

# **Workbook of Organic Spectroscopy**

Using simulated spectra to learn how to determine organic structures.

**Phil Beauchamp,  
California State Polytechnic University, Pomona**

## **Introduction**

Humankind has probably always been fascinated with colors. A rainbow in the sky during a rain or floating across a raging waterfall or even in a bit of oil spread on a pool of water, all provide visible evidence that light is more than the bright absence of darkness. In the last 300 years humankind has learned how to use the entire spectrum of electromagnetic radiation to probe the unknown worlds of the universe - both outward and inward.

Spectroscopy is a tool which revolutionized the way scientists look at not only our immediate world, but the universe around us. It is somewhat paradoxical that we use the same tools to look at the utter vastness of the universe and the infinitesimally small world of atoms. We can probe the macroscopic and microscopic worlds of our imagination and construct theoretical models to make these worlds understandable because they both are composed of matter. The tool of electromagnetic radiation spans a wide spectrum and it has the ability to interact with matter in a variety of ways. We are, perhaps, most familiar with a small portion called visible light because we have exquisitely developed visible light detectors, called eyes. If you quickly scan about where you are currently sitting, you can easily make extremely fine distinctions of colors, contrasts, edges and shapes that would be difficult to duplicate in an instrument. This, indeed, is where scientists first began as well. Acid/base color indicators are used to determine endpoints of titrations and different natural product extracts can, at least in part, be separated by color.

New elements were discovered by spectral line patterns generated when the elements were burned in flames. As early as the 1750's the bright spectral lines of metallic salts were noticed. Characteristic colors could be generated by placing different materials in a flame of fire and when these colors were passed through a prism, individual colored lines of characteristic patterns were resolved. Around 1850 Bunsen invented a burner which mixed air and gas more efficiently to provide a colorless flame so that he could obtain clearer results in similar flame tests. Many new elements were discovered through the unique patterns of spectral lines using these techniques. Even one element not known on earth was observed in the spectrum of sunlight taken during an eclipse in India in 1868 and so became known as helium (Greek, for sun). It wasn't until 1895 that helium was discovered on earth as an inert gas formed from radioactive decay and which was released from natural gas wells deep within the earth.

Just after 1800 a heating effect was observed beyond red light in the visible spectrum and it was realized that some form of energetic radiation was present that was not visible to the eyes, but somehow generated heat. This became known as infrared (below red) radiation or light. It was also noticed that beyond the violet end of the visible spectrum, a blackening effect was produced on silver chloride. Again some invisible energetic form of radiation was present. This became known as ultraviolet (beyond the violet) radiation or light. These early tools (ultraviolet, visible and infrared radiation) were some of the most important methods available to scientists to study matter. They revolutionized physics and chemistry and led the way to the characterization of matter and even the development of quantum mechanics.

However, the high quality, simple to use instruments that current researchers are familiar with, only became available in the 1940-1950's. The development of such instrumentation rapidly accelerated our understanding of chemistry. Most likely you have used some of the older and newer techniques in your freshman chemistry labs: acid/base colorimetric titrations, flame tests of elements and/or colorimetric determination of concentrations with a UV-Vis spectrophotometer.

In modern times the use of the electromagnetic spectrum has been extended far beyond the earlier used methods. We have the ultrahigh energy radiation of x-rays that can probe the world of solid structures and the low energy radiation of microwaves, which can cook our popcorn. Even lower energy radiation, radiowaves, can carry our TV and radio signals to our eager senses. It is

interesting that humankind has learned to probe inside our very bodies using these same tools. Computed Axial Tomography (CAT) scans, using very high energy x-rays, create an internal image of the body and Magnetic Resonance Imaging (MRI) using very low energy radiowaves also creates an internal image of the body. However, for the chemist, it is the image of molecules that we seek to know.

As far as we are aware, there are only about 90 stable elements comprising the universe. Fortunately for us, in organic chemistry, our typical “organic universe” consists of about 10 elements (C, H, O, N, S, P, F, Cl, Br and I are common). However, there is infinity of possible arrangements for this handful of elements. Our goal as newly budding organic chemists is to understand how a chemist goes about using these tools to deduce a structure. There are several spectroscopic methods available to us, each providing clues in bits and pieces. Our job is much like a detective, piecing together these clues, sometimes using them to suggest the next bit of data to acquire, until we have enough information to conclusively declare our ultimate answer to the mystery before us. If you like reading stories about Sherlock Holmes, you will enjoy, so much more, being the organic Sherlock Holmes yourself. It is truly elementary, my dear student.

We will not present every detail and method available for organic chemists to determine structures. Whole courses and careers are built around this pursuit. We will develop the essential tools used by organic chemists to make reasonable, straight forward structure determinations. These will include proton ( $^1\text{H}$ ) and carbon-13 ( $^{13}\text{C}$ ) nuclear magnetic resonance spectroscopy (NMR) and some of the modern variations of these methods. Infrared spectroscopy (IR) is useful in identifying functional groups and substitution patterns of alkenes and aromatics. Additionally, mass spectroscopy (MS) will also be discussed, though this method uses a high energy electron beam to smash a molecule to cationic pieces, which are then accelerated to a detector where they are sized according to their masses, with the molecular weight being the most valuable mass. At one time UV-Vis was a common tool of organic structure determination, but with the advent of NMR it is not as commonly used now. It is still an important tool in other chemical sciences, but we will not cover the use of UV-Vis here.

Why do we need to know the structures of organic and biological molecules? First, to discuss organic molecules and organic reactions we must know the structure of the molecules we are studying. After all, old bonds are broken and new bonds are formed in chemical reactions, and we must determine what has changed to understand those reactions. Second, to know what molecules nature has created, we also must know how to determine the structure of molecules. If new medicinal compounds are to be isolated, studied and synthesized, their structures must be determined. Before the theories of organic chemistry and biochemistry could reasonably progress, chemists had to know how the atoms are connected together.

Even with the powerful spectroscopic tools available to chemists, determining a structure of a complicated molecule can be a challenging task. By using a combination of strategies, a chemist can piece together even incredibly complicated structures. This usually requires persistence, patience and an understanding of the spectroscopic tools available. It can take hours, days, weeks or even months. Of course, even months is vastly better than the decades it sometimes took in the first half of the 20<sup>th</sup> century. On the other hand, there are many simple structures that can be determined in less than a minute by an experienced chemist with the appropriate data available. We will start with simple structures and work our way towards more complicated molecules.

As you progress through this workbook you will become a chemical Sherlock Holmes. Endless mysteries lie before you, providing endless hours of enjoyment.

### A Special Note About This Book –

The hope in writing this book is that budding organic chemists will be able to use organic spectra (IR, MS,  $^1\text{H}$ ,  $^{13}\text{C}$  and a few other variations of NMR) to determine the structure of organic molecules. It is written for organic students taking their first year of organic chemistry, not seasoned researchers. I am not an expert on theory and instrumentation, but I try to explain enough of each technique so that students have an essential idea about how it works. There are better authors who have written informative and helpful books for learning the practical skills of instrumentation and the theoretical knowledge of spectroscopy.

This book arose as a result of teaching spectroscopy to first year organic lab students over a 35 year period. I began teaching with the usual very simple example molecules, e.g. 1-bromopropane, propan-2-ol, etc. Because of the excitement from my own research, in collaboration with Dr. Vasu Dev in determining structures of natural products isolated from plants, I kept increasing the level of complexity of problems in my teaching labs. Always, I was thinking that the next level would be too complicated for the students to do. I moved from the very simple molecules of my early years to  $\text{C}_{10}$  compounds, then  $\text{C}_{15}$ , then  $\text{C}_{20}$ , all the way to more than 25 carbon atoms in our homework problems.

Because I did not have access to real molecules that were simple enough for my students, yet had the complexity that required a sustained effort to solve, I made them up myself. In fact, I did not want real molecules, which often have the difficulties of overlapping peaks and/or extraneous peaks that should not be there and/or missing peaks that should be there. As is the case with real molecules, it is the various types of NMR spectra that solve a structure. In my problems, I include  $^1\text{H}$ ,  $^{13}\text{C}$ , DEPT, COSY, HETCOR/HSQC and HMBC. An IR is included because it can provide some very helpful functional group clues and maybe details about how an alkene or aromatic ring are substituted. In my experience mass spectra are useful for finding a molecular weight or the presence of halogens, but I have never solved a structure based on clues from mass spec. I do want students to understand fragmentation patterns of EI mass spectra and I discuss those possibilities, probably more than any book I have read on the topic. I go through the most common functional groups studied in organic chemistry, but in my structure problems, the main purpose of MS is to provide a molecular weight.

In creating my NMR structures I am always careful to minimize overlap of proton and carbon NMR signals. I use molecules from synthetic papers and natural product elucidation papers as my starting points. If a molecule is a really big structure, I cut out an interesting portion as a starting point. I use ChemDraw to create a starting proton NMR spectrum, and then I add a double bond or a substituted phenyl ring (to keep it interesting), or an oxygen (alcohol, ether, ester), or nitrogen (amine, amide or nitrile), or halogen or sulfur atom at key locations so that chemical shifts are different enough to distinguish in the  $^1\text{H}$ ,  $^{13}\text{C}$ , COSY, HETCOR/HSQC and HMBC spectra.

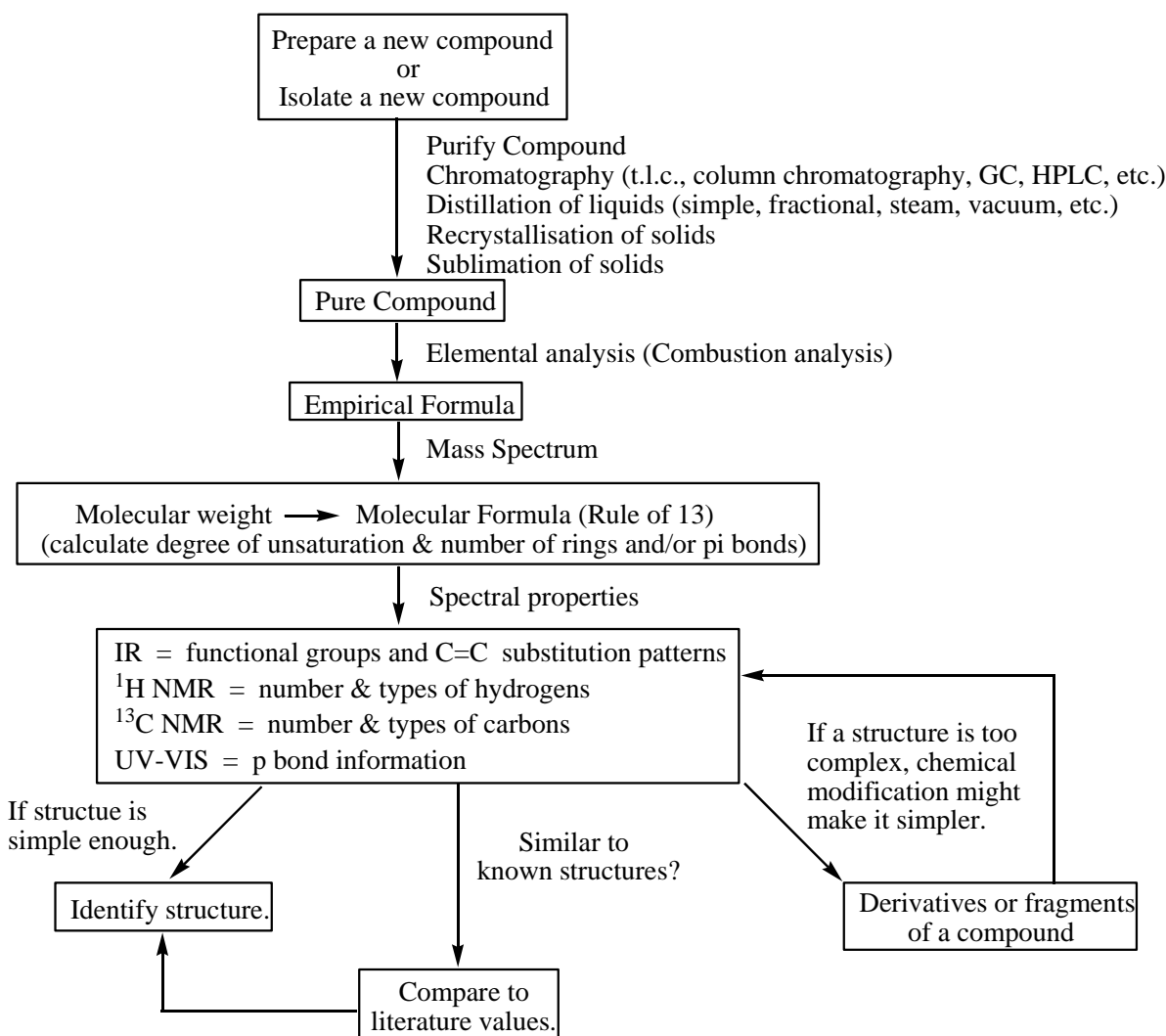
I was continually amazed each time I increased the difficulty of the problems by what the students could accomplish. I developed a very consistent, specific plan of attack to approach every problem (summarized in a one page worksheet). The structure problems in the last chapter were designed to be solved in hours, following the directed plan of attack, not days or weeks or months of research level work. Maybe, 1/5 of the students would actually get the structure completely correct. Most would get varying portions correct, and there would be a few (maybe 1/5) who thought I was completely insane and unreasonable.

My goal, usually met, was to assign a new problem every week of the quarter, but when I would not have time to make up a problem in a particular week (it takes a lot of time), many of the students would be disappointed. On the other hand, if I did give them a problem, they would complain about how much time they spent on these problems when they turned in their homework. But, by the end of the quarter, most students commented that the problems were fun. I occasionally see students after the quarter is over and some will comment how they miss doing those problems. It was feedback like

this that gave me the inclination to put forth this approach in a book so that others might also enjoy this pursuit. I hope you are in the 4/5 that finds some fun here.

### General Procedure For Structure Identification

New organic compounds are most often encountered as a sequential progression of steps in a chemical synthesis, or alternatively in natural product isolation from plants or animals or other environmental source in nature. In a synthetic sequence, usually a known starting material is mixed with reagents of well understood chemistry in a highly purified solvent under controlled reaction conditions (i.e. temperature, pressure, etc.). The researchers have reasonable expectations of what possible products could form. Usually they are confirming what they already suspect. However, surprises are common enough and these can often lead to new directions for a research project. In natural product isolation, the world is the limit. The nature of the extraction procedure may suggest classes of compounds such as proteins, carbohydrates, lipids, nucleic acids, terpenoids, steroids, alkaloids and the like. But rarely will there be much of a clue concerning specific structure until we actually begin to acquire spectroscopic data. In either case, we must obtain highly purified material for our spectra to be useful. From this starting point, an overview of a possible strategy from preparation or isolation of a compound to identification of its structure is presented below. You usually learn about some of the purification techniques listed below in the organic laboratory.



## Elemental/Combustion Analysis - Empirical Formulas

Elemental or combustion analysis is a very old procedure, which is performed today in a 'qualitatively' similar manner to that of 150 years ago. A chemist today sends a small amount (maybe 50 mg) of the highly purified sample out to a commercial lab for analysis (150 years ago you would have to do it yourself). A modern commercial analytical lab analyzes for any requested elements (C,H,N,S and halogens are common possibilities). Notice that oxygen is not listed and is often obtained by difference. The analytical lab generally mails or emails back the results for a reasonable fee.

The first step in the elemental analysis is to burn the sample in a flow of O<sub>2</sub> gas passed over a CuO catalyst to ensure complete combustion of all the carbon to CO<sub>2</sub> and all the hydrogen to H<sub>2</sub>O.

The fraction of carbon in CO<sub>2</sub> (12.01g/44.01g = 0.2729) multiplied times the mass of CO<sub>2</sub> produced equals the mass of carbon in our original sample. The fraction of hydrogen in H<sub>2</sub>O (2.016g/18.015g = 0.1119) multiplied times the mass of H<sub>2</sub>O produced equals the amount of hydrogen in the original sample.

If the unknown sample was a hydrocarbon, then the two masses should add up to the total mass combusted and we could proceed to solve for an empirical formula (lowest whole number mole ratio or atom ratio of the elements present).

If only oxygen was also present, then we could determine the mass of oxygen by difference between the mass of the unknown sample and the total mass of carbon and hydrogen.

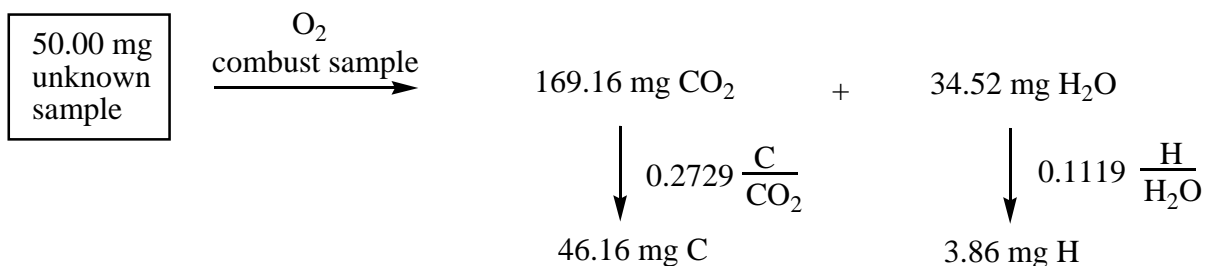
If nitrogen is also present, we will report its amount as a weight percent based on the original mass of the sample. You can solve for the mass of nitrogen in the original sample by multiplying the decimal fraction of nitrogen times the original mass of the sample.

The masses of carbon and hydrogen (or any other element considered) can be converted to mole values by dividing by the appropriate atomic weight. This can be accomplished in grams and moles or mg and mmols.

$\frac{(\text{grams})}{(\text{grams/mole})} = \text{mole}$ $\frac{(\text{mg})}{(\text{mg/mmol})} = \text{millimole}$
--

### Common atomic weights for organic chemistry

hydrogen	=	1.008
carbon	=	12.01
nitrogen	=	14.007
oxygen	=	15.999
sulfur	=	32.06
fluorine	=	18.998
chlorine	=	35.453
bromine	=	79.904
iodine	=	126.904

**Example 1 – only C and H**

total mass = 46.16 mg + 3.86 mg = 50.02 mg (This equals the entire sample weight within experimental error, so no other elements appear to be present.)

$$\text{mass formula} = \text{C}_{46.16 \text{ mg}} \text{H}_{3.86 \text{ mg}}$$

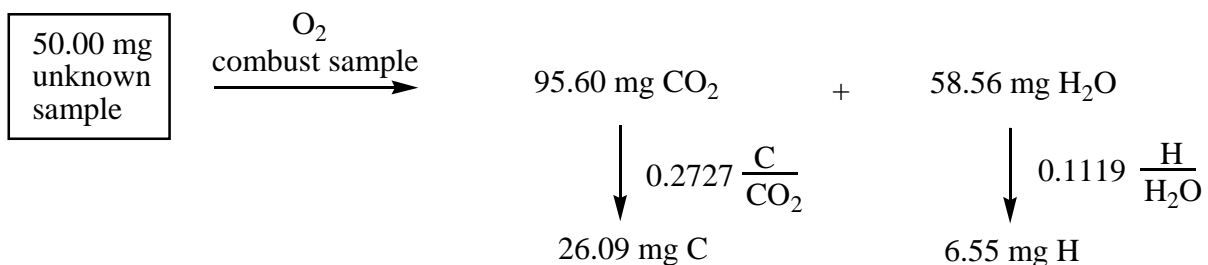
$$\text{mole ratio} = \text{C}_{(46.16 \text{ mg})/(12.01 \text{ mg/mmol})} \text{H}_{(3.86 \text{ mg})/(1.008 \text{ mg/mmol})}$$

$$\text{mole ratio} = \text{C}_{3.844 \text{ mmol}} \text{H}_{3.829 \text{ mmol}}$$

$$\text{Empirical formula whole number ratio} = \text{C}_{3.844/3.829} \text{H}_{3.829/3.829} = \text{C}_1\text{H}_1$$

↑  
Divide by smallest mole  
value to obtain integer ratios.

This is an empirical formula. We need the molecular weight to obtain the molecular formula.

**Example 2 - C, H and O**

$$\text{mass of carbon + hydrogen} = (26.09 + 6.55) \text{ mg} = 32.64 \text{ mg}$$

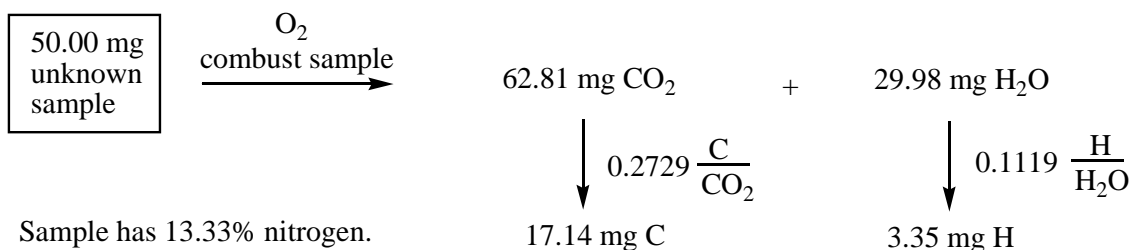
$$\text{mass of oxygen (by difference)} = (50.00 - 32.64) \text{ mg} = 17.36 \text{ mg}$$

$$\text{mass formula} = \text{C}_{26.09 \text{ mg}} \text{H}_{6.55 \text{ mg}} \text{O}_{17.36 \text{ mg}}$$

$$\text{mole ratio} = \text{C}_{(26.09 \text{ mg})/(12.01 \text{ mg/mmol})} \text{H}_{(6.55 \text{ mg})/(1.008 \text{ mg/mmol})} \text{O}_{(17.36 \text{ mg})/(16.00 \text{ mg/mmol})}$$

$$\text{mole ratio} = \text{C}_{2.17 \text{ mmol}} \text{H}_{6.50 \text{ mmol}} \text{O}_{1.09 \text{ mmol}}$$

$$\text{Empirical formula whole number ratio} = \text{C}_{2.17/1.09} \text{H}_{6.50/1.09} \text{O}_{1.09/1.09} = \text{C}_2\text{H}_6\text{O}_1$$

**Example 3 - C, H, N and O**

$$\left(0.1333 \frac{\text{nitrogen}}{\text{sample}}\right) \left(50.00 \text{ mg sample}\right) = 6.66 \text{ mg N}$$

$$\text{mass of carbon + hydrogen + nitrogen} = (17.14 + 3.35 + 6.66) \text{ mg} = 27.15 \text{ mg}$$

$$\text{mass of oxygen (by difference)} = (50.00 - 27.15) \text{ mg} = 22.85 \text{ mg}$$

$$\text{mass formula} = \text{C}_{17.14 \text{ mg}} \text{H}_{3.35 \text{ mg}} \text{N}_{6.66 \text{ mg}} \text{O}_{22.85 \text{ mg}}$$

$$\text{mole ratio} = \text{C}_{(17.14 \text{ mg})/(12.01 \text{ mg/mmol})} \text{H}_{(3.35 \text{ mg})/(1.008 \text{ mg/mmol})} \text{N}_{(6.66 \text{ mg})/(14.007 \text{ mg/mmol})} \text{O}_{(22.85 \text{ mg})/(16.00 \text{ mg/mmol})}$$

$$\text{mole ratio} = \text{C}_{1.43 \text{ mmol}} \text{H}_{3.32 \text{ mmol}} \text{N}_{0.476 \text{ mmol}} \text{O}_{1.43 \text{ mmol}}$$

$$\text{Empirical formula whole number ratio} = \text{C}_{1.43/0.476} \text{H}_{3.32/0.476} \text{N}_{0.476/0.476} \text{O}_{1.43/0.476} = \text{C}_3\text{H}_7\text{N}_1\text{O}_3$$

Problem 1 - 50.00mg of an unknown sample was combusted in excess oxygen with the following results. Determine an empirical formula.



Problem 2 - Assume 50.00mg of unknown is combusted in each problem below. The mg of CO<sub>2</sub> and H<sub>2</sub>O are provided. Find an empirical formula.

- a. 99.96 mg CO<sub>2</sub> and 17.52 mg H<sub>2</sub>O
- b. 73.29 mg CO<sub>2</sub> and 29.98 mg H<sub>2</sub>O
- c. 138.53 mg CO<sub>2</sub> and 18.90 mg H<sub>2</sub>O
- d. 142.23 mg CO<sub>2</sub> and 55.00 mg H<sub>2</sub>O and 10.06% nitrogen (multiply this percent times the 50.00 mg mass to determine how much nitrogen is in the sample and then continue as with carbon and hydrogen).



## Molecular Formula

The procedure above provides an empirical formula which is the lowest whole number ratio of the elements present in the unknown. The actual number of moles of each element in an unknown can be any integer multiple of this ratio,  $n$ . To decide which integer is needed, the molecular weight is required. This is most often obtained from the mass spectrum of the unknown compound in a separate analysis. Since the molecular weight is some integer multiple,  $n$ , of the empirical formula weight, you can calculate the value of  $n$  by dividing the molecular weight by the empirical formula weight. Until we cover mass spectroscopy, the molecular weight will be given.

The molecular formula has to equal some integer multiple,  $n$ , of the empirical formula.

$$\text{molecular formula} = n \left( \text{empirical formula} \right)$$

$$n = \frac{\text{molecular formula weight}}{\text{empirical formula weight}} = \frac{\text{molecular formula weight}}{\text{empirical formula weight}}$$

← obtain from mass spec  
← obtain from elemental analysis

1. In the first example above (hydrocarbon: only C & H), the empirical formula was  $C_1H_1$ :

<u>Possible Molecular Formulas</u>	<u>Molecular Weights</u>	mass of empirical formula = 13 g/formula
$(C_1H_1)_1$	$(13.02 \text{ g}) \times 1 = 13.02$	An odd number of hydrogen atoms is not possible in the molecular formula of a hydrocarbon.
$(C_1H_1)_2$	$(13.02 \text{ g}) \times 2 = 26.04$	
$(C_1H_1)_3$	$(13.02 \text{ g}) \times 3 = 39.06$	
etc.	etc.	
$(C_1H_1)_n$	$(13.02 \text{ g}) \times (n) = ?$	

2. In the second example (C, H & O present) above, the empirical formula was:  $C_2H_6O_1$  :

mass of empirical formula = 48 g/formula

if MW = 48, then  $n = 48 / 48 = 1$  and molecular formula =  $C_2H_6O_1$

if MW = 96, then  $n = 96 / 48 = 2$  and molecular formula =  $C_4H_{12}O_2$

if MW = 144, then  $n = 144 / 48 = 3$  and molecular formula =  $C_6H_{18}O_3$

if MW = 192, then  $n = 192 / 48 = 4$  and molecular formula =  $C_8H_{24}O_4$

← Impossible formulae, because there are too many hydrogen atoms for the number of carbon atoms

Problem 3 - What are some possible structures for the above empirical formula  $(C_1H_1)_n$  in example 1? (Stable molecular hydrocarbons have to have an even number of hydrogen atoms, so "n" must be an even number in this problem). Is there a systematic way to approach a problem like this? See the next section for some possibilities.

Molecular weight = 26 g/mol (There is only one answer.)

Molecular weight = 52 g/mol (I thought of 7 molecules, try and draw at least 2.)

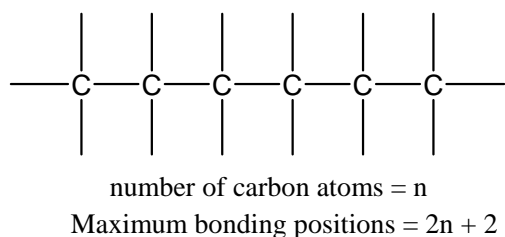
Molecular weight = 78 g/mol (Who knows how many are possible? Not me. Try and draw at least 4.)

Problem 4 – Redo problem 2 above and use the molecular weight provided below to generate a molecular formula for each part. Draw at least one possible structure using your molecular formula.

- 99.96 mg CO<sub>2</sub> and 17.52 mg H<sub>2</sub>O; MW = 154 g/mol
- 73.29 mg CO<sub>2</sub> and 29.98 mg H<sub>2</sub>O; MW = 180 g/mol
- 138.53 mg CO<sub>2</sub> and 18.90 mg H<sub>2</sub>O; MW = 238 g/mol
- 142.23 mg CO<sub>2</sub> and 55.00 mg H<sub>2</sub>O and 10.06% nitrogen; MW = 139 g/mol

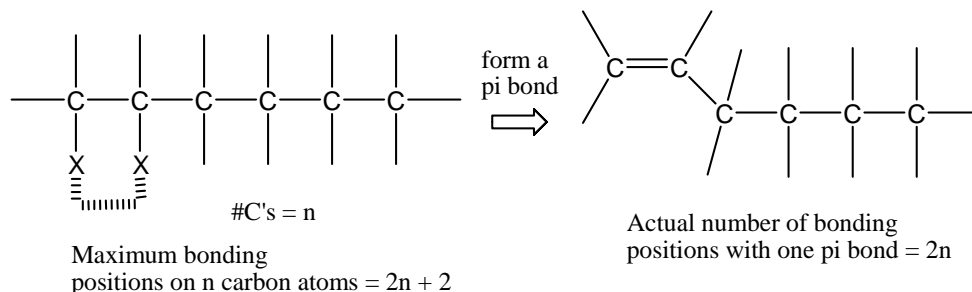
### Degrees of Unsaturation

There are two bonding positions on every carbon, with two additional positions on the end carbons. This produces  $(2n + 2)$  bonding positions on an alkane, where  $n$  is the number of carbons. This is the maximum number of bonding positions in an alkane, so when this number of single bonding groups are actually present, the formula is referred to as *saturated*. Count all of the hydrogen and the halogen atoms (F, Cl, Br, I) in the total number of atoms forming only one bond.



This is referred to as saturated when the total number of single bonding groups equals the maximum number of bonded positions. All of the bonded atoms would be hydrogen atoms in an alkane. However, we will add halogen atoms in with hydrogen atoms because they both only form single bonds and occupy a single bonding position on the carbon skeleton.

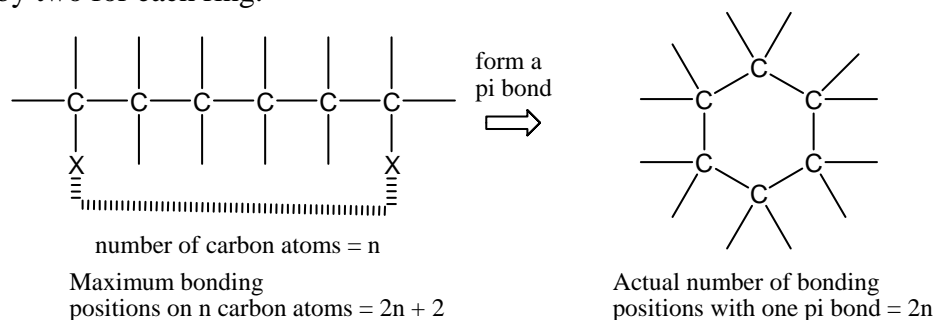
What happens if there is a pi bond? The maximum number of single bonding groups (hydrogen and halogen atoms) is reduced by two for each pi bond.



This structure is referred to as unsaturated. Each pi bond represents one degree of unsaturation ( $1^\circ$  unsaturation) and takes away two single bonding groups from the formula.

$$\text{Degree of unsaturation} = \frac{(2n + 2) - (2n)}{2} = \frac{2}{2} = 1 \text{ degree of unsaturation}$$

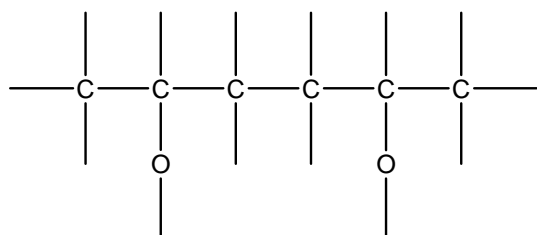
What happens if there is a ring? The maximum number of single bonded atoms is again reduced by two for each ring.



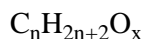
This structure is referred to as unsaturated. Each ring represents one degree of unsaturation ( $1^\circ$  unsaturation) and takes away two single bonding groups from the formula.

$$\text{Degree of unsaturation in both of the examples above} = \frac{(2n + 2) - (2n)}{2} = \frac{2}{2} = 1 \text{ degree of unsaturation}$$

What happens if there is an oxygen atom added to the carbon skeleton? Since oxygen makes two bonds, the bond that it takes is replaced with the second bond that it forms. There is no change in the calculation no matter how many oxygen atoms there are, and we can ignore them in our calculations. Divalent sulfur is similar to oxygen in this regard.

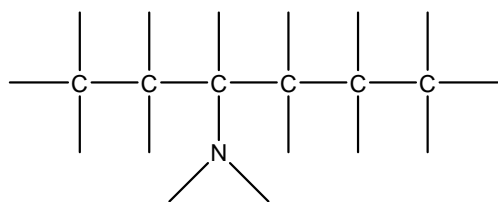


#C's = n      Maximum bonding positions on n carbon atoms =  $2n + 2$



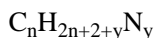
Oxygen atoms, in any amount, do not change the above calculation. They merely act as spacer atoms. We just ignore them when calculation the degree of unsaturation.

What happens if there is a nitrogen atom? Since a nitrogen atom makes three bonds, the bond that it occupies on the carbon skeleton is replaced by two additional bonds and that produces a net increase of one bond per nitrogen atom.



#C's = n

Maximum bonding positions on n carbon atoms with nitrogen present =  $2n + 2 + \#N$  atoms



Every single nitrogen atom will add an extra bonding position. Also, an odd number of nitrogen atoms (1,3,5...) will lead to an odd molecular weight.

The actual number of single bonded atoms (hydrogen and halogen atoms) is compared to the calculated maximum number of bonding positions for the number of carbon atoms and nitrogen atoms in the formula ( $= 2n + 2 + \#N$ ). If the two numbers are the same, then there are zero degrees of unsaturation, because every bonding position is filled. For every two bonding groups less than the maximum, there is one degree of unsaturation, which could be a pi bond or a ring in any combination. The spectroscopic techniques discussed below will usually clarify the number of pi bonds versus rings. Carbon-13 NMR is particularly helpful in this regard.

Maximum bonding positions =  $2n + 2 + \#N$ , (where n = the number of carbon atoms and #N is the number of nitrogen atoms)

– Subtract the actual number of single bonding groups (hydrogen and halogen atoms) from the maximum number.

difference

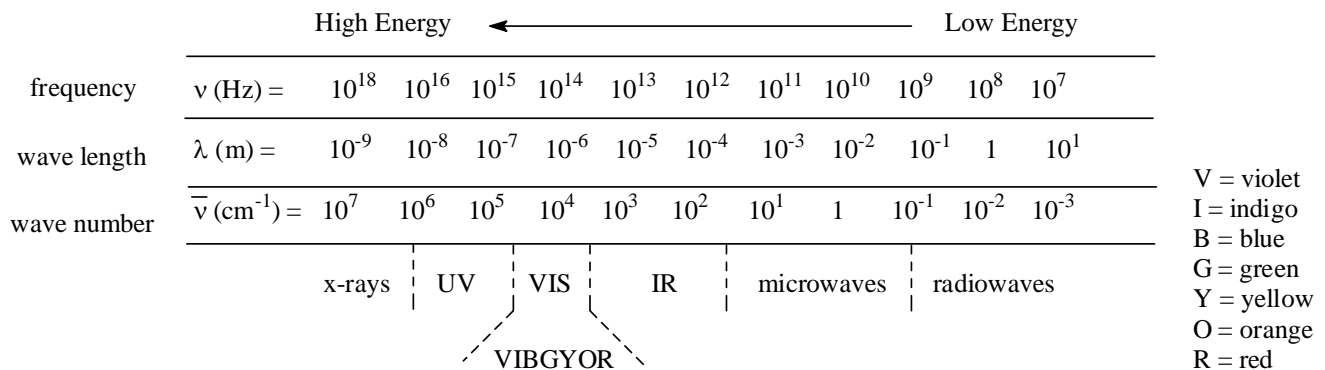
$$\frac{\text{difference}}{2} = \text{degrees of unsaturation}$$

Problem 5 - Determine the degrees of unsaturation for each of the following formulas. What arrangements of pi bonds and rings are possible in each case? Is it possible for any of the following formulas to have an alkene, alkyne, carboxylic acid, ester, amide, nitrile, aromatic ring, ketone, aldehyde, ether, amine or alcohol? Try and draw some examples of such structures.

- a.  $C_7H_8$       b.  $C_5H_{10}O$       c.  $C_4H_8O_2$       d.  $C_6H_{11}N$       e.  $C_8H_{17}NO$   
 f.  $C_{10}H_9ClN_2O$       g.  $C_9H_9NO_2$       h.  $C_{12}H_8Cl_2$       i.  $C_7H_5N$       j.  $C_6H_{10}O_6$

## Common Features of Electromagnetic Radiation

All of the spectroscopic techniques in this workbook, except mass spectroscopy, involve the interaction of electromagnetic radiation with matter. The responses of matter to electromagnetic radiation allow us to probe beyond our senses into the world of molecules and atoms. The following figure illustrates the usual spectroscopic divisions of the electromagnetic spectrum. Even though every designated region is a term in common everyday usage, you are probably unfamiliar with these terms as methods to study the structure of molecules.



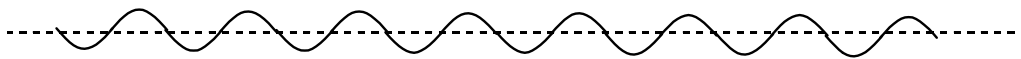
While the electromagnetic spectrum is divided into separate convenient spectroscopic regions (techniques), there are a few aspects common to the entire electromagnetic spectrum that we will review here.

First, the speed of the electromagnetic radiation is a constant value of  $3.0 \times 10^8$  m/sec in a vacuum and essentially the same in air. There are only two parameters associated with the velocity of light, which vary inversely with one another. Light has wave properties, so each wave will have a wavelength,  $\lambda$ , (lambda = distance) and a frequency,  $\nu$ , (nu = number/sec. = Hertz = Hz). The product of these two variables equals the speed of light,  $c$ , (a constant in a particular medium). Because of their inverse relationship, if one of these variables gets larger, then the other variable has to get smaller.

a.  $\nu = \text{frequency} = \text{number} / \text{time} = (\# / \text{sec})$

These units (Hz) are used in NMR.

$\nu = \frac{c}{\lambda}$	$c = (\nu)(\lambda) = 3.0 \times 10^8 \frac{\text{m}}{\text{sec}}$	$\nu_{\text{red}} = 3.8 \times 10^{14}$ Hz (lower energy) $\nu_{\text{violet}} = 7.5 \times 10^{14}$ Hz (higher energy)	}	visible light
---------------------------	--	--	---	---------------



$\nu = \text{number} / \text{sec}$  (Hz, and you better count really fast!)

$\lambda$  = wavelength = distance (m, cm, mm,  $\mu\text{m}$ , nm, pm)

$$\lambda = \frac{c}{\nu}$$

$$c = (\nu)(\lambda) = 3.0 \times 10^8 \frac{\text{m}}{\text{sec}}$$

These units (nm) are used in UV-Vis.

$\lambda_{\text{red}} = 800 \text{ nm}$  (lower energy)

$\lambda_{\text{violet}} = 400 \text{ nm}$  (higher energy)

} visible light

m = meter

cm =  $10^{-2}$  m (centi)

mm =  $10^{-3}$  m (milli)

$\mu\text{m}$  =  $10^{-6}$  m (micro)

nm =  $10^{-9}$  m (nano)

pm =  $10^{-12}$  m (pico)

fm =  $10^{-15}$  m (femto)

am =  $10^{-18}$  m (atto)

- b. A common variation of wavelength is wavenumber, which counts the number of waves per unit distance (e.g. #/cm =  $\text{cm}^{-1}$ ). The symbol is confusing because it is similar in appearance to frequency. Frequency is number per time, while wavenumber is number per distance (and the distance has to be specified, e.g. "cm"). Note that the Greek letter nu for frequency and wavenumber is the same. A bar is drawn over the wavenumber to distinguish it from frequency. (Since my word processing program does not have this symbol, I will write  $\nu$ -bar in the text part of this book for wave numbers.)

distance = 1 cm

$$\bar{\nu} = \frac{1}{\lambda}$$

$$\bar{\nu} = \frac{\text{number}}{\text{cm}} = \# \text{ cm}^{-1}$$

← These units ( $\text{cm}^{-1}$ ) are used in IR.

$$c = \frac{\nu}{\bar{\nu}}$$

$\bar{\nu}_{\text{red}} = 12,500 \text{ cm}^{-1}$  (lower energy)

$\bar{\nu}_{\text{violet}} = 25,000 \text{ cm}^{-1}$  (higher energy)

$\lambda_{\text{red}} = 800 \text{ nm}$  (lower energy)

$\lambda_{\text{violet}} = 400 \text{ nm}$  (higher energy)

} visible light

A moment's thought will suggest that if the frequency gets larger (more per second), then the wavelength must get shorter. The opposite is also true; a smaller frequency is associated with a longer wavelength.

$c = \text{constant}$

high energy  
high frequency  
high wavenumber  
short wavelength

low energy  
low frequency  
low wavenumber  
long wavelength

Since light travels so fast ( $3.0 \times 10^8 \text{ m/sec} = 186,000 \text{ miles/sec}$ ) even a very long wavelength has a reasonably high frequency. For example, a low energy radio wave of 1m/sec has a frequency of  $3 \times 10^8 \text{ Hz}$ . A much shorter wavelength of visible light is about  $3 \times 10^{-7} \text{ m}$  (0.00001 inch) and has a frequency of  $5 \times 10^{14} \text{ Hz}$ . To try and give this some perspective, a piece of copy paper is

approximately 0.009 cm (0.003 inch). The width of such paper would be 300 times longer than wavelength of visible light discussed above!

Problem 6 - a. Which photon of electromagnetic radiation below would have the longer wavelength? Convert both values to meters.

$$\bar{\nu} = 3500 \text{ cm}^{-1} \quad \nu = 4 \times 10^{14} \text{ Hz}$$

b. Which photon of electromagnetic radiation below would have the higher frequency? Convert both values to Hz.

$$\bar{\nu} = 400 \text{ cm}^{-1} \quad \lambda = 300 \text{ nm}$$

c. Which photon of electromagnetic radiation below would have the smaller wavenumber? Convert both values to  $\text{cm}^{-1}$ .

$$\lambda = 1 \text{ m} \quad \nu = 6 \times 10^{10} \text{ Hz}$$

Helpful Equations:

$$c = (\nu)(\lambda) \quad \text{and} \quad \bar{\nu} = (1/\lambda) \quad \text{so} \quad c = (\nu)/(\bar{\nu})$$

$$c = 3.00 \times 10^8 \text{ m/sec} = 3.00 \times 10^{10} \text{ cm/sec}$$

### Electromagnetic Radiation as Energy

Light is also a form of energy. Getting in a closed car on a hot summer day or walking barefoot across hot beach sand at high noon provides proof enough. There are additional equations relating energy to the parameters of either frequency, wavelength or wavenumber. Wavenumber,  $\text{cm}^{-1}$ , is the commonly used unit of infrared radiation (IR) and indirectly specifies the energy in this region. Nuclear magnetic spectroscopy uses frequency,  $\nu$ , in hertz (Hz) as the measure of energy. The instrumental techniques of ultraviolet and visible spectroscopies use wavelength,  $\lambda$ , in nm as the most common measurement of energy. Notice that in these equations the energy of electromagnetic radiation increases as the frequency and wavenumber get larger, while the energy decreases as the wavelength gets larger. It is certainly an inconvenience for students to have so many ways of categorizing the energy transitions of the various techniques that are used in science. However, there are only 3 simple equations and a little practice will soon make them understandable.

$$E = h \nu$$

$$E = h (c / \lambda) = h c (1 / \lambda)$$

$$E = h c \bar{\nu}$$

The variables are  $\nu$ ,  $\lambda$  and  $\bar{\nu}$ . Changes in these values will change the energy of electromagnetic radiation.

$$h = 6.62 \times 10^{-34} \text{ joule-sec}$$

$$c = 3.0 \times 10^{10} \text{ cm/sec} = 3.0 \times 10^8 \text{ m/sec}$$

The symbol,  $h$ , is called Planck's constant. Planck's constant can be considered as the smallest packet of quantized energy in a second of a particular frequency (#/sec) of electromagnetic radiation.

$$h = 6.62 \times 10^{-34} \text{ joule-sec}$$

This incredibly small energy parameter is magnified by how many wave units pass by in a second. It is truly a parameter from the world of atoms. Consider the frequency of visible light, above,  $5 \times 10^{14}$  Hz. A single photon would have the following small energy value (joule =  $\text{kg}\cdot\text{m}^2/\text{sec}^2$ ).

$$E = h\nu = (6.62 \times 10^{-34} \text{ joule}\cdot\text{sec})(5 \times 10^{14} / \text{sec}) = 3 \times 10^{-19} \text{ joule}$$

However, a mole of these photons would have a considerable amount of energy, because Avogadro's number is huge ( $6.02 \times 10^{23}$ )!

$$E_{\text{mole}} = (3 \times 10^{-19} \text{ joule / photon})(6.02 \times 10^{23} \text{ photons / mole}) = 2 \times 10^5 \text{ joule / mole}$$

$$E_{\text{mole}} = (2 \times 10^5 \text{ joule / mole})(1 \text{ kJ / 1000 joules}) = 200 \text{ kJ / mole}$$

$$E_{\text{mole}} = (200 \text{ kJ / mole})(1 \text{ kcal / 4.18 kJ}) = 50 \text{ kcal}$$

This amount of energy is in the range of weak chemical bonds. Light of this frequency would be sufficiently energetic to break weak bonds. For example the energy of a Br-Br bond is 46 kcal/mole,  $\text{sp}^3$  C-H bonds are about 95 kcal/mole and C=O bonds are about 175 kcal/mole and CN triple bonds are about 212 kcal/mole.

Problem 7 - Order the following photons from lowest to highest energy (first convert each value to kJoules). What is the energy of each photon in kcal/mole?

$$\text{a. } \bar{\nu} = 10^5 \text{ cm}^{-1} \quad \lambda = 10^3 \text{ nm} \quad \nu = 10^9 \text{ Hz}$$

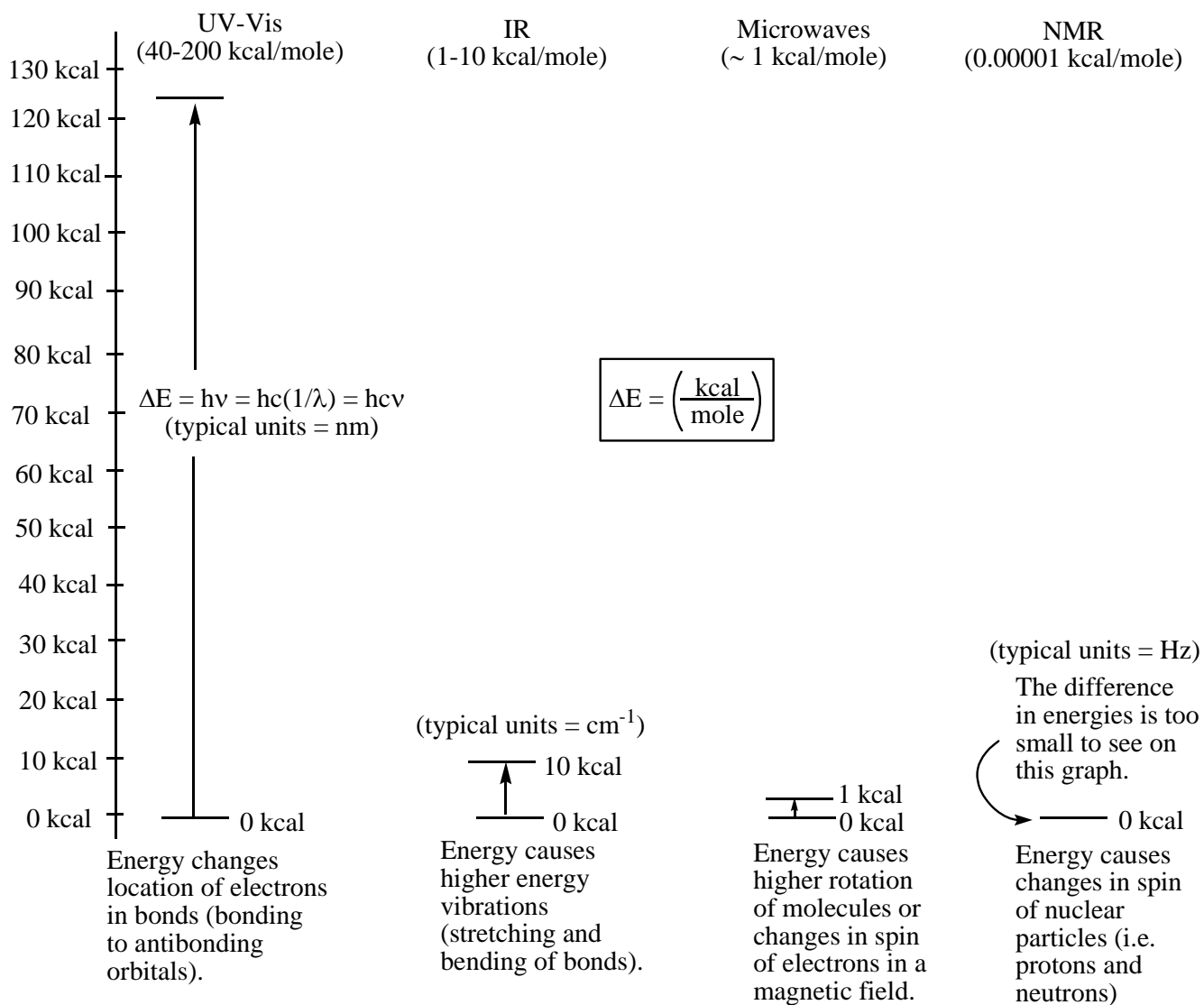
$$\text{b. } \bar{\nu} = 1 \text{ cm}^{-1} \quad \lambda = 10^{10} \text{ nm} \quad \nu = 10^{15} \text{ Hz}$$

### **Where Does the Energy Go?**

The energy of the light absorbed is transferred into a particular energy transition of the molecule with a matching (resonant) frequency. You might think of the matching frequencies as analogous to you pushing someone on a swing. If you time your pushes to the frequency of the person being pushed, you can increase the energy of their oscillation, moving them to higher amplitudes. In a molecule, this increase in energy can be electronic excitation by ultraviolet-visible light, vibrational stretching and bending by infrared light or proton and carbon-13 nuclear spin inversion in the presence of a magnetic field with radio waves of nuclear magnetic resonance spectroscopy.

The figure below shows the electromagnetic spectrum with relevant energies, frequencies, wavelengths and wavenumbers. The effects on molecules, atoms, electrons and nuclei are listed in the appropriate regions.

## Spectroscopic Techniques

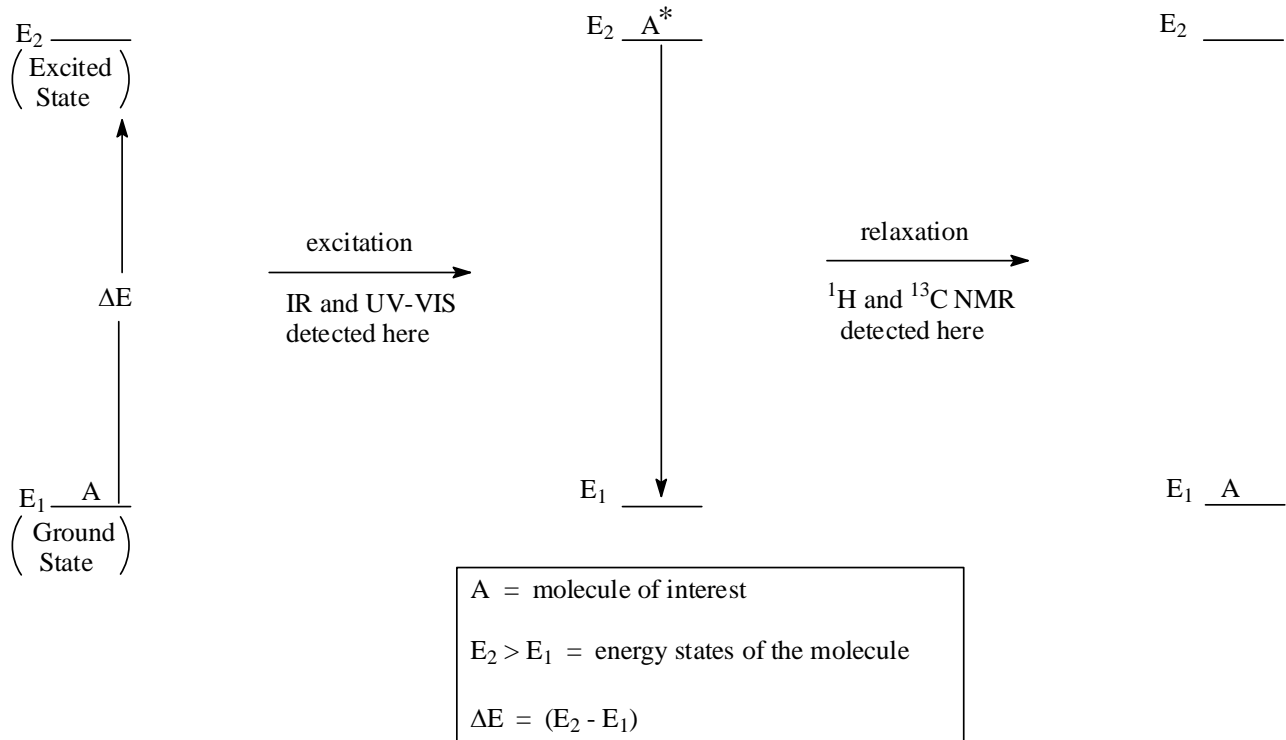


### Other Ways of Looking at Energy ( $\nu$ = frequency, $\bar{\nu}$ = wave number, $\lambda$ = wavelength)

Parameter	X-rays	UV	Vis	IR	Microwave	Radiowaves
E (kcal/mole)	24,000	200	50	10	$3 \times 10^{-3}$	$6 \times 10^{-6}$
E (kJ/mole)	100,000	800	200	40	$1.2 \times 10^{-2}$	$2 \times 10^{-5}$
E (eV/photon)	1,200	8	2	0.4	$1 \times 10^{-4}$	$3 \times 10^{-7}$
$\nu$ (Hz)	$3 \times 10^{17}$	$2 \times 10^{15}$	$5 \times 10^{14}$	$1 \times 10^{14}$	$3 \times 10^{10}$	$3 \times 10^8$
$\bar{\nu}$ ( $\text{cm}^{-1}$ )	$1 \times 10^7$	50,000	17,000	3,000	1	0.01
$\lambda$ (nm)	1	200	600	3,000	$1 \times 10^7$	$1 \times 10^9$



From the moment a molecule gets in an excited state (electronic, vibrational, rotational or nuclear spin), it is seeking a way to get back to the lower energy ground state (radiationless heat transfer, fluorescence, phosphorescence). This process is called relaxation. Relaxation can occur by a number of mechanisms, which include producing heat or emitting a photon of energy (fluorescence or phosphorescence). Our observation of the interaction of the photon with the molecule is sometimes detected in the event of excitation (UV-Vis and IR) and sometimes detected in the relaxation of the event ( $^1\text{H}$  and  $^{13}\text{C}$  NMR).



$$\Delta E \approx 50-100 \text{ kcal/mole}$$

Electron excitation occurs from a bonding to an antibonding orbital. Usually in pi bonds or conjugated pi systems, but it also can be from lone pair electrons or weak sigma bonds. } UV-VIS

$$\Delta E \approx 5 \text{ kcal/mole}$$

Excitation of stretching and bending vibrations of functional group patterns. } IR

$$\Delta E \approx 10^{-5} \text{ kcal/mole}$$

Excitation corresponds to nuclear particle spin flips in the presence of a magnetic field:  $^1\text{H}$  isotope of hydrogen and  $^{13}\text{C}$  isotope of carbon. } NMR

## Spectrometers

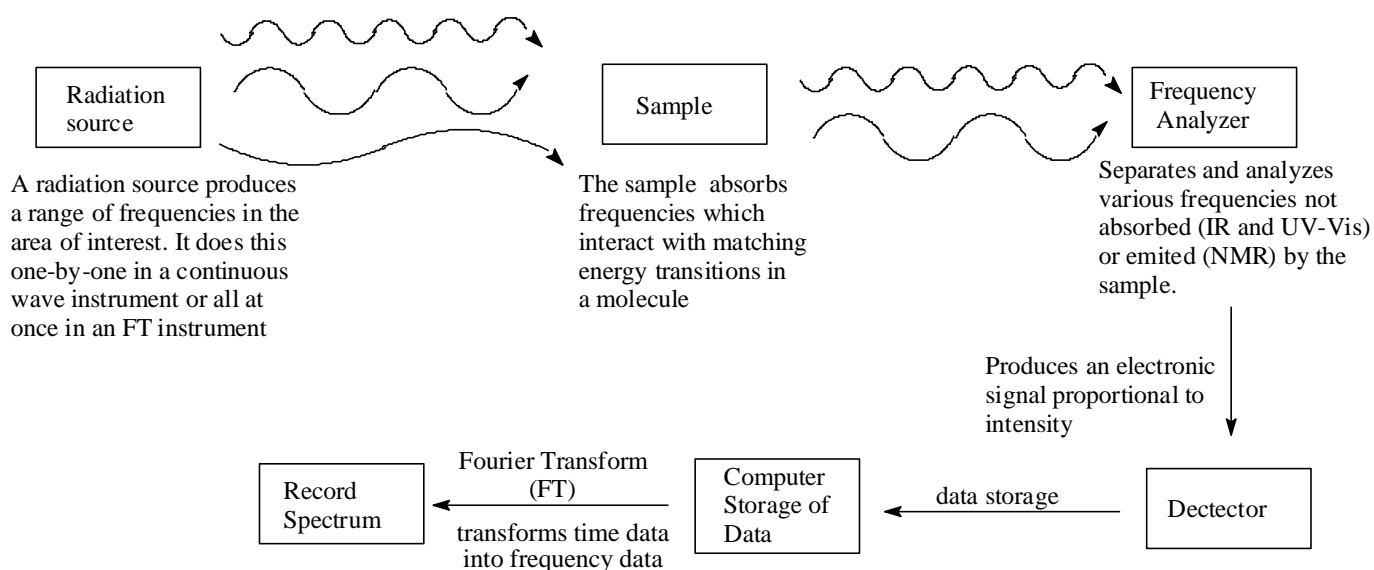
In each spectroscopic technique there are essential elements of instrumentation. It is not possible to cover the details of such instrumentation in a workbook such as this. As stated earlier, our ultimate goal is interpretation. However, there are some common general features that can be pointed out, with a caveat that I am not an analytical chemist and do not have extensive expertise in instrumentation.

All of the instruments that we use have a source of electromagnetic radiation (except mass spec.). This can be ultraviolet light, visible light, infrared light or radiowaves in NMR. There is a sample holder which contains the sample to be studied and allows the radiation to pass through the sample. This allows for any relevant interactions to occur. Any frequencies that are absorbed are converted into energetic transitions in the sample that is irradiated.

The efficiency of energy transfer to the sample determines the strength of absorption that occurs, for a particular frequency of radiation. A very efficient transfer will lead to a strong absorption and a less efficient transfer will produce a weak absorption. If a particular frequency does not interact with the sample at all, then none of the radiation will be absorbed. Alternatively, we could say all of the electromagnetic radiation is transmitted. Absorption and transmission are inversely related, as shown below. Some instruments record absorption and some record transmission. Absorbance units are usually given as 2 minus the log scale value of the percent transmission.

100% transmission	0% absorption (Absorbance = $2 - \log(100\%) = 0.00$ )
80% transmission	20% absorption (Absorbance = $2 - \log(80\%) = 0.10$ )
60% transmission	40% absorption (Absorbance = $2 - \log(60\%) = 0.21$ )
40% transmission	60% absorption (Absorbance = $2 - \log(40\%) = 0.40$ )
20% transmission	80% absorption (Absorbance = $2 - \log(20\%) = 0.70$ )
1% transmission	99% absorption (Absorbance = $2 - \log(1\%) = 2.00$ )

In addition to detecting the intensity of transmission (or absorption), the instrument must also separate the many different frequencies to be recorded (referred to as resolution). This requires a frequency analyzer of some sort. One that you are probably familiar with is a glass prism that can separate visible light into its rainbow of colors. Modern spectroscopic instruments allow extremely fine divisions to be recorded. The finer the detail, the greater the resolution that is possible for the chemist to make distinguishing determinations. Once the frequencies have been separated, they must be detected in a manner that also allows the intensity to be measured. There are a variety of detectors that stir up electrons (excite them) to generate electrical signals which can be amplified. These signals are routed to either a computer data storage area or a recording chart which can print out the final result which is called a spectrum. An experienced chemist can then analyze the details in the spectrum to develop conclusions about structural features of the unknown sample. This is shown in the simplistic diagram below.



### Fourier Transform (FT) Spectroscopy

Many current instruments (FT instruments are more modern) use a technique where all frequencies are excited at once and detected at once, instead of going through each frequency point-by-point (continuous wave instruments are older). The excitation and collection of data are much quicker with this approach. From the perspective of the chemist, the raw data is very confusing. Each individual frequency is mixed in with all of the other frequencies and no detailed analysis can be made. However, thanks to a mathematical manipulation that most of us will never understand, the mixed frequencies can be separated from one another as sines and cosines. This mathematical procedure is called a Fourier Transform. It is usually accomplished by the clever computer so that the chemist can get the data in a form which can be interpreted. This means that there is usually an additional step to the procedure diagrammed above adding a computational translation of the time data into frequency data, called a Fourier transformation (or FT transform).

An analogy to these two approaches of data collection can be made with a guitar. If you played all of the notes of a chord, one-by-one, you would be recording a continuous wave spectrum, where each frequency is detected (heard) a single note at a time. If you spent one second playing each note and 4 seconds fixing its sound in your mind, it would take  $6 \times (1 + 4) = 30$  seconds to mentally picture the entire chord. However, if you strummed the entire chord at once (1 sec) and could permanently fix the sound in your mind or a computer (4 sec), you would have saved 25 seconds. It would be more difficult to distinguish each individual frequency (note) with this approach, however. The magic of a Fourier transformation is that it can take the entire mixture of frequencies in the chord and unravel them to their individual frequencies. It does this with combinations of sine and cosine functions and calculus that will remain a black box for us here.

We will now examine IR, MS and several NMR methods to see what they can tell us about the structures of organic molecules.