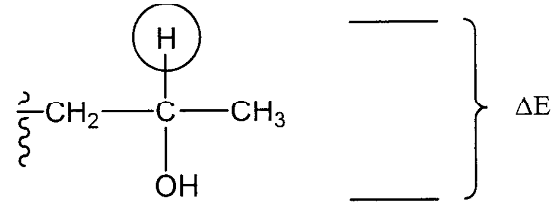
Electrons around the nuclei can "shield" the nucleus from the effects of the external magnetic field, lowering ΔE (Figure 7.5). Thus, the magnetic field felt by any specific nucleus can be expressed as in Equation 7.1

$$H_{nuc} = H_{ext} - H_{shielding} \qquad \text{(Eq. 7.1)}$$

where H_{nuc} is the field felt by the nucleus, H_{ext} is the applied external magnetic field, and $H_{shielding}$ is the shielding or opposing magnetic field due to electrons in the vicinity of the nucleus.



δ 0.9 ppm



δ 3.8 ppm

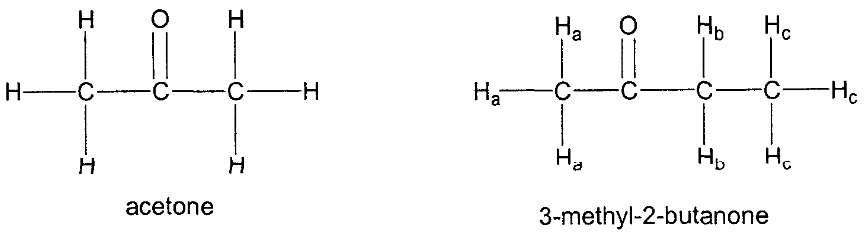
Chemical Shift

ΔE is proportional to the chemical shift, δ (delta) which is expressed in units of parts per million (ppm). The less shielding around a nuclei, the larger the delta E, and the larger the chemical shift. Tetramethylsilane (TMS) is used as a reference compound (δ = 0 ppm) because all of the hydrogen nuclei are very strongly shielded by the large and uniform cloud of electrons in this molecule.

The chemical shift of a proton signal can give valuable information about the shielding, which in turn can provide an indication of the types of nearby atoms or functional groups. Electronegative atoms such as O, N, X, or double bonds can **decrease** shielding ("deshield") resulting in an increase in chemical shift. Table 7.2 (at the end of this chapter) provides typical chemical shift ranges for hydrogen nuclei in the vicinity of various functional groups. This type of chemical shift correlation table is a powerful tool for use in determining structures of compounds from their ^1H NMR spectra.

Equivalent Nuclei

The symmetry of molecules plays a very important role in determining the number of signals observed in the NMR spectrum. When two or more hydrogen nuclei are equivalent by symmetry they will have the same chemical shift and they will give rise to one signal (but not necessarily a single peak - see "splitting" below) in the NMR spectrum. For example, the hydrogen nuclei in 2-Propanone (acetone) are all equivalent by symmetry and give rise to one NMR signal whereas the hydrogen nuclei in 3-Methyl-2-butanone (isopropyl methyl ketone) can be divided into three different groups (a, b, c, Figure 7.6) where the nuclei within each group are equivalent by symmetry, but the groups are not equivalent to each other by symmetry. The NMR spectrum contains 3 signals, one for each group. A NMR signal may be a single peak (singlet) or a closely spaced group of peaks (doublet, triplet, quartet, or other multiplet) which has a distinct chemical shift and represents one or more equivalent nuclei.


acetone

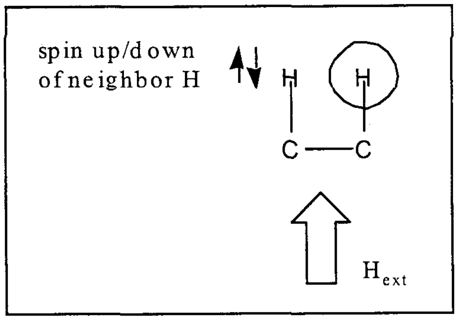
3-methyl-2-butanone

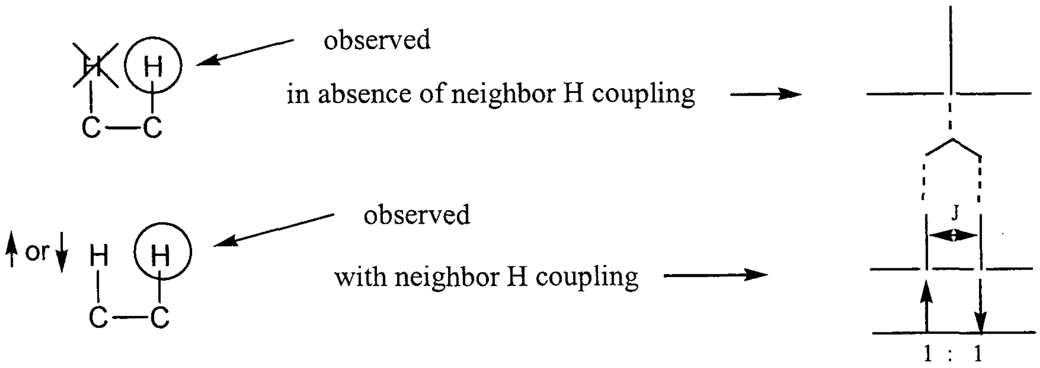
Figure 7.6: Structures of 2-propanone (acetone) and 3-methyl-2-butanone.

Splitting

In addition to chemical shift, the multiplicity or "splitting" of peaks can give valuable information of help in determining molecular structure. The presence of atoms with spin in close proximity to the observed nuclei can affect the signal of that nuclei.

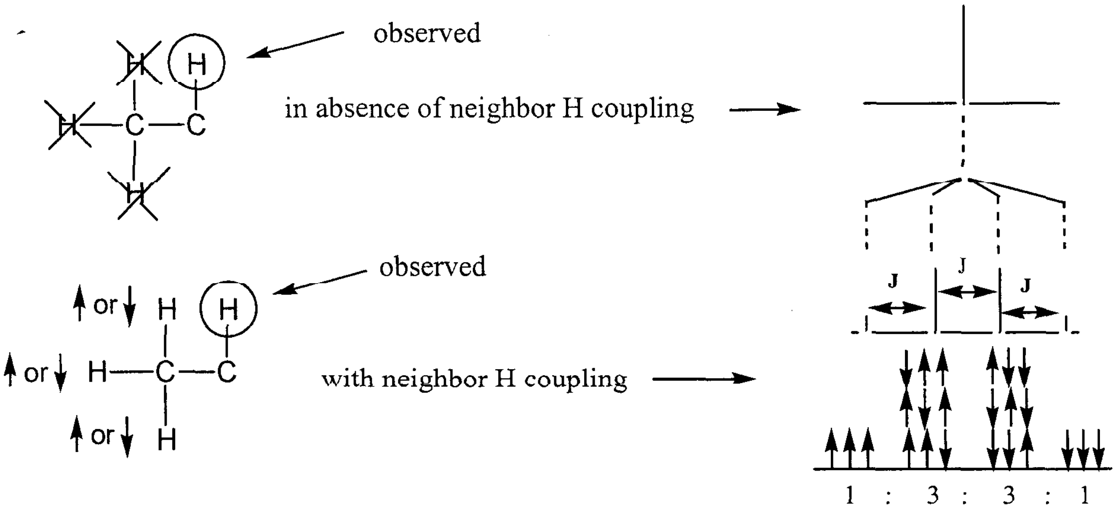
The H observed will have a specific chemical shift due to the shielding around the nuclei. The H adjacent (3 bonds away) will also align its spin either with or against the external applied magnetic field. If the spin aligns with the external field, this increases the field felt by the observed nuclei and increases ΔE (increases the chemical shift). If the spin aligns against the external field, this decreases the field felt by the observed nuclei and decreases ΔE (decreases the chemical shift). Since it is equally likely that the neighbor nuclei with allign with or against the external field, two equivalent height signals are observed. The ratio of intensities is 1:1





The separation between these two peaks (which arise from observing a single type of nuclei) is called the coupling constant, *J*. The observed nuclei is said to "couple" with the adjacent nuclei that causes the splitting. This signal is called a "doublet".

Now consider an example where three equivalent nuclei are neighbors (3 bonds away) from the observed nuclei. Each of these nuclei has a spin that can either align with or against the external applied magnetic field. The resulting signal is a statistical population of all possible combinations. This signal is called a quartet. The ratio of intensities is 1:3:3:1

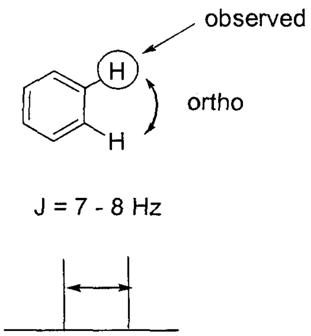


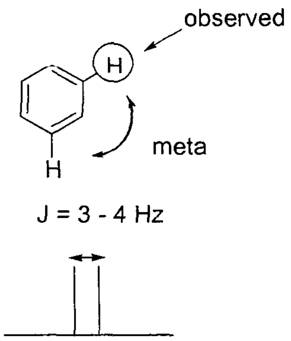
The intensities of the peaks from coupling due to the number of neighboring hydrogens can be followed by Pascal's Triangle.

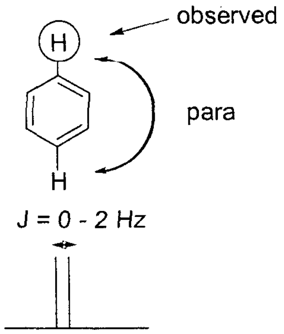
Number of Neighbors	Number of Peaks in Multiplet	Name of Multiplet	Relative Intensities within Muliplet
0	1	singlet	1
1	2	doublet	1:1
2	3	triplet	1:2:1
3	4	quartet	1:3:3:1
4	5	quintet	1:4:6:4:1
5	6	sextet	1:5:10:10:5:1
:	:	:	
N	N+1		

Other Splitting Examples

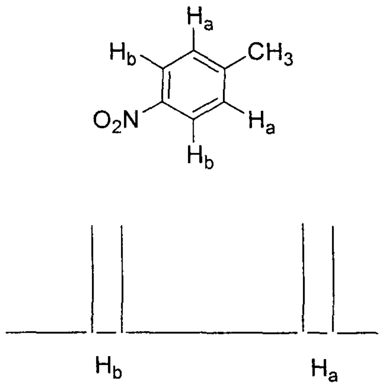
Typical splitting patterns are observed for neighboring nuclei 3-bonds away from the observed nuclei. However, extended coupling can be observed through pi-bonds. In the case of a phenyl ring, splitting can be seen around the ring. Ortho splitting is the largest (*J*), then meta, and finally para splitting is the smallest.







A para substituted phenyl ring gives rise to a very distinct coupling patern. The signal looks like two doublets. However, if the chemical shifts of the protons on the ring are very similar, then the doublets will not be of equal height; they will lean towards each other.



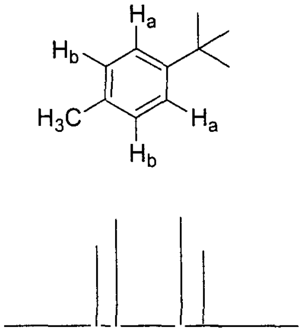
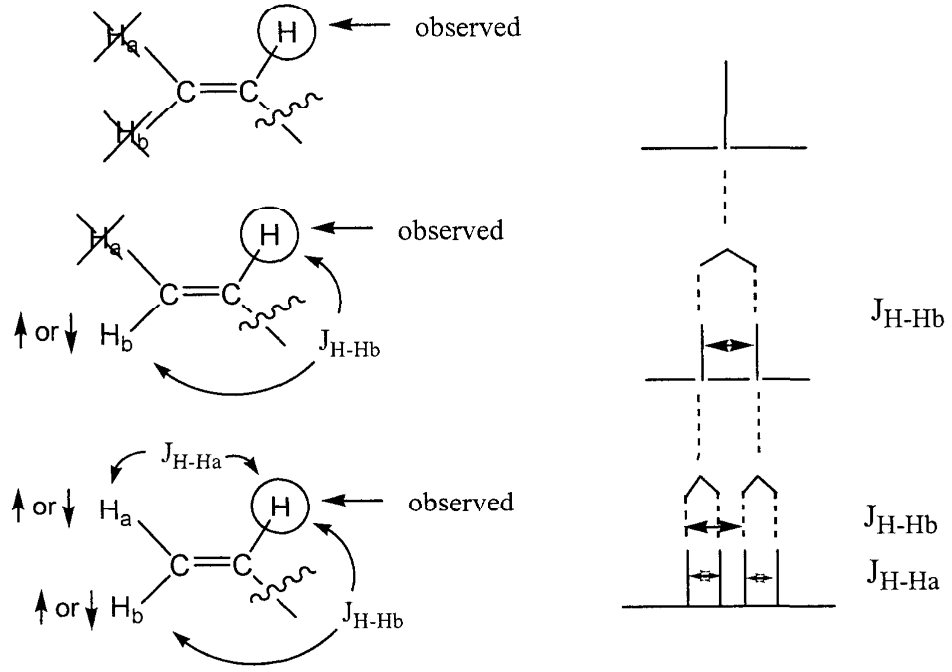


Figure out which are which?

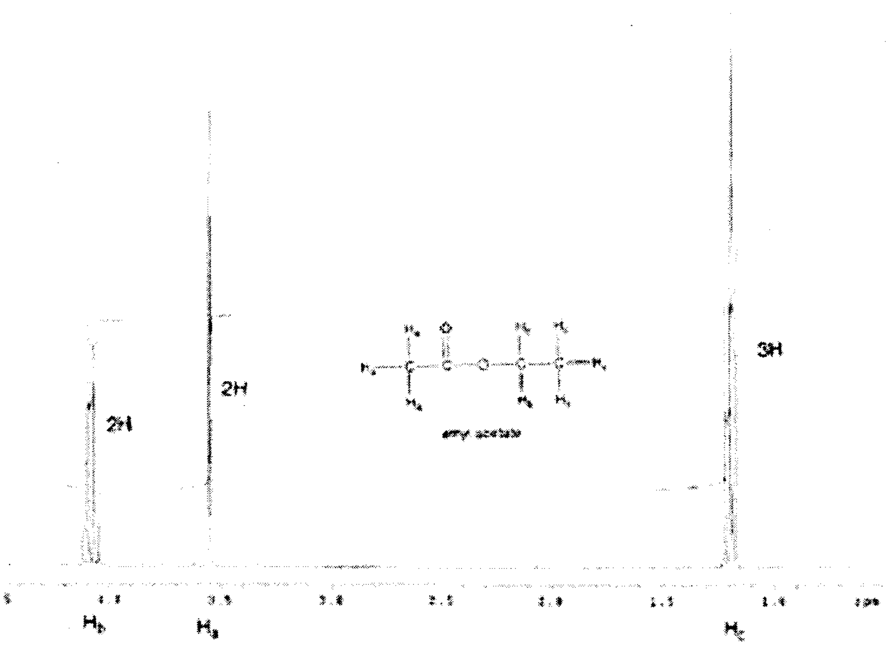
Finally, if an observed nucleus has non-equivalent neighboring nuclei, then a complicated patern can be observed. The nuclei will be split differently by each distinct group of neighbors. This is commonly seen when observing a proton on a double bond that has both a cis ($J = 8$ Hz) and a trans ($J = 15$ Hz) H neighbor. The resulting signal is called a doublet of doublets.



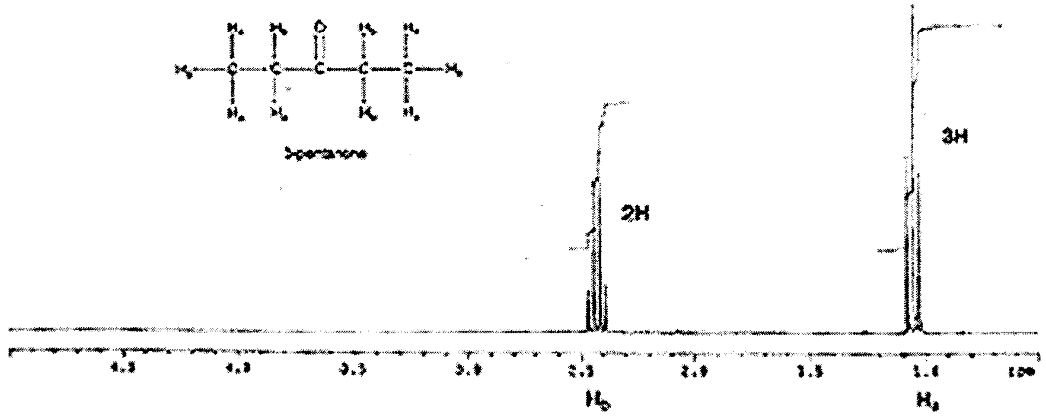
The Integral

A final important piece of information obtainable by NMR is an integration each signal. Integration of the area under the curve gives a relative amount (a ratio) of the protons giving rise to that signal. The difference in height of the "steps" of the integration can be used to determine a ratio of protons between peaks.

Keep in mind that the integration gives a ratio of nuclei giving rise to each signal, **NOT** an absolute number of nuclei. For example, integration of 3-petanone gives a ratio of 2:3, even though there are 4 H at 2.4 ppm and 6H at 1.0 ppm.



^{1}H NMR Spectrum of ethyl acetate.



^{1}H NMR Spectrum of 3-pentanone

Sample Preparation

Solvent

It is important that the solvent used in NMR does not have protons. This is because since there is much more solvent than sample, any signal from solvent protons would be much larger than from the protons in the sample, making the spectrum difficult to interpret. The deuterium resonance of deuterochloroform ($CDCl_3$ singlet , 7.24 ppm) is far from the resonances of the protons. Among other potential solvents are deuterated acetone (CD_3COCD_3, mulitplet, 2.10 ppm) and deuterated dimethylsulfoxide (d_6-DMSO, Sepetet, 2.49 ppm).

NMR Tube

The spectrum is determined with the sample in an NMR tube, a thin-walled glass tube 5mm in diameter and 180mm long, sealed at the bottom. A tight-fitting plastic cap closes the top of the tube.

To prepare the NMR sample:

1. Place a small amount of compound in a small disposable vial.
2. Transfer solvent by glass pipet into the vial to dissolve the compound.
3. Then transfer the solvent by the same glass pipet into the NMR tube.

If there is some insoluble material in the vial, then filter the solution through a pipet with glass wool or cotton.

7.4 Solving Structures using NMR/IR

1. If the molecular formula is given, calculate the number of double bond equivalents (also called units of unsaturation). Remember: the number of double bond equivalents is the number of double bonds and/or rings present in the compound. If the # of DBE is 4 or greater, consider a benzene ring substructure.

For hydrocarbons or compounds containing only C, H, and O:

$$\#\text{ of DBE} = \frac{(2n + 2) - (\text{actual }\#\text{ of H's})}{2}$$

For each halogen in formula, add 1 to actual # of H's.

For each nitrogen in formula, subtract 1 from actual # of H's.

2. If the infrared spectrum is given, look for the presence (or ab-sence) of common functional groups. In particular, look for the C=O stretch of ketones, aldehydes, esters, etc. (1650-1850 cm^{-1}). The O-H stretch of alcohols and carboxylic acids, the N-H stretch of amines, and the C=C stretch of alkenes also have characteristic absorption peaks.

3. Look at the integrations in the NMR spectrum. Determine how many protons are represented by each signal (i.e. each peak or multiplet) .

4. Look at the chemical shifts of each set of peaks and compare them to those of common structure groups as shown in an NMR correlation table.

5. Look at the splitting patterns. For simple multiplets (i.e. doublets, triplets, quartets, etc.) use the n + 1 rule to determine the number of nearest neighbor H's.

6. Write down partial structures which can be deduced from the chemical shifts, integrations, and splitting patterns.

7. Connect the pieces (partial structures) together.

8. If there is more than one possible structure, draw each possible structure and determine which one is more fully consistent with all of the NMR and IR data.