

# 11: INFRARED SPECTROSCOPY AND MASS SPECTROMETRY



## CHAPTER OVERVIEW

### 11: INFRARED SPECTROSCOPY AND MASS SPECTROMETRY

#### Learning Objectives

After reading this chapter and completing ALL the exercises, a student can be able to

- correlate regions of the electromagnetic spectrum to spectroscopic techniques - refer to section 11.1
- explain how an IR spectrometer works and the IR region interacts with organic compounds - refer to section 11.2
- explain the role of asymmetry in IR absorption - refer to section 11.3
- interpret IR spectra - refer to section 11.4, 11.5, and 11.6
- explain how a mass spectrometer works - refer to section 11.7
- explain the source of the base peak and molecular ion in a mass spectrum - refer to section 11.7
- correlate bond strength to fragmentation patterns - refer to section 11.8
- use fragmentation patterns to elucidate structural features of organic compounds - refer to section 11.9
- explain how high-resolution mass can be used to determine chemical formulas - refer to section 11.10

[11.1: The Electromagnetic Spectrum and Spectroscopy](#)

[11.2: Infrared \(IR\) Spectroscopy](#)

[11.3: IR-Active and IR-Inactive Vibrations](#)

[11.4: Interpreting IR Spectra](#)

[11.5: Infrared Spectra of Some Common Functional Groups](#)

[11.6: Summary and Tips to Distinguish between Carbonyl Functional Groups](#)

[11.7: Mass Spectrometry - an introduction](#)

[11.8: Fragmentation Patterns in Mass Spectrometry](#)

[11.9: Useful Patterns for Structure Elucidation](#)

[11.10: Determination of the Molecular Formula by High Resolution Mass Spectrometry](#)

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## 11.1: THE ELECTROMAGNETIC SPECTRUM AND SPECTROSCOPY

### Objectives

After completing this section, you should be able to

1. write a brief paragraph discussing the nature of electromagnetic radiation.
2. write the equations that relate energy to frequency, frequency to wavelength and energy to wavelength, and perform calculations using these relationships.
3. describe, in general terms, how absorption spectra are obtained.

### Key Terms

Make certain that you can define, and use in context, the key terms below.

- electromagnetic radiation
- electromagnetic spectrum
- hertz (Hz)
- infrared spectroscopy
- photon
- quantum

### Study Notes

From your studies in general chemistry or physics, you should be familiar with the idea that electromagnetic radiation is a form of energy that possesses wave character and travels through space at a speed of  $3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1}$ . However, such radiation also displays some of the properties of particles, and on occasion it is more convenient to think of electromagnetic radiation as consisting of a stream of particles called *photons*.

In spectroscopy, the frequency of the electromagnetic radiation being used is usually expressed in *hertz (Hz)*, that is, cycles per second. Note that  $1 \text{ Hz} = \text{s}^{-1}$ .

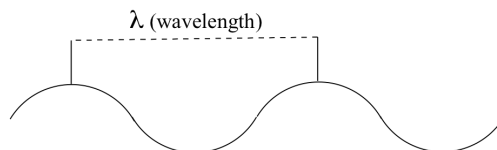
A *quantum* is a small, definite quantity of electromagnetic radiation whose energy is directly proportional to its frequency. (The plural is “quanta.”) If you wish, you can read about the properties of [electromagnetic radiation](#) and the relationships among wavelength, frequency and energy, or refer to your general chemistry textbook if you still have it.

Note also that in SI units, Planck’s constant is  $6.626 \times 10^{-34} \text{ J} \cdot \text{s}$ .

### THE ELECTROMAGNETIC SPECTRUM

Electromagnetic radiation, as you may recall from a previous chemistry or physics class, is composed of electrical and magnetic waves which oscillate on perpendicular planes. Visible light is electromagnetic radiation. So are the gamma rays that are emitted by spent nuclear fuel, the x-rays that a doctor uses to visualize your bones, the ultraviolet light that causes a painful sunburn when you forget to apply sun block, the infrared light that the army uses in night-vision goggles, the microwaves that you use to heat up your frozen burritos, and the radio-frequency waves that bring music to anybody who is old-fashioned enough to still listen to FM or AM radio.

Just like ocean waves, electromagnetic waves travel in a defined direction. While the speed of ocean waves can vary, however, the speed of electromagnetic waves – commonly referred to as the speed of light – is essentially a constant, approximately 300 million meters per second. This is true whether we are talking about gamma radiation or visible light. Obviously, there is a big difference between these two types of waves – we are surrounded by the latter for more than half of our time on earth, whereas we hopefully never become exposed to the former to any significant degree. The different properties of the various types of electromagnetic radiation are due to differences in their wavelengths, and the corresponding differences in their energies: *shorter wavelengths correspond to higher energy*.



High-energy radiation (such as gamma- and x-rays) is composed of very short waves – as short as  $10^{-16}$  meter from crest to crest. Longer waves are far less energetic, and thus are less dangerous to living things. Visible light waves are in the range of 400 – 700 nm (nanometers, or  $10^{-9}$  m), while radio waves can be several hundred meters in length.

The notion that electromagnetic radiation contains a quantifiable amount of energy can perhaps be better understood if we talk about light as a stream of *particles*, called **photons**, rather than as a wave. (Recall the concept known as ‘wave-particle duality’: at the quantum level, wave behavior and particle behavior become indistinguishable, and very small particles have an observable ‘wavelength’). If we describe light as a stream of photons, the energy of a particular wavelength can be expressed as:

$$E = \frac{hc}{\lambda} \quad (12.5.1)$$

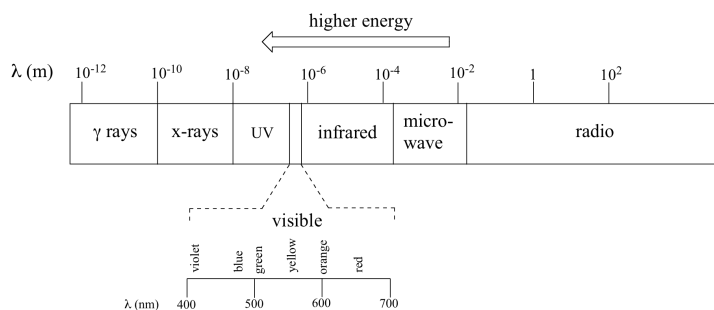
where E is energy in kcal/mol,  $\lambda$  (the Greek letter *lambda*) is wavelength in meters, c is  $3.00 \times 10^8$  m/s (the speed of light), and h is  $9.537 \times 10^{-14}$  kcal•s•mol<sup>-1</sup>, a number known as Planck’s constant.

Because electromagnetic radiation travels at a constant speed, each wavelength corresponds to a given frequency, which is the number of times per second that a crest passes a given point. Longer waves have lower frequencies, and shorter waves have higher frequencies. Frequency is commonly reported in hertz (Hz), meaning ‘cycles per second’, or ‘waves per second’. The standard unit for frequency is s<sup>-1</sup>.

When talking about electromagnetic waves, we can refer either to wavelength or to frequency - the two values are interconverted using the simple expression:

$$\lambda \nu = c \quad (12.5.2)$$

where  $\nu$  (the Greek letter ‘nu’) is frequency in s<sup>-1</sup>. Visible red light with a wavelength of 700 nm, for example, has a frequency of  $4.29 \times 10^{14}$  Hz, and an energy of 40.9 kcal per mole of photons. The full range of electromagnetic radiation wavelengths is referred to as the **electromagnetic spectrum**.



Notice in the figure above that visible light takes up just a narrow band of the full spectrum. White light from the sun or a light bulb is a mixture of all of the visible wavelengths. You see the visible region of the electromagnetic spectrum divided into its different wavelengths every time you see a rainbow: violet light has the shortest wavelength, and red light has the longest.

### Example

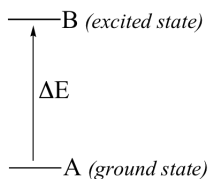
Visible light has a wavelength range of about 400-700 nm. What is the corresponding frequency range? What is the corresponding energy range, in kcal/mol of photons?

Solution

## MOLECULAR SPECTROSCOPY – THE BASIC IDEA

In a spectroscopy experiment, electromagnetic radiation of a specified range of wavelengths is allowed to pass through a sample containing a compound of interest. The sample molecules absorb energy from some of the wavelengths, and as a result jump from a low energy ‘ground state’ to some higher energy ‘excited state’. Other wavelengths are *not* absorbed by the sample molecule, so they pass on through. A detector on the other side of the sample records which wavelengths were absorbed, and to what extent they were absorbed.

Here is the key to molecular spectroscopy: *a given molecule will specifically absorb only those wavelengths which have energies that correspond to the energy difference of the transition that is occurring*. Thus, if the transition involves the molecule jumping from ground state A to excited state B, with an energy difference of  $\Delta E$ , the molecule will specifically absorb radiation with wavelength that corresponds to  $\Delta E$ , while allowing other wavelengths to pass through unabsorbed.



By observing which wavelengths a molecule absorbs, and to what extent it absorbs them, we can gain information about the nature of the energetic transitions that a molecule is able to undergo, and thus information about its structure.

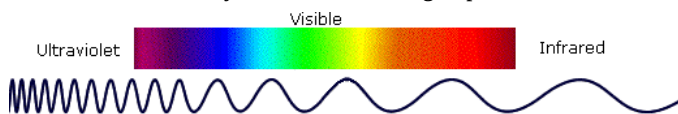
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## 11.2: INFRARED (IR) SPECTROSCOPY

### INTRODUCTION

Photon energies associated with the infrared (from 1 to 15 kcal/mole) are not large enough to excite electrons, but may induce vibrational excitation of covalently bonded atoms and groups.

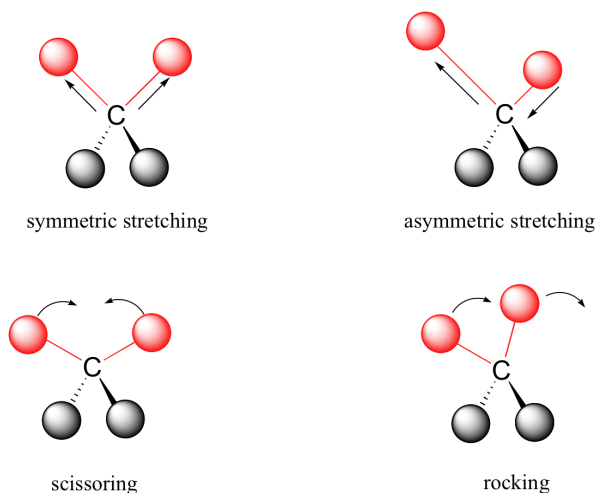


The covalent bonds in molecules are not rigid sticks or rods, such as found in molecular model kits, but are more like stiff springs that can be stretched and bent. The mobile nature of organic molecules was noted in the chapter concerning conformational isomers. We must now recognize that, in addition to the facile rotation of groups about single bonds, molecules experience a wide variety of vibrational motions, characteristic of their component atoms. Consequently, virtually all organic compounds will absorb infrared radiation that corresponds in energy to these vibrations. Infrared spectrometers, similar in principle to the UV-Visible spectrometer described elsewhere, permit chemists to obtain absorption spectra of compounds that are a unique reflection of their molecular structure.

### VIBRATIONAL SPECTROSCOPY

A molecule composed of  $n$ -atoms has  $3n$  degrees of freedom, six of which are translations and rotations of the molecule itself. This leaves  $3n-6$  degrees of vibrational freedom ( $3n-5$  if the molecule is linear). Vibrational modes are often given descriptive names, such as stretching, bending, scissoring, rocking and twisting. The four-atom molecule of formaldehyde, the gas phase spectrum of which is shown below, provides an example of these terms. If a ball & stick model of formaldehyde is not displayed to the right of the spectrum, press the **view ball&stick model** button on the right. We expect six fundamental vibrations (12 minus 6), and these have been assigned to the spectrum absorptions. To see the formaldehyde molecule display a vibration, click one of the buttons under the spectrum, or click on one of the absorption peaks in the spectrum.

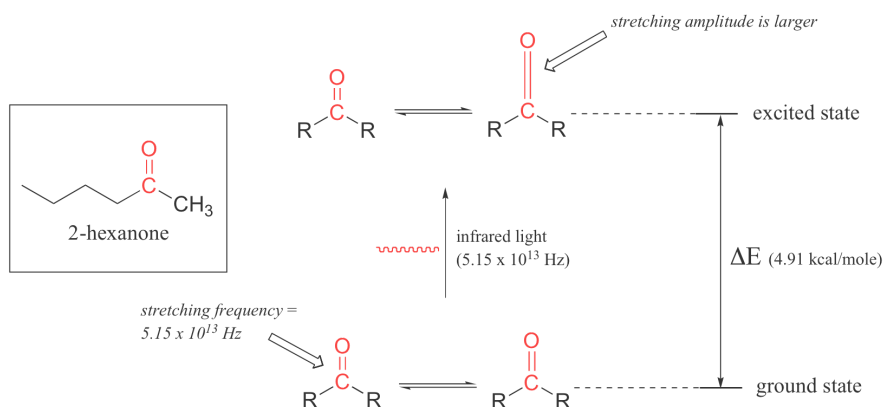
Covalent bonds in organic molecules are not rigid sticks – rather, they behave more like springs. At room temperature, organic molecules are always in motion, as their bonds stretch, bend, and twist. These complex vibrations can be broken down mathematically into individual **vibrational modes**, a few of which are illustrated below.



The energy of molecular vibration is *quantized* rather than continuous, meaning that a molecule can only stretch and bend at certain 'allowed' frequencies. If a molecule is exposed to electromagnetic radiation that matches the frequency of one of its vibrational modes, it will in most cases absorb energy from the radiation and jump to a higher vibrational energy state - what this means is that the *amplitude* of the vibration will increase, but the vibrational *frequency* will remain the same. The difference in energy between the two vibrational states is equal to the energy associated with the wavelength of radiation that was absorbed. It turns out that it is the *infrared* region of the electromagnetic spectrum which contains frequencies corresponding to the vibrational frequencies of organic bonds.

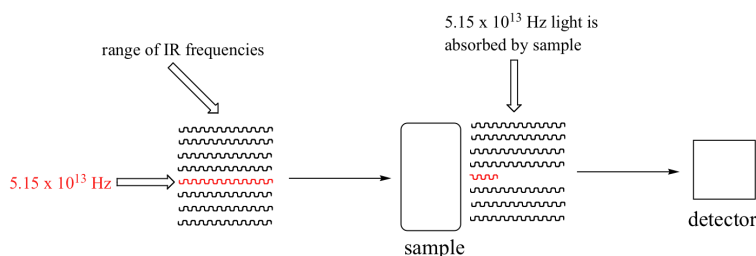
#### An IR Spectrum

We will use a ketone sample to illustrate this process. The sample is irradiated with infrared light and the carbonyl bond will specifically absorb light with this same frequency, which by equations 4.1 and 4.2 corresponds to a wavelength of  $5.83 \times 10^{-6}$  m and an energy of 4.91 kcal/mol. When the carbonyl bond absorbs this energy, it jumps up to an excited vibrational state.



The value of  $\Delta E$  - the energy difference between the low energy (ground) and high energy (excited) vibrational states - is equal to 4.91 kcal/mol, the same as the energy associated with the absorbed light frequency. The molecule does not remain in its excited vibrational state for very long, but quickly releases energy to the surrounding environment in form of heat, and returns to the ground state.

With an instrument called an infrared spectrophotometer, we can 'see' this vibrational transition. In the spectrophotometer, infrared light with frequencies ranging from about  $10^{13}$  to  $10^{14}$  Hz is passed through our sample of cyclohexane. Most frequencies pass right through the sample and are recorded by a detector on the other side.

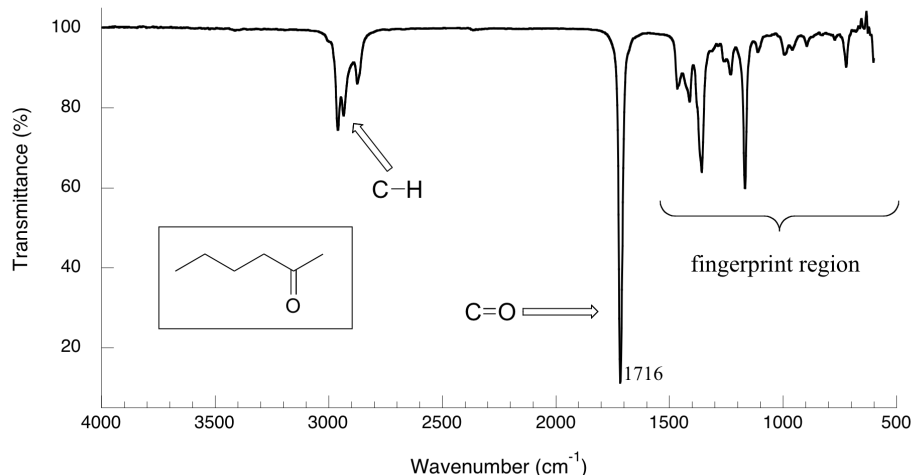


Our  $5.15 \times 10^{13}$  Hz carbonyl stretching frequency, however, is absorbed by the 2-hexanone sample, and so the detector records that the intensity of this frequency, after having passed through the sample, is something less than 100% of its initial intensity.

The vibrations of a 2-hexanone molecule are not, of course, limited to the simple stretching of the carbonyl bond. The various carbon-carbon bonds also stretch and bend, as do the carbon-hydrogen bonds, and all of these vibrational modes also absorb different frequencies of infrared light.

The power of infrared spectroscopy arises from the observation that *different functional groups have different characteristic absorption frequencies*. The carbonyl bond in a ketone, as we saw with our 2-hexanone example, typically absorbs in the range of  $5.11 - 5.18 \times 10^{13}$  Hz, depending on the molecule. The carbon-carbon triple bond of an alkyne, on the other hand, absorbs in the range  $6.30 - 6.80 \times 10^{13}$  Hz. The technique is therefore very useful as a means of identifying which functional groups are present in a molecule of interest. If we pass infrared light through an unknown sample and find that it absorbs in the carbonyl frequency range but not in the alkyne range, we can infer that the molecule contains a carbonyl group but not an alkyne.

Now, let's look at some actual output from IR spectroscopy experiments. Below is the IR spectrum for 2-hexanone.



There are a number of things that need to be explained in order for you to understand what it is that we are looking at. On the horizontal axis we see IR wavelengths expressed in terms of a unit called **wavenumber** (cm<sup>-1</sup>), which tells us how many waves fit into one centimeter. On the vertical axis we see ‘% **transmittance**’, which tells us how strongly light was absorbed at each frequency (100% transmittance means no absorption occurred at that frequency). The solid line traces the values of % transmittance for every wavelength – the ‘peaks’ (which are actually pointing down) show regions of strong absorption. For some reason, it is typical in IR spectroscopy to report wavenumber values rather than wavelength (in meters) or frequency (in Hz). The ‘upside down’ vertical axis, with absorbance peaks pointing down rather than up, is also a curious convention in IR spectroscopy. We wouldn’t want to make things too easy for you!

A calculator for interconverting these frequency and wavelength values is provided on the right. Simply enter the value to be converted in the appropriate box, press "Calculate" and the equivalent number will appear in the empty box.

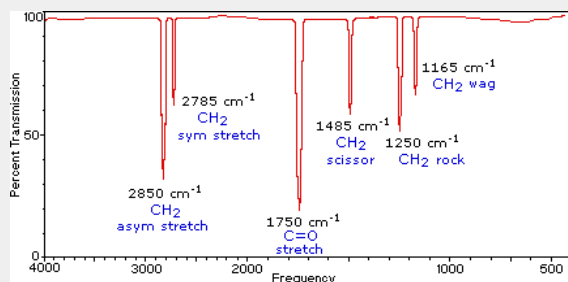
Infrared spectra may be obtained from samples in all phases (liquid, solid and gaseous). Liquids are usually examined as a thin film sandwiched between two polished salt plates (note that glass absorbs infrared radiation, whereas NaCl is transparent). If solvents are used to dissolve solids, care must be taken to avoid obscuring important spectral regions by solvent absorption. Perchlorinated solvents such as carbon tetrachloride, chloroform and tetrachloroethene are commonly used. Alternatively, solids may either be incorporated in a thin KBr disk, prepared under high pressure, or mixed with a little non-volatile liquid and ground to a paste (or mull) that is smeared between salt plates.

### FREQUENCY - WAVELENGTH CONVERTER

<input type="text"/>	Frequency in cm <sup>-1</sup>
<input type="text"/>	Wavelength in μ
<input type="button" value="Calculate"/>	



## GAS PHASE INFRARED SPECTRUM OF FORMALDEHYDE, H<sub>2</sub>C=O



- View CH<sub>2</sub> Asymmetric Stretch
- View CH<sub>2</sub> Symmetric Stretch
- View C=O Stretch
- View CH<sub>2</sub> Scissoring
- View CH<sub>2</sub> Rocking
- View CH<sub>2</sub> Wagging

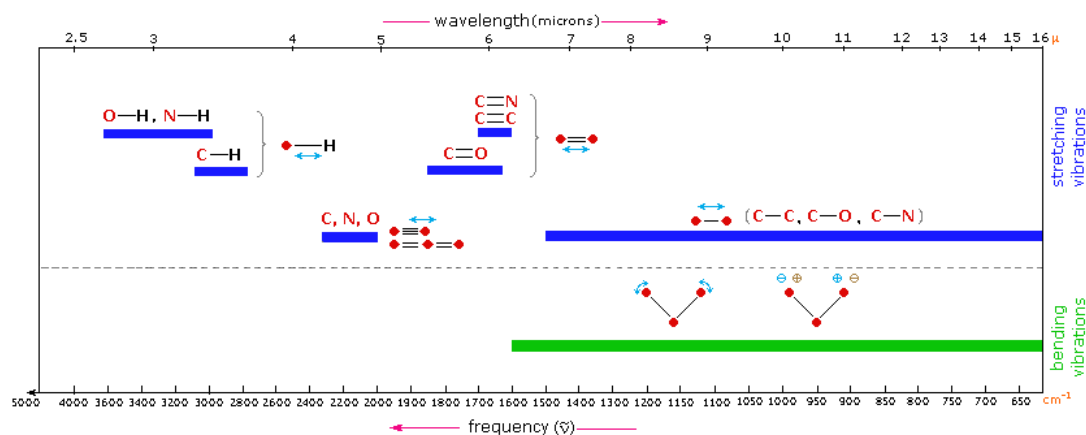
- Ball&Stick Model
- Spacefill Model
- Stick Model
- Motion Off

The exact frequency at which a given vibration occurs is determined by the strengths of the bonds involved and the mass of the component atoms. For a more detailed discussion of these factors [Click Here](#). In practice, infrared spectra do not normally display separate absorption signals for each of the  $3n-6$  fundamental vibrational modes of a molecule. The number of observed absorptions may be increased by additive and subtractive interactions leading to combination tones and overtones of the fundamental vibrations, in much the same way that sound vibrations from a musical instrument interact. Furthermore, the number of observed absorptions may be decreased by molecular symmetry, spectrometer limitations, and spectroscopic selection rules. One selection rule that influences the intensity of infrared absorptions, is that a change in dipole moment should occur for a vibration to absorb infrared energy. Absorption bands associated with C=O bond stretching are usually very strong because a large change in the dipole takes place in that mode.

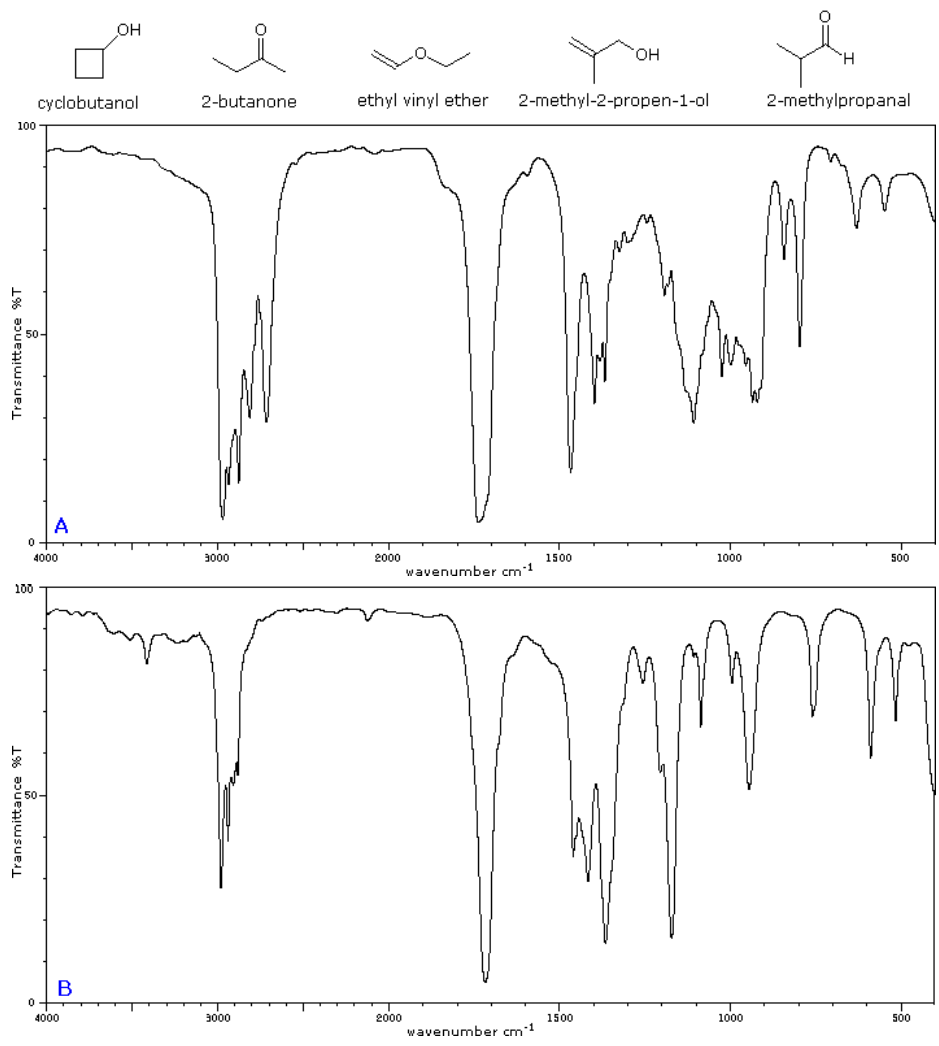
### Some General Trends:

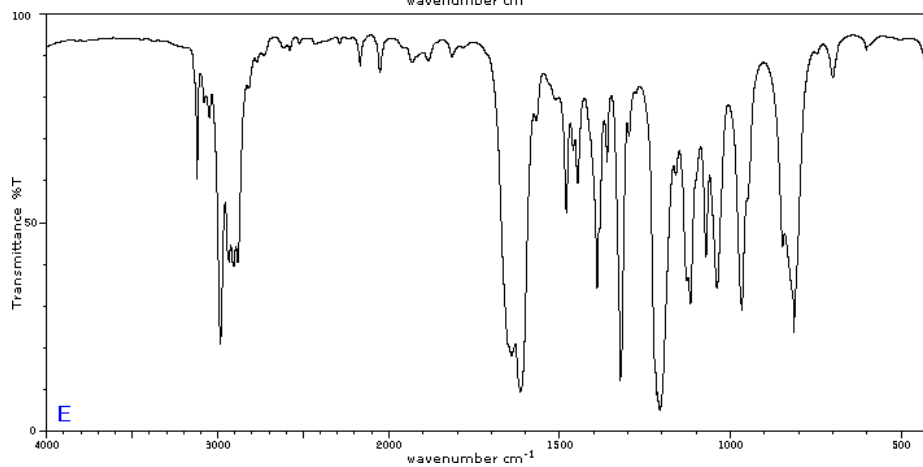
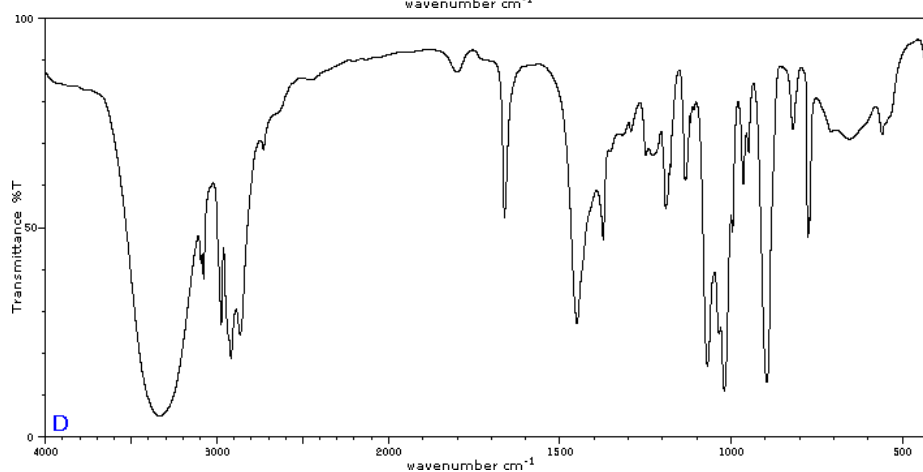
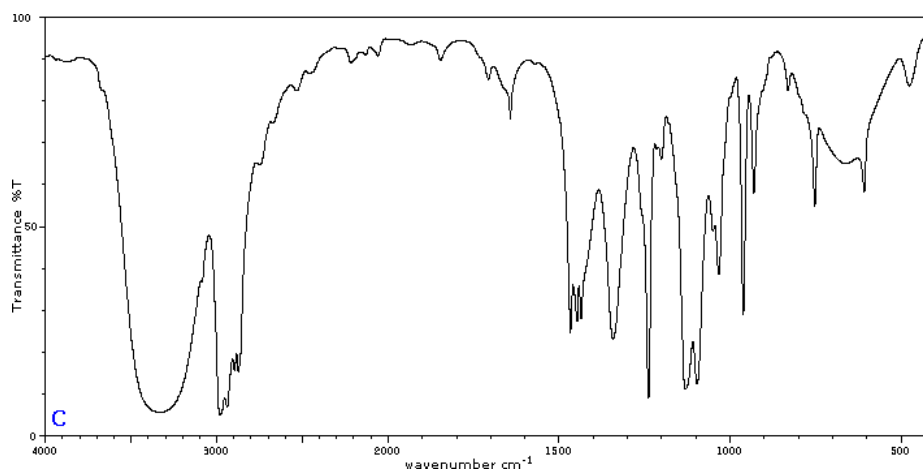
- Stretching frequencies are higher than corresponding bending frequencies. (It is easier to bend a bond than to stretch or compress it.)
- Bonds to hydrogen have higher stretching frequencies than those to heavier atoms.
- Triple bonds have higher stretching frequencies than corresponding double bonds, which in turn have higher frequencies than single bonds. (Except for bonds to hydrogen).

The general regions of the infrared spectrum in which various kinds of vibrational bands are observed are outlined in the following chart. Note that the blue colored sections above the dashed line refer to stretching vibrations, and the green colored band below the line encompasses bending vibrations. The complexity of infrared spectra in the 1450 to 600  $\text{cm}^{-1}$  region makes it difficult to assign all the absorption bands, and because of the unique patterns found there, it is often called the **fingerprint** region. Absorption bands in the 4000 to 1450  $\text{cm}^{-1}$  region are usually due to stretching vibrations of diatomic units, and this is sometimes called the **group frequency** region.



To illustrate the usefulness of infrared absorption spectra, examples for five C<sub>4</sub>H<sub>8</sub>O isomers are presented below their corresponding structural formulas. Try to associate each spectrum (A - E) with one of the isomers in the row above it.





## Answers

### INTERNAL LINKS

- [Organic Chemistry With a Biological Emphasis](#)

### CONTRIBUTORS

- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)

### CONTRIBUTORS AND ATTRIBUTIONS

- [Dr. Dietmar Kennepohl](#) FCIC (Professor of Chemistry, [Athabasca University](#))
- [Prof. Steven Farmer](#) ([Sonoma State University](#))
- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)

- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)

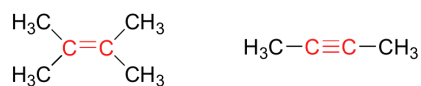
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## 11.3: IR-ACTIVE AND IR-INACTIVE VIBRATIONS

Some bonds absorb infrared light more strongly than others, and some bonds do not absorb at all. *In order for a vibrational mode to absorb infrared light, it must result in a periodic change in the dipole moment of the molecule.* Such vibrations are said to be **infrared active**. In general, the greater the polarity of the bond, the stronger its IR absorption. The carbonyl bond is very polar, and absorbs very strongly. The carbon-carbon triple bond in most alkynes, in contrast, is much less polar, and thus a stretching vibration does not result in a large change in the overall dipole moment of the molecule. Alkyne groups absorb rather weakly compared to carbonyls.

Some kinds of vibrations are **infrared inactive**. The stretching vibrations of completely symmetrical double and triple bonds, for example, do not result in a change in dipole moment, and therefore do not result in any absorption of light (but other bonds and vibrational modes in these molecules *do* absorb IR light).



infrared-inactive double and triple bonds

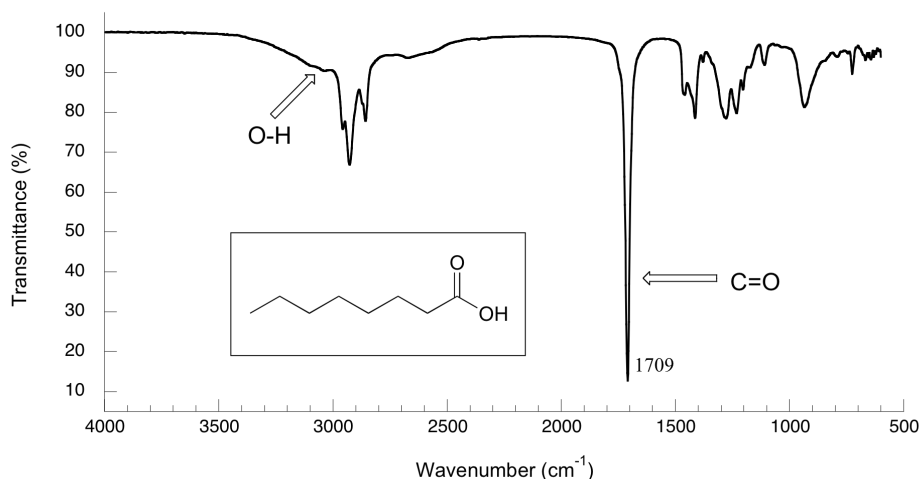
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## 11.4: INTERPRETTING IR SPECTRA

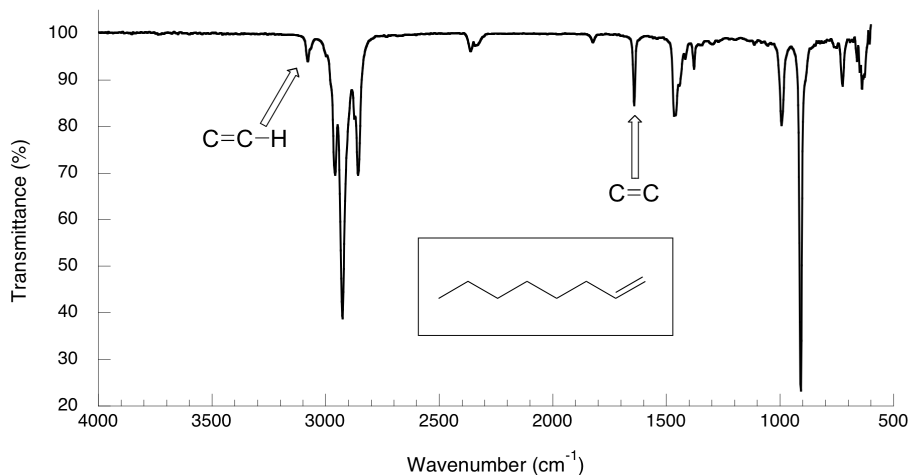
### GUIDED IR SPECTRUM INTERPRETATION

Now, let's take a look at the IR spectrum for 1-hexanol. There is a very broad 'mountain' centered at about  $3400\text{ cm}^{-1}$ . This signal is characteristic of the O-H stretching mode of alcohols, and is a dead giveaway for the presence of an alcohol group. The breadth of this signal is a consequence of hydrogen bonding between molecules.

In the spectrum of octanoic acid we see, as expected, the characteristic carbonyl peak, this time at  $1709\text{ cm}^{-1}$ . We also see a low, broad absorbance band that looks like an alcohol, except that it is displaced slightly to the right (long-wavelength) side of the spectrum, causing it to overlap to some degree with the C-H region. This is the characteristic carboxylic acid O-H single bond stretching absorbance.



The spectrum for 1-octene shows two peaks that are characteristic of alkenes: the one at  $1642\text{ cm}^{-1}$  is due to stretching of the carbon-carbon double bond, and the one at  $3079\text{ cm}^{-1}$  is due to stretching of the s bond between the alkene carbons and their attached hydrogens.



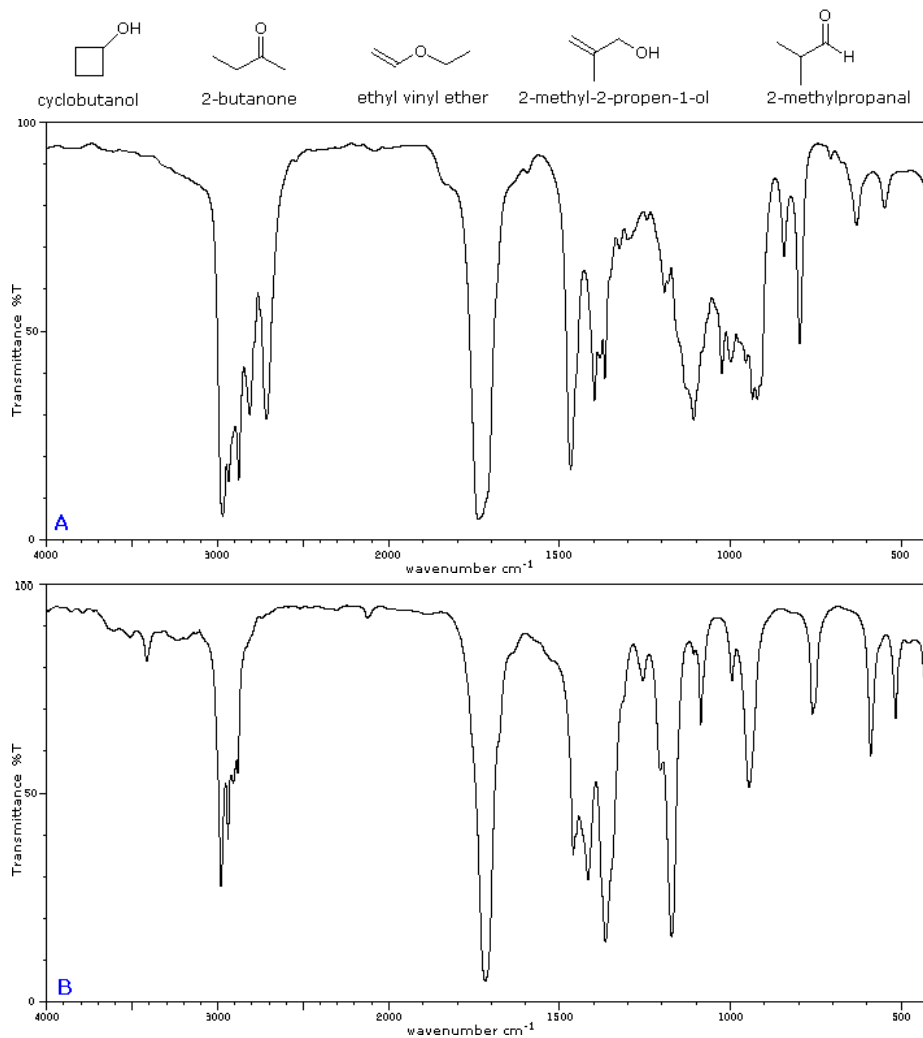
Alkynes have characteristic IR absorbance peaks in the range of  $2100\text{--}2250\text{ cm}^{-1}$  due to stretching of the carbon-carbon triple bond, and terminal alkenes can be identified by their absorbance at about  $3300\text{ cm}^{-1}$ , due to stretching of the bond between the  $\text{sp}$ -hybridized carbon and the terminal hydrogen.

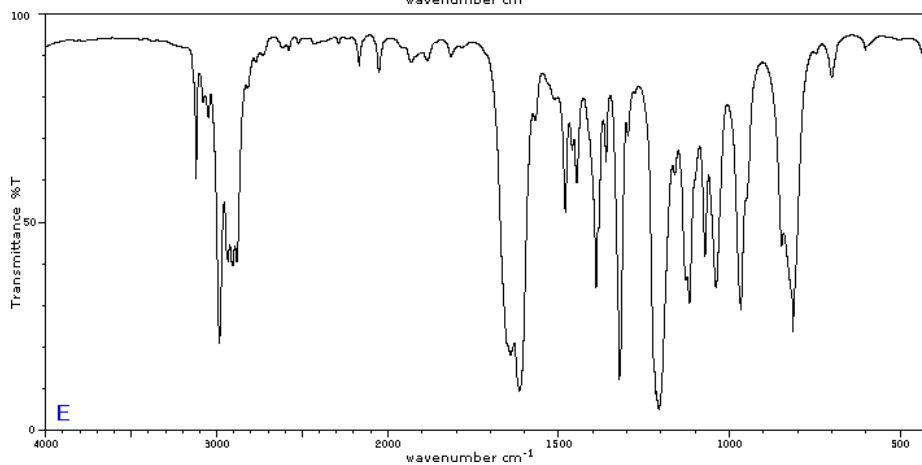
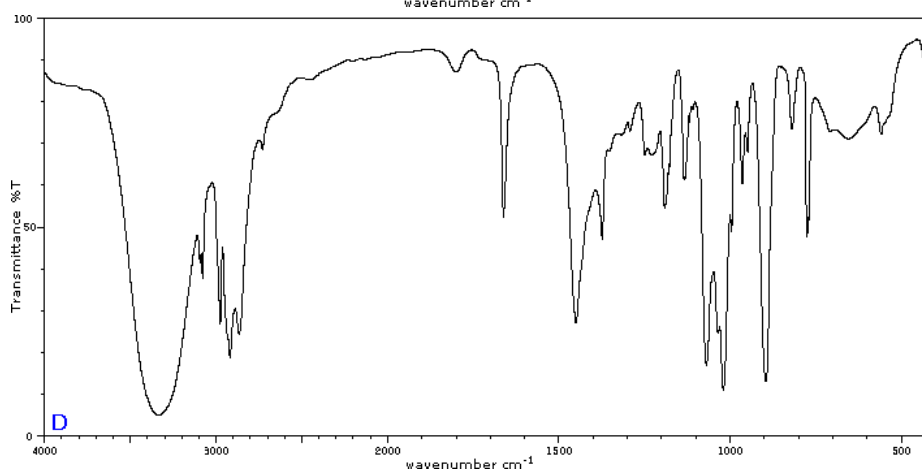
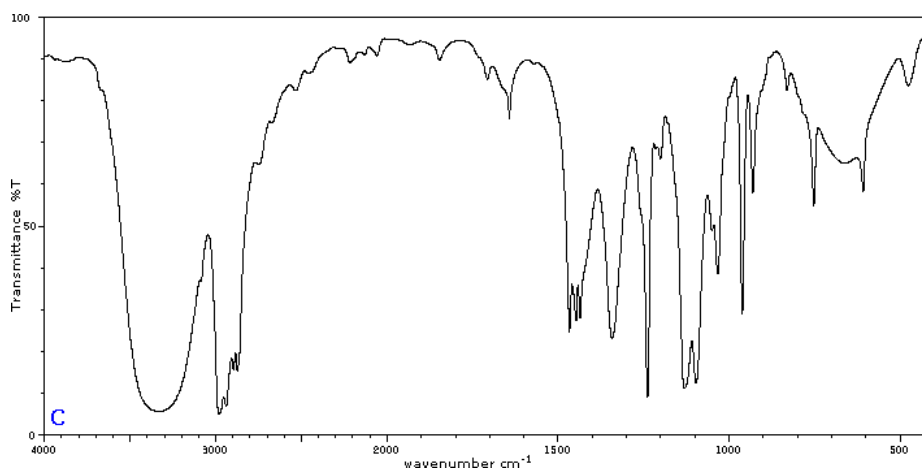
It is possible to identify other functional groups such as amines and ethers, but the characteristic peaks for these groups are considerably more subtle and/or variable, and often are overlapped with peaks from the fingerprint region. For this reason, we will limit our discussion here to the most easily recognized functional groups, which are summarized in this [table](#).

As you can imagine, obtaining an IR spectrum for a compound will not allow us to figure out the complete structure of even a simple molecule, unless we happen to have a reference spectrum for comparison. In conjunction with other analytical methods, however, IR spectroscopy can prove to be a very valuable tool, given the information it provides about the presence or absence of key functional groups. IR can also be a quick and convenient way for a chemist to check to see if a reaction has proceeded as planned. If we were to run a reaction in which we wished to convert cyclohexanone to cyclohexanol, for example, a quick comparison of the IR spectra of starting compound and product would tell us if we had successfully converted the ketone group to an alcohol.

### MORE EXAMPLES OF IR SPECTRA

To illustrate the usefulness of infrared absorption spectra, examples for five  $C_4H_8O$  isomers are presented below their corresponding structural formulas. Try to associate each spectrum with one of the isomers in the row above it.





## EXERCISES

### QUESTIONS

#### Q12.7.1

What functional groups give the following signals in an IR spectrum?

- A) 1700 cm<sup>-1</sup>
- B) 1550 cm<sup>-1</sup>
- C) 1700 cm<sup>-1</sup> and 2510-3000 cm<sup>-1</sup>

#### Q12.7.2

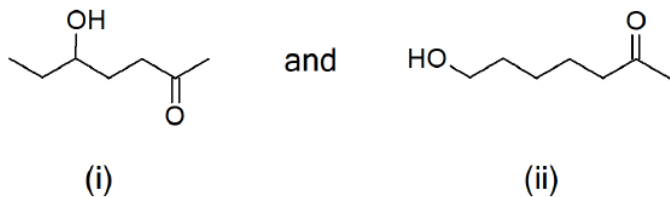
How can you distinguish the following pairs of compounds through IR analysis?

- A) CH<sub>3</sub>OH (Methanol) and CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub> (Diethylether)



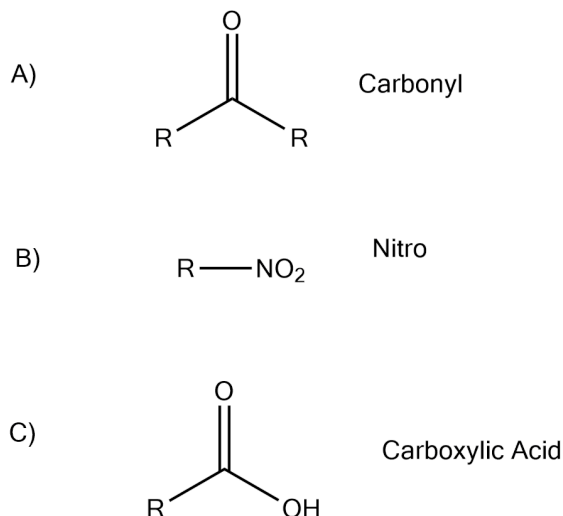
B) Cyclopentane and 1-pentene.

C)



### SOLUTIONS

#### S12.7.1



#### S12.7.2

A) A OH peak will be present around  $3300\text{ cm}^{-1}$  for methanol and will be absent in the ether.

B) 1-pentene will have a alkene peak around  $1650\text{ cm}^{-1}$  for the C=C and there will be another peak around  $3100\text{ cm}^{-1}$  for the  $\text{sp}^2$  C-H group on the alkene

C) Cannot distinguish these two isomers. They both have the same functional groups and therefore would have the same peaks on an IR spectra.

### CONTRIBUTORS AND ATTRIBUTIONS

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- Prof. Steven Farmer ([Sonoma State University](#))
- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)
- **Organic Chemistry With a Biological Emphasis** by [Tim Soderberg](#) (University of Minnesota, Morris)

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## 11.5: INFRARED SPECTRA OF SOME COMMON FUNCTIONAL GROUPS

### COMMON GROUP FREQUENCIES SUMMARY

When analyzing an IR spectrum, it is helpful to overlay the diagram below onto the spectrum with our mind to help recognize functional groups.

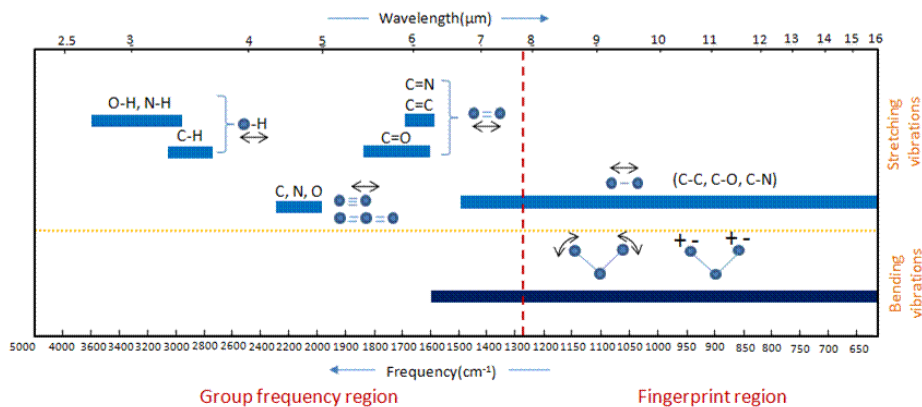


Figure 1. Group frequency and fingerprint regions of the mid-infrared spectrum

The region of the infrared spectrum from 1200 to 700 cm<sup>-1</sup> is called the fingerprint region. This region is notable for the large number of infrared bands that are found there. Many different vibrations, including C-O, C-C and C-N single bond stretches, C-H bending vibrations, and some bands due to benzene rings are found in this region. The fingerprint region is often the most complex and confusing region to interpret, and is usually the last section of a spectrum to be interpreted. However, the utility of the fingerprint region is that the many bands there provide a fingerprint for a molecule.

### GROUP FREQUENCIES - A CLOSER LOOK

Detailed information about the infrared absorptions observed for various bonded atoms and groups is usually presented in tabular form. The following table provides a collection of such data for the most common functional groups. Following the color scheme of the chart, stretching absorptions are listed in the blue-shaded section and bending absorptions in the green shaded part. **More detailed descriptions for certain groups (e.g. alkenes, arenes, alcohols, amines & carbonyl compounds) may be viewed by clicking on the functional class name.** Since most organic compounds have C-H bonds, a useful rule is that absorption in the 2850 to 3000 cm<sup>-1</sup> is due to sp<sup>3</sup> C-H stretching; whereas, absorption above 3000 cm<sup>-1</sup> is from sp<sup>2</sup> C-H stretching or sp C-H stretching if it is near 3300 cm<sup>-1</sup>.

Functional Class	Stretching Vibrations			Bending Vibrations		
	Range ( $\text{cm}^{-1}$ )	Intensity	Assignment	Range ( $\text{cm}^{-1}$ )	Intensity	Assignment
Alkanes	2850-3000	str	CH <sub>3</sub> , CH <sub>2</sub> & CH 2 or 3 bands	1350-1470	med	CH <sub>2</sub> & CH <sub>3</sub> deformation
				1370-1390	med	CH <sub>3</sub> deformation
				720-725	wk	CH <sub>2</sub> rocking
Alkenes	3020-3100 1630-1680	med	=C-H & =CH <sub>2</sub> (usually sharp) C=C (symmetry reduces intensity)	880-995	str	=C-H & =CH <sub>2</sub>
		var		780-850	med	(out-of-plane bending)
		str		675-730	med	cis-RCH=CHR
Alkynes	3300 2100-2250	str	C≡C (symmetry reduces intensity)	600-700	str	C-H deformation
		var				
Arenes	3030 1600 & 1500	var	C-H (may be several bands) C=C (in ring) (2 bands) (3 if conjugated)	690-900	str-med	C-H bending & ring puckering
		med-wk				
Alcohols & Phenols	3580-3650 3200-3550 970-1250	var	O-H (free), usually sharp O-H (H-bonded), usually broad C-O	1330-1430	med	O-H bending (in-plane)
		str		650-770	var-wk	O-H bend (out-of-plane)
		str				
Amines	3400-3500 (dil. soln.) 3300-3400 (dil. soln.) 1000-1250	wk	N-H (1°-amines), 2 bands N-H (2°-amines) C-N	1550-1650 660-900	med-str	NH <sub>2</sub> scissoring (1°-amines)
		wk			var	NH <sub>2</sub> & N-H wagging (shifts on H-bonding)
		med				
Aldehydes & Ketones	2690-2840(2 bands) 1720-1740 1710-1720	med str str  str str str str	C-H (aldehyde C-H) C=O (saturated aldehyde) C=O (saturated ketone)  aryl ketone α, β-unsaturation cyclopentanone cyclobutanone	1350- 1360 1400- 1450 1100	str str med	α-CH <sub>3</sub> bending α-CH <sub>2</sub> bending C-C-C bending
Carboxylic Derivatives	Acids & 2500-3300 (acids) overlap 1705-1720 (acids) 1210-1320 (acids)	str str med-str  str str str str str	C-H O-H (very broad) C=O (H-bonded) O-C (sometimes 2-peaks)  C=O C=O (2-bands) O-C C=O O-C (2-bands) C=O (amide I band)	1395- 1440   1590- 1650 1500- 1560	med	C-O-H bending    N-H (1°-amide) II band N-H (2°-amide) II band
Nitriles	2240-2260	med	C≡N (sharp)			
Isocyanates, Isothiocyanates, Diimides, Azides & Ketenes	2100-2270	med	-N=C=O, -N=C=S -N=C=N-, -N <sub>3</sub> , C=C=O			

## RECOGNIZING GROUP FREQUENCIES IN IR SPECTRA - A VERY CLOSE LOOK

### HYDROCARBONS

Hydrocarbons compounds contain only C-H and C-C bonds, but there is plenty of information to be obtained from the infrared spectra arising from C-H stretching and C-H bending.

In alkanes, which have very few bands, each band in the spectrum can be assigned:

- C-H stretch from 3000–2850  $\text{cm}^{-1}$
- C-H bend or scissoring from 1470-1450  $\text{cm}^{-1}$
- C-H rock, methyl from 1370-1350  $\text{cm}^{-1}$
- C-H rock, methyl, seen only in long chain alkanes, from 725-720  $\text{cm}^{-1}$

Figure 3. shows the IR spectrum of octane. Since most organic compounds have these features, these C-H vibrations are usually not noted when interpreting a routine IR spectrum. Note that the change in dipole moment with respect to distance for the C-H stretching is greater than that for others shown, which is why the C-H stretch band is the more intense.

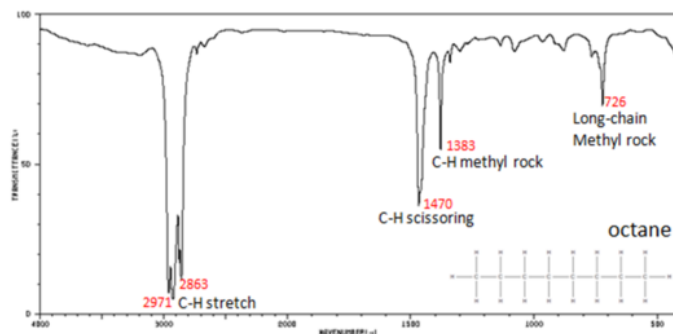


Figure 3. Infrared Spectrum of Octane

In alkenes compounds, each band in the spectrum can be assigned:

- C=C stretch from  $1680-1640\text{ cm}^{-1}$
- =C-H stretch from  $3100-3000\text{ cm}^{-1}$
- =C-H bend from  $1000-650\text{ cm}^{-1}$

Figure 4. shows the IR spectrum of 1-octene. As alkenes compounds, these bands are not specific and are generally not noted because they are present in almost all organic molecules.

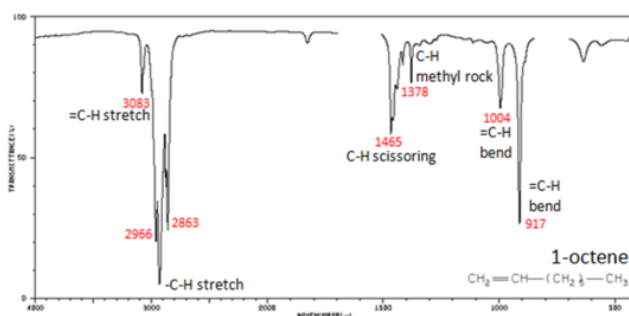


Figure 4. Infrared Spectrum of 1-Octene

In alkynes, each band in the spectrum can be assigned:

- $\text{-C}\equiv\text{C-}$  stretch from  $2260-2100\text{ cm}^{-1}$
- $\text{-C}\equiv\text{C-H}$ : C-H stretch from  $3330-3270\text{ cm}^{-1}$
- $\text{-C}\equiv\text{C-H}$ : C-H bend from  $700-610\text{ cm}^{-1}$

The spectrum of 1-hexyne, a terminal alkyne, is shown below.

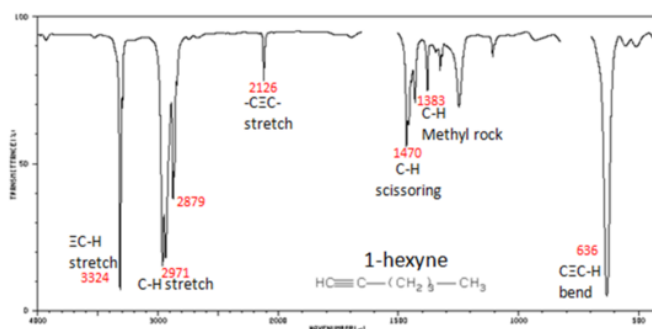


Figure 5. Infrared Spectrum of 1-Hexyne

In aromatic compounds, each band in the spectrum can be assigned:

- C-H stretch from  $3100-3000\text{ cm}^{-1}$
- overtones, weak, from  $2000-1665\text{ cm}^{-1}$
- C-C stretch (in-ring) from  $1600-1585\text{ cm}^{-1}$

- C–C stretch (in-ring) from 1500-1400  $\text{cm}^{-1}$
- C–H "oop" from 900-675  $\text{cm}^{-1}$

Note that this is at slightly higher frequency than is the C–H stretch in alkanes. This is a very useful tool for interpreting IR spectra. Only alkenes and aromatics show a C–H stretch slightly higher than 3000  $\text{cm}^{-1}$ .

Figure 6. shows the spectrum of toluene.

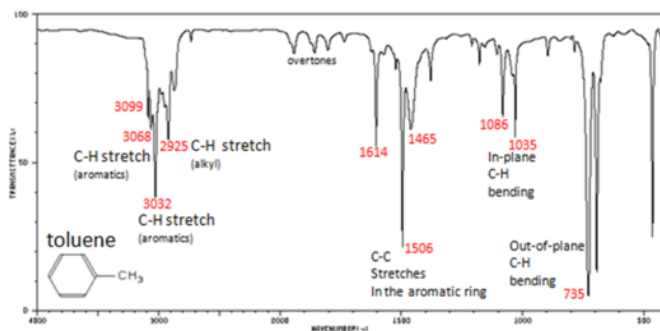


Figure 6. Infrared Spectrum of Toluene

#### FUNCTIONAL GROUPS CONTAINING THE C-O BOND

Alcohols have IR absorptions associated with both the O–H and the C–O stretching vibrations.

- O–H stretch, hydrogen bonded 3500-3200  $\text{cm}^{-1}$
- C–O stretch 1260-1050  $\text{cm}^{-1}$  (s)

Figure 7. shows the spectrum of ethanol. Note the very broad, strong band of the O–H stretch.

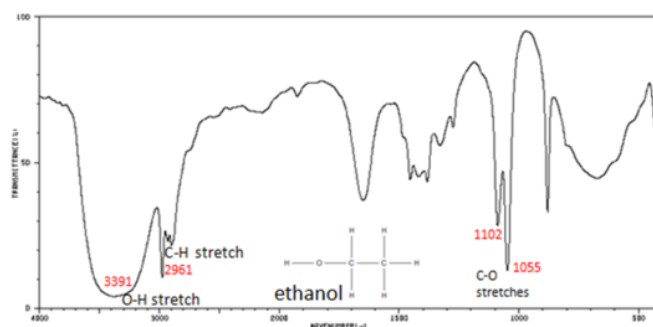


Figure 7. Infrared Spectrum of Ethanol

The carbonyl stretching vibration band C=O of saturated aliphatic ketones appears:

- C=O stretch - aliphatic ketones 1715  $\text{cm}^{-1}$
- ?, ?-unsaturated ketones 1685-1666  $\text{cm}^{-1}$

Figure 8. shows the spectrum of 2-butanone. This is a saturated ketone, and the C=O band appears at 1715.

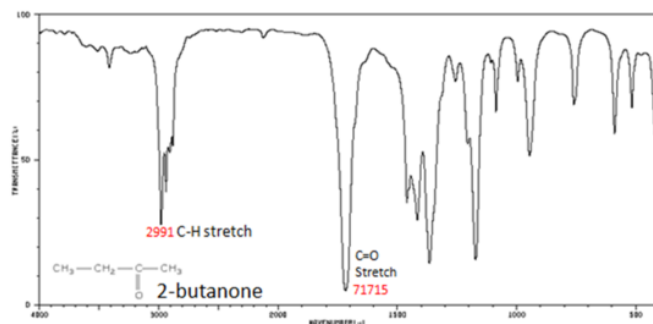


Figure 8. Infrared Spectrum of 2-Butanone

If a compound is suspected to be an aldehyde, a peak always appears around 2720  $\text{cm}^{-1}$  which often appears as a shoulder-type peak just to the right of the alkyl C–H stretches.

- H-C=O stretch 2830-2695  $\text{cm}^{-1}$
- C=O stretch:
  - aliphatic aldehydes 1740-1720  $\text{cm}^{-1}$
  - alpha, beta-unsaturated aldehydes 1710-1685  $\text{cm}^{-1}$

Figure 9. shows the spectrum of butyraldehyde.

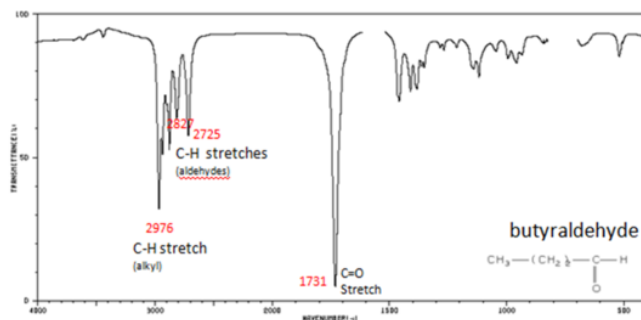


Figure 9. Infrared Spectrum of Butyraldehyde

The carbonyl stretch C=O of esters appears:

- C=O stretch
  - aliphatic from 1750-1735  $\text{cm}^{-1}$
  - $\alpha, \beta$ -unsaturated from 1730-1715  $\text{cm}^{-1}$
- C-O stretch from 1300-1000  $\text{cm}^{-1}$

Figure 10. shows the spectrum of ethyl benzoate.

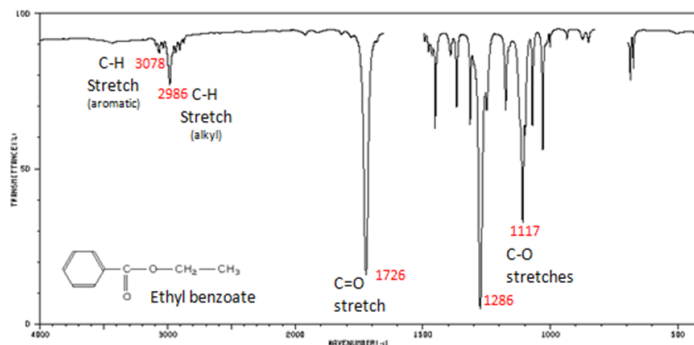


Figure 10. Infrared Spectrum of Ethyl benzoate

The carbonyl stretch C=O of a carboxylic acid appears as an intense band from 1760-1690  $\text{cm}^{-1}$ . The exact position of this broad band depends on whether the carboxylic acid is saturated or unsaturated, dimerized, or has internal hydrogen bonding.

- O-H stretch from 3300-2500  $\text{cm}^{-1}$
- C=O stretch from 1760-1690  $\text{cm}^{-1}$
- C-O stretch from 1320-1210  $\text{cm}^{-1}$
- O-H bend from 1440-1395 and 950-910  $\text{cm}^{-1}$

Figure 11. shows the spectrum of hexanoic acid.

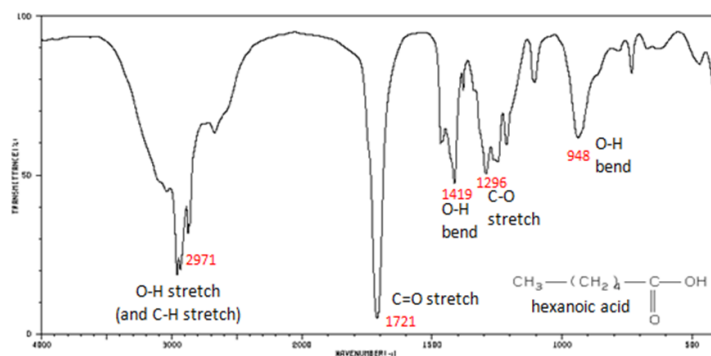


Figure 11. Infrared Spectrum of Hexanoic acid

### ORGANIC NITROGEN COMPOUNDS

- N–O asymmetric stretch from  $1550\text{--}1475\text{ cm}^{-1}$
- N–O symmetric stretch from  $1360\text{--}1290\text{ cm}^{-1}$

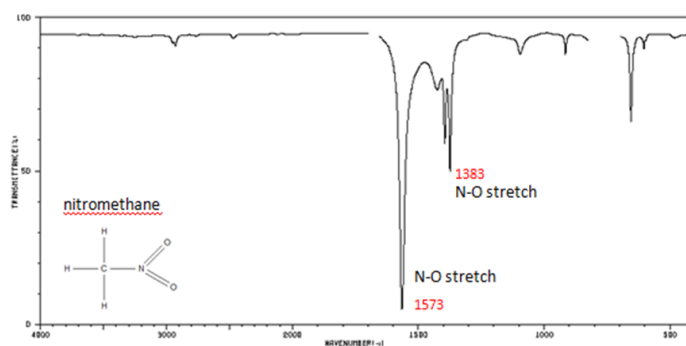


Figure 12. Infrared Spectrum of Nitromethane

### ORGANIC COMPOUNDS CONTAINING HALOGENS

Alkyl halides are compounds that have a C–X bond, where X is a halogen: bromine, chlorine, fluorene, or iodine.

- C–H wag ( $-\text{CH}_2\text{X}$ ) from  $1300\text{--}1150\text{ cm}^{-1}$
- C–X stretches (general) from  $850\text{--}515\text{ cm}^{-1}$ 
  - C–Cl stretch  $850\text{--}550\text{ cm}^{-1}$
  - C–Br stretch  $690\text{--}515\text{ cm}^{-1}$

The spectrum of 1-chloro-2-methylpropane are shown below.

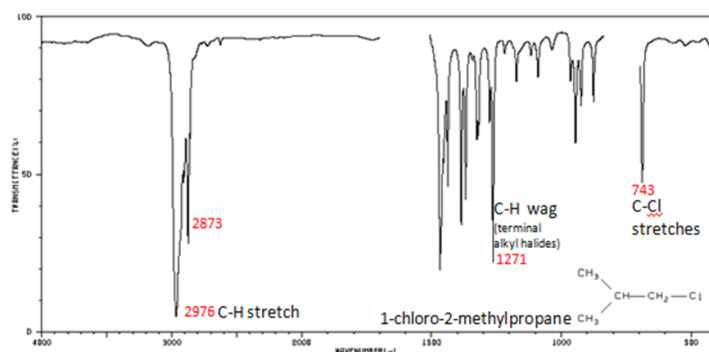


Figure 13. Infrared Spectrum of 1-chloro-2-methylpropane

For more Infrared spectra Spectral database of organic molecules is introduced to use free database. Also, the infrared spectroscopy correlation table is linked on bottom of page to find other assigned IR peaks.

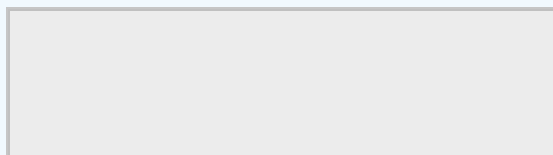
Exercise

1. What functional groups give the following signals in an IR spectrum?

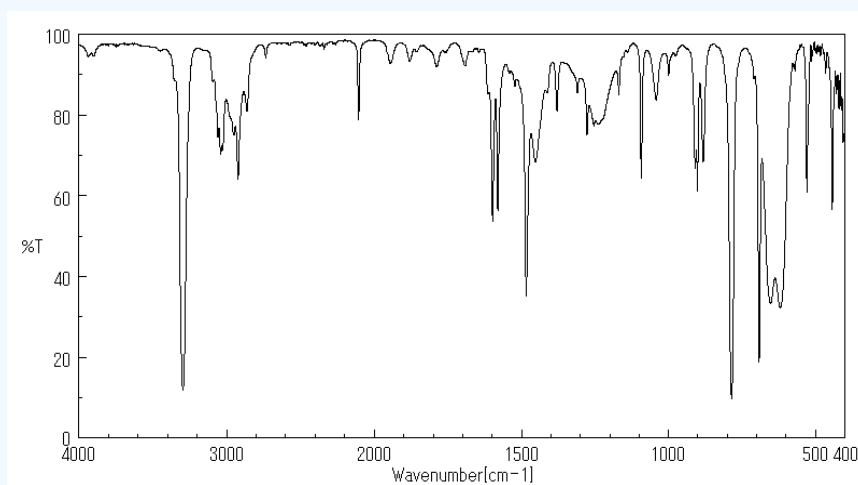
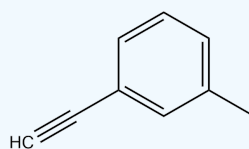
- A)  $1700\text{ cm}^{-1}$
- B)  $1550\text{ cm}^{-1}$
- C)  $1700\text{ cm}^{-1}$  and  $2510\text{-}3000\text{ cm}^{-1}$

2. How can you distinguish the following pairs of compounds through IR analysis?

- A)  $\text{CH}_3\text{OH}$  (Methanol) and  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$  (Diethylether)
- B) Cyclopentane and 1-pentene.
- C)

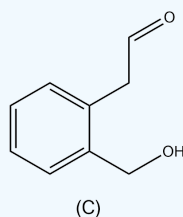
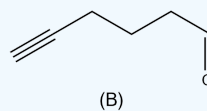
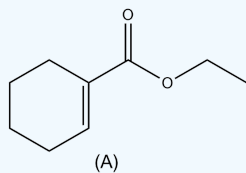


3. The following spectra is for the accompanying compound. What are the peaks that you can identify in the spectrum?

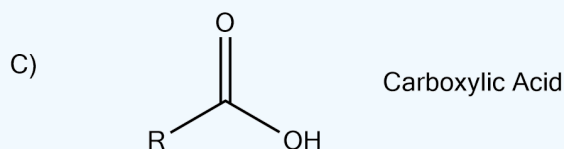
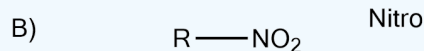
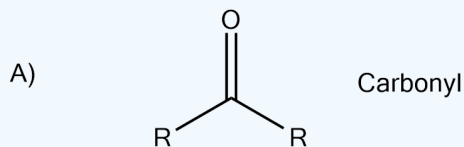


Source: SDBSWeb : <http://sdb.s.db.aist.go.jp> (National Institute of Advanced Industrial Science and Technology, 2 December 2016)

4. What absorptions would the following compounds have in an IR spectra?





**Answer**
**1.**

**2.**

A) A OH peak will be present around  $3300\text{ cm}^{-1}$  for methanol and will be absent in the ether.

B) 1-pentene will have a alkene peak around  $1650\text{ cm}^{-1}$  for the C=C and there will be another peak around  $3100\text{ cm}^{-1}$  for the  $\text{sp}^2$  C-H group on the alkene

C) Cannot distinguish these two isomers. They both have the same functional groups and therefore would have the same peaks on an IR spectra.

**3.**
**Frequency (cm-1) Functional Group**

3200 C≡C-H

2900-3000 C-C-H, C=C-H

2100 C≡C

1610 C=C

(There is also an aromatic undertone region between 2000-1600 which describes the substitution on the phenyl ring.)

**4.**
**A)**
**Frequency (cm-1) Functional Group**

2900-3000 C-C-H, C=C-H

1710 C=O

1610 C=C

1100 C-O

**B)**
**Frequency (cm-1) Functional Group**

3200 C≡C-H

2900-3000 C-C-H, C=C-H

2100 C≡C

1710 C=O

**C)**
**Frequency (cm-1) Functional Group**

3300 (broad) O-H

2900-3000 C-C-H, C=C-H

2000-1800 Aromatic Overtones

1710 C=O

1610 C=C

## CONTRIBUTORS AND ATTRIBUTIONS

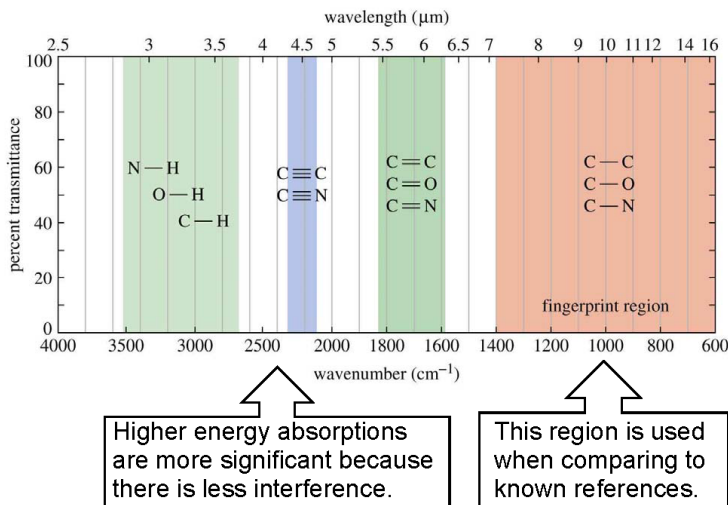
- [Dr. Dietmar Kennepohl](#) FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)

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## 11.6: SUMMARY AND TIPS TO DISTINGUISH BETWEEN CARBONYL FUNCTIONAL GROUPS

### Summary for Interpreting IR Spectra



### IR Absorption Bands to Memorize

- ≈ 3400 cm<sup>-1</sup>: O-H and N-H stretch
- ≈ 3100 cm<sup>-1</sup>: sp and sp<sup>2</sup> C-H stretch
- ≈ 2900 cm<sup>-1</sup>: sp<sup>3</sup> C-H stretch
- ≈ 2700 cm<sup>-1</sup>: aldehyde C-H stretch (fangs)
- ≈ 2200 cm<sup>-1</sup>: C≡C & C≡N stretch  
(primarily for terminal C≡C & C≡N)
- ≈ 1700 cm<sup>-1</sup>: C=O stretch
- ≈ 1600 cm<sup>-1</sup>: C=C stretch (primarily for terminal C=C)
- ≈ 1200 cm<sup>-1</sup>: C-O stretch

## Distinguishing between Functional Groups with Carbonyls C=O's

While there may be subtle differences in the wavenumbers of the carbonyl stretch between some of the functional groups, it is the secondary features of the IR spectrum that help with discernment.

Functional Grp	Carbonyl Stretch	Secondary IR Spectral Feature
Aldehyde	1710 $\text{cm}^{-1}$	fingers at 2700 & 2800 $\text{cm}^{-1}$
Ketone	1710 $\text{cm}^{-1}$	
Acid	1710 $\text{cm}^{-1}$	broad O-H stretch between 3500-2500 $\text{cm}^{-1}$
Ester	1735 $\text{cm}^{-1}$	C-O stretch $\approx$ 1200 $\text{cm}^{-1}$
Amide	1660 $\text{cm}^{-1}$ (doublet)	N-H stretch $\approx$ 3300 $\text{cm}^{-1}$ 2 peaks for $\text{RCONH}_2$ 1 peak for $\text{RCONHR}'$
Acid Chloride	1800 $\text{cm}^{-1}$	energy of carbonyl stretch
Anhydride	1800 & 1750 $\text{cm}^{-1}$	energy of carbonyl doublet

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## 11.7: MASS SPECTROMETRY - AN INTRODUCTION

### Learning Objectives

After completing this section, you should be able to

1. sketch a simple diagram to show the essential features of a mass spectrometer.
2. identify peaks in a simple mass spectrum, and explain how they arise.

### Key Terms

Make certain that you can define, and use in context, the key terms below.

- parent peak (molecular ion peak)
- relative abundance
- mass spectroscopy
- molecular ion ( $M^{+\cdot}$ )
- mass-to-charge ratio ( $m/z$ )

### Study Notes

You may remember from general first-year chemistry how mass spectroscopy has been used to establish the atomic mass and abundance of isotopes.

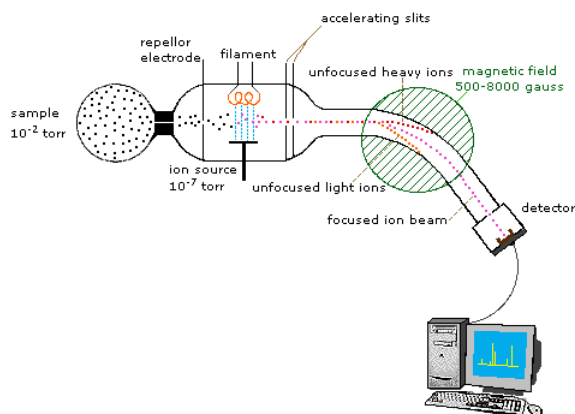
Mass spectrometers are large and expensive, and usually operated only by fully trained personnel, so you will not have the opportunity to use such an instrument as part of this course. Research chemists often rely quite heavily on mass spectra to assist them in the identification of compounds, and you will be required to interpret simple mass spectra both in assignments and on examinations. Note that in most attempts to identify an unknown compound, chemists do not rely exclusively on the results obtained from a single spectroscopic technique. A combination of chemical and physical properties and spectral evidence is usually employed.

### THE MASS SPECTROMETER

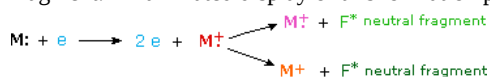
In order to measure the characteristics of individual molecules, a mass spectrometer converts them to ions so that they can be moved about and manipulated by external electric and magnetic fields. The three essential functions of a mass spectrometer, and the associated components, are:

1. The ions are sorted and separated according to their mass and charge. **The Mass Analyzer**
2. The separated ions are then measured, and the results displayed on a chart. **The Detector**

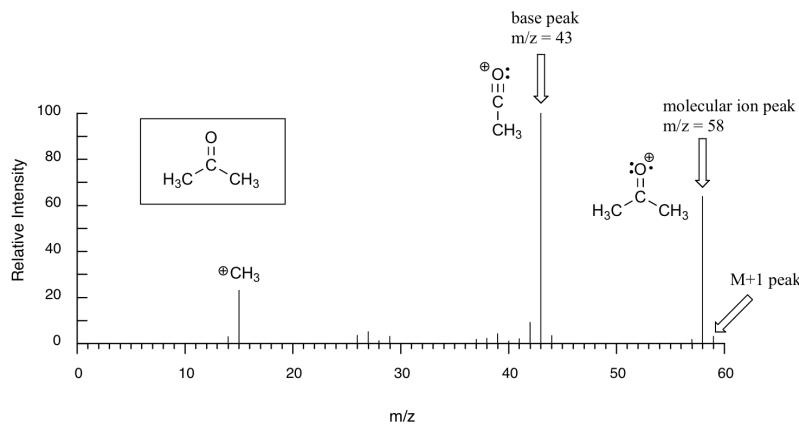
Because ions are very reactive and short-lived, their formation and manipulation must be conducted in a vacuum. Atmospheric pressure is around 760 torr (mm of mercury). The pressure under which ions may be handled is roughly  $10^{-5}$  to  $10^{-8}$  torr (less than a billionth of an atmosphere). Each of the three tasks listed above may be accomplished in different ways. In one common procedure, ionization is effected by a high energy beam of electrons, and ion separation is achieved by accelerating and focusing the ions in a beam, which is then bent by an external magnetic field. The ions are then detected electronically and the resulting information is stored and analyzed in a computer. A mass spectrometer operating in this fashion is outlined in the following diagram. The heart of the spectrometer is the **ion source**. Here molecules of the sample (black dots) are bombarded by electrons (light blue lines) issuing from a heated filament. This is called an **EI** (electron-impact) source. Gases and volatile liquid samples are allowed to leak into the ion source from a reservoir (as shown). Non-volatile solids and liquids may be introduced directly. Cations formed by the electron bombardment (red dots) are pushed away by a charged repeller plate (anions are attracted to it), and accelerated toward other electrodes, having slits through which the ions pass as a beam. Some of these ions fragment into smaller cations and neutral fragments. A perpendicular magnetic field deflects the ion beam in an arc whose radius is inversely proportional to the mass of each ion. Lighter ions are deflected more than heavier ions. By varying the strength of the magnetic field, ions of different mass can be focused progressively on a detector fixed at the end of a curved tube (also under a high vacuum).



When a high energy electron collides with a molecule it often ionizes it by knocking away one of the molecular electrons (either bonding or non-bonding). This leaves behind a **molecular ion** (colored red in the following diagram). Residual energy from the collision may cause the molecular ion to fragment into neutral pieces (colored green) and smaller **fragment ions** (colored pink and orange). The molecular ion is a radical cation, but the fragment ions may either be radical cations (pink) or carbocations (orange), depending on the nature of the neutral fragment. An animated display of this ionization process will appear if you click on the ion source of the mass spectrometer diagram.



Below is typical output for an electron-ionization MS experiment (MS data below is derived from the Spectral Database for Organic Compounds, a free, web-based service provided by AIST in Japan).



The sample is acetone. On the horizontal axis is the value for  $m/z$  (as we stated above, the charge  $z$  is almost always  $+1$ , so in practice this is the same as mass). On the vertical axis is the relative abundance of each ion detected. On this scale, the most abundant ion, called the **base peak**, is set to 100%, and all other peaks are recorded relative to this value. For acetone, the base peak corresponds to a fragment with  $m/z = 43$ . The molecular weight of acetone is 58, so we can identify the peak at  $m/z = 58$  as that corresponding to the **molecular ion peak**, or **parent peak**. Notice that there is a small peak at  $m/z = 59$ : this is referred to as the **M+1 peak**. How can there be an ion that has a greater mass than the molecular ion? Simple: a small fraction - about 1.1% - of all carbon atoms in nature are actually the  $^{13}\text{C}$  rather than the  $^{12}\text{C}$  isotope. The  $^{13}\text{C}$  isotope is, of course, heavier than  $^{12}\text{C}$  by 1 mass unit. In addition, about 0.015% of all hydrogen atoms are actually deuterium, the  $^2\text{H}$  isotope. So the M+1 peak represents those few acetone molecules in the sample which contained either a  $^{13}\text{C}$  or  $^2\text{H}$ .

## CONTRIBUTORS

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## 11.8: FRAGMENTATION PATTERNS IN MASS SPECTROMETRY

### Objectives

After completing this section, you should be able to

1. suggest possible molecular formulas for a compound, given the  $m/z$  value for the molecular ion, or a mass spectrum from which this value can be obtained.
2. predict the relative heights of the  $M^+$ ,  $(M + 1)^+$ , etc., peaks in the mass spectrum of a compound, given the natural abundance of the isotopes of carbon and the other elements present in the compound.
3. interpret the fragmentation pattern of the mass spectrum of a relatively simple, known compound (e.g., hexane).
4. use the fragmentation pattern in a given mass spectrum to assist in the identification of a relatively simple, unknown compound (e.g., an unknown alkane).

### Study Notes

When interpreting fragmentation patterns, you may find it helpful to know that, as you might expect, the weakest carbon-carbon bonds are the ones most likely to break. You might wish to refer to the table of [bond dissociation energies](#) when attempting problems involving the interpretation of mass spectra.

This page looks at how fragmentation patterns are formed when organic molecules are fed into a mass spectrometer, and how you can get information from the mass spectrum.

### THE ORIGIN OF FRAGMENTATION PATTERNS

When the vaporized organic sample passes into the ionization chamber of a mass spectrometer, it is bombarded by a stream of electrons. These electrons have a high enough energy to knock an electron off an organic molecule to form a positive ion. This ion is called the **molecular ion - or sometimes the parent ion** and is often given the symbol  $M^+$  or  $M\dot{+}$ . The dot in this second version represents the fact that somewhere in the ion there will be a single unpaired electron. That's one half of what was originally a pair of electrons - the other half is the electron which was removed in the ionization process.

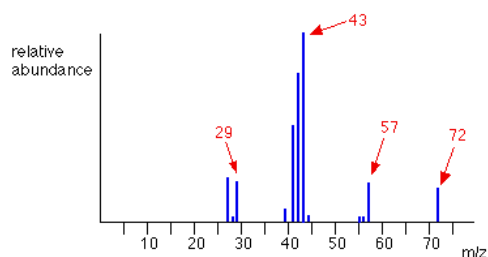
The molecular ions are energetically unstable, and some of them will break up into smaller pieces. The simplest case is that a molecular ion breaks into two parts - one of which is another positive ion, and the other is an uncharged free radical.



The uncharged free radical will **not** produce a line on the mass spectrum. Only charged particles will be accelerated, deflected and detected by the mass spectrometer. These uncharged particles will simply get lost in the machine - eventually, they get removed by the vacuum pump.

The ion,  $X^+$ , will travel through the mass spectrometer just like any other positive ion - and will produce a line on the stick diagram. All sorts of fragmentations of the original molecular ion are possible - and that means that you will get a whole host of lines in the mass spectrum. For example, the mass spectrum of pentane looks like this:

simplified mass spectrum of pentane -  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$



#### Note

The pattern of lines in the mass spectrum of an *organic compound* tells you something quite different from the pattern of lines in the mass spectrum of an *element*. With an element, each line represents a different isotope of that element. With a compound, each line represents a different fragment produced when the molecular ion breaks up.

In the stick diagram showing the mass spectrum of pentane, the line produced by the heaviest ion passing through the machine (at  $m/z = 72$ ) is due to the **molecular ion**. The tallest line in the stick diagram (in this case at  $m/z = 43$ ) is called the **base peak**. This is usually given an arbitrary height of 100, and the height of everything else is measured relative to this. The base peak is the tallest peak because it represents the commonest fragment ion to be formed - either because there are several ways in which it could be produced during fragmentation of the parent ion, or because it is a particularly stable ion.

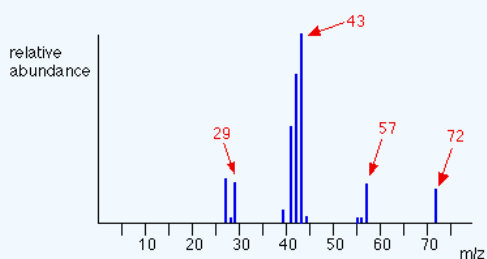
#### USING FRAGMENTATION PATTERNS

This section will ignore the information you can get from the molecular ion (or ions). That is covered in three other pages which you can get at via the mass spectrometry menu. You will find a link at the bottom of the page.

#### Example: Pentane

Let's have another look at the mass spectrum for pentane:

simplified mass spectrum of pentane -  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$



What causes the line at  $m/z = 57$ ?

How many carbon atoms are there in this ion? There cannot be 5 because  $5 \times 12 = 60$ . What about 4?  $4 \times 12 = 48$ . That leaves 9 to make up a total of 57. How about  $\text{C}_4\text{H}_9^+$  then?

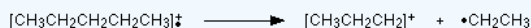
$\text{C}_4\text{H}_9^+$  would be  $[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2]^+$ , and this would be produced by the following fragmentation:





The methyl radical produced will simply get lost in the machine.

The line at  $m/z = 43$  can be worked out similarly. If you play around with the numbers, you will find that this corresponds to a break producing a 3-carbon ion:



The line at  $m/z = 29$  is typical of an ethyl ion,  $[\text{CH}_3\text{CH}_2]^+$ :

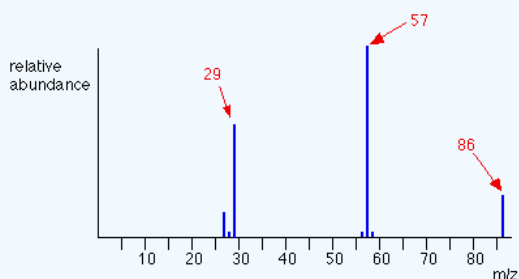


The other lines in the mass spectrum are more difficult to explain. For example, lines with  $m/z$  values 1 or 2 less than one of the easy lines are often due to loss of one or more hydrogen atoms during the fragmentation process.

### Example: Pentan-3-one

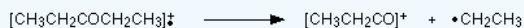
This time the base peak (the tallest peak - and so the commonest fragment ion) is at  $m/z = 57$ . But this is not produced by the same ion as the same  $m/z$  value peak in pentane.

simplified mass spectrum of pentan-3-one -  $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$

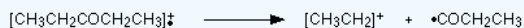


If you remember, the  $m/z = 57$  peak in pentane was produced by  $[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2]^+$ . If you look at the structure of pentan-3-one, it's impossible to get that particular fragment from it.

Work along the molecule mentally chopping bits off until you come up with something that adds up to 57. With a small amount of patience, you'll eventually find  $[\text{CH}_3\text{CH}_2\text{CO}]^+$  - which is produced by this fragmentation:



You would get exactly the same products whichever side of the CO group you split the molecular ion. The  $m/z = 29$  peak is produced by the ethyl ion - which once again could be formed by splitting the molecular ion either side of the CO group.



### PEAK HEIGHTS AND STABILITY

The more stable an ion is, the more likely it is to form. The more of a particular sort of ion that's formed, the higher its peak height will be. We'll look at two common examples of this.

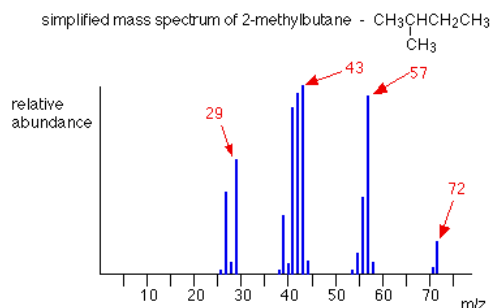
### CARBOCATIONS (CARBONIUM IONS)

Summarizing the most important conclusion from the page on carbocations:

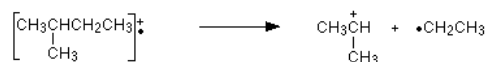
#### Order of stability of carbocations

primary < secondary < tertiary

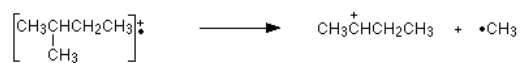
Applying the logic of this to fragmentation patterns, it means that a split which produces a secondary carbocation is going to be more successful than one producing a primary one. A split producing a tertiary carbocation will be more successful still. Let's look at the mass spectrum of 2-methylbutane. 2-methylbutane is an isomer of pentane - isomers are molecules with the same molecular formula, but a different spatial arrangement of the atoms.



Look first at the very strong peak at  $m/z = 43$ . This is caused by a different ion than the corresponding peak in the pentane mass spectrum. This peak in 2-methylbutane is caused by:



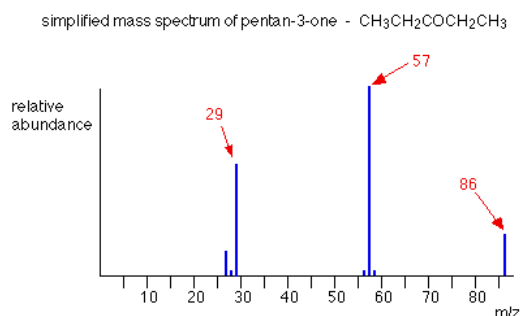
The ion formed is a secondary carbocation - it has two alkyl groups attached to the carbon with the positive charge. As such, it is relatively stable. The peak at  $m/z = 57$  is much taller than the corresponding line in pentane. Again a secondary carbocation is formed - this time, by:



You would get the same ion, of course, if the left-hand  $\text{CH}_3$  group broke off instead of the bottom one as we've drawn it. In these two spectra, this is probably the most dramatic example of the extra stability of a secondary carbocation.

### ACYLIUM IONS, $[\text{RCO}]^+$

Ions with the positive charge on the carbon of a carbonyl group,  $\text{C}=\text{O}$ , are also relatively stable. This is fairly clearly seen in the mass spectra of ketones like pentan-3-one.



The base peak, at  $m/z=57$ , is due to the  $[\text{CH}_3\text{CH}_2\text{CO}]^+$  ion. We've already discussed the fragmentation that produces this.

Note

The more stable an ion is, the more likely it is to form. The more of a particular ion that is formed, the higher will be its peak height.

### USING MASS SPECTRA TO DISTINGUISH BETWEEN COMPOUNDS

Suppose you had to suggest a way of distinguishing between pentan-2-one and pentan-3-one using their mass spectra.

pentan-2-one	$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$
pentan-3-one	$\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$

Each of these is likely to split to produce ions with a positive charge on the CO group. In the pentan-2-one case, there are two different ions like this:

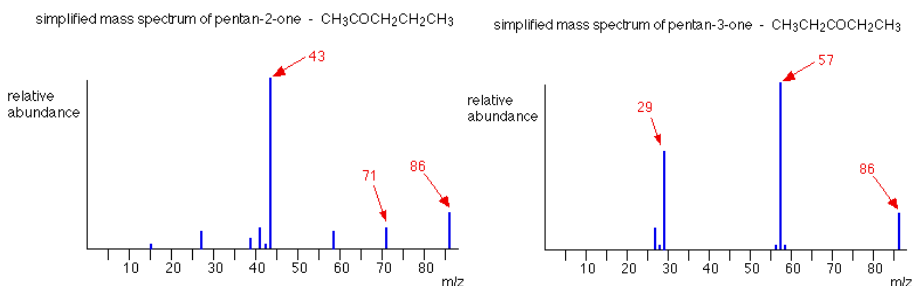
- $[\text{CH}_3\text{CO}]^+$
- $[\text{COCH}_2\text{CH}_2\text{CH}_3]^+$

That would give you strong lines at  $m/z = 43$  and  $71$ . With pentan-3-one, you would only get one ion of this kind:

- $[\text{CH}_3\text{CH}_2\text{CO}]^+$

In that case, you would get a strong line at  $57$ . You don't need to worry about the other lines in the spectra - the  $43$ ,  $57$  and  $71$  lines give you plenty of difference between the two. The  $43$  and  $71$  lines are missing from the pentan-3-one spectrum, and the  $57$  line is missing from the pentan-2-one one.

The two mass spectra look like this:

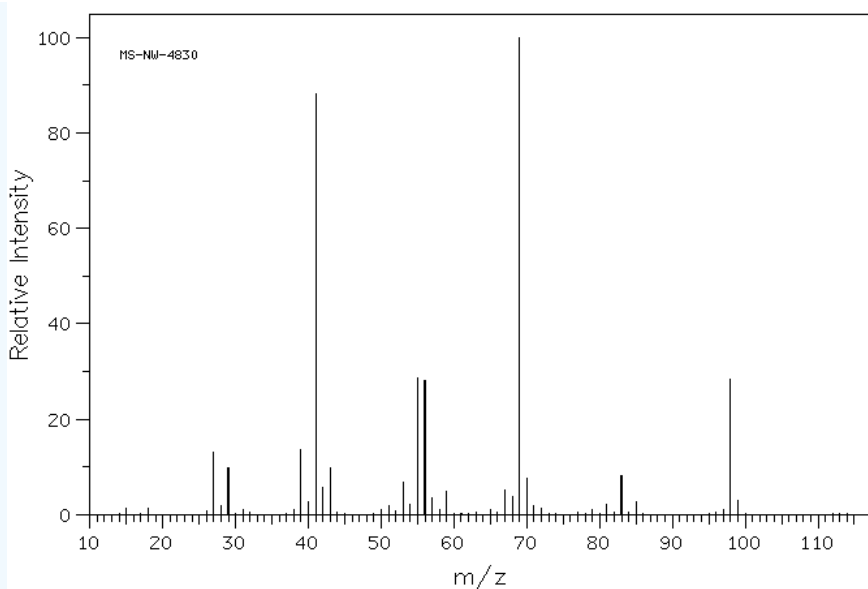


As you've seen, the mass spectrum of even very similar organic compounds will be quite different because of the different fragmentation patterns that can occur. Provided you have a computer data base of mass spectra, any unknown spectrum can be computer analyzed and simply matched against the data base.

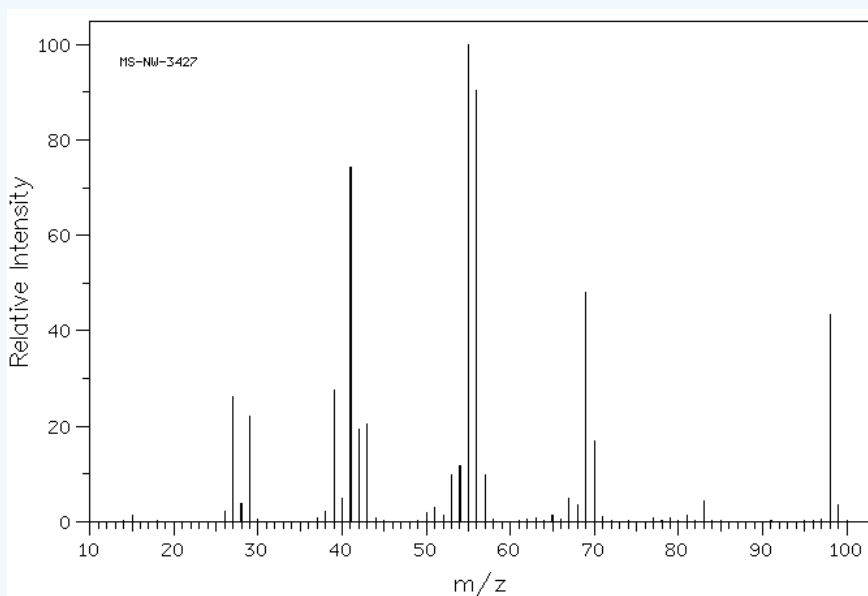
### Exercise

5. Caffeine has a mass of  $194.19$  amu, determined by mass spectrometry, and contains C, N, H, O. What is a molecular formula for this molecule?
6. The following are the spectra for 2-methyl-2-hexene and 2-heptene, which spectra belongs to the correct molecule. Explain.

A:

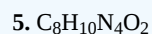


B:



Source: SDBSWeb : <http://sdb.sdb.aist.go.jp> (National Institute of Advanced Industrial Science and Technology, 2 December 2016)

**Answer**



$C = 12 \times 8 = 96$

$N = 14 \times 4 = 56$

$H = 1 \times 10 = 10$

$O = 2 \times 16 = 32$

$96+56+10+32 = 194 \text{ g/mol}$

6. The (A) spectrum is 2-methyl-2-hexene and the (B) spectrum is 2-heptene. Looking at (A) the peak at 68  $m/z$  is the fractioned molecule with just the tri-substituted alkene present. While (B) has a strong peak around the 56  $m/z$ , which in this case is the di-substituted alkene left behind from the linear heptene.

## CONTRIBUTORS AND ATTRIBUTIONS

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- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)
- Jim Clark ([Chemguide.co.uk](#))

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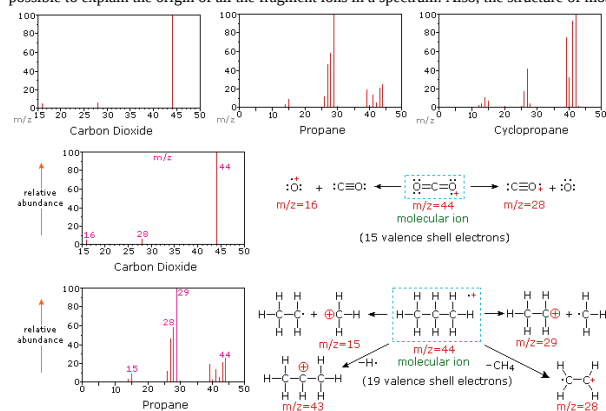
## 11.9: USEFUL PATTERNS FOR STRUCTURE ELUCIDATION

### THE NATURE OF MASS SPECTRA

A mass spectrum will usually be presented as a vertical bar graph, in which each bar represents an ion having a specific mass-to-charge ratio ( $m/z$ ) and the length of the bar indicates the relative abundance of the ion. The most intense ion is assigned an abundance of 100, and it is referred to as the **base peak**. Most of the ions formed in a mass spectrometer have a single charge, so the  $m/z$  value is equivalent to mass itself. Modern mass spectrometers easily distinguish (resolve) ions differing by only a single atomic mass unit, and thus provide completely accurate values for the molecular mass of a compound. The highest-mass ion in a spectrum is normally considered to be the molecular ion, and lower-mass ions are fragments from the molecular ion, assuming the sample is a single pure compound.

Atomic mass is given in terms of the **unified atomic mass unit** (symbol:  $\mu$ ) or **dalton** (symbol: Da). In recent years there has been a gradual change towards using the dalton in preference to the unified atomic mass unit. The dalton is classified as a "non-SI unit whose values in SI units must be obtained experimentally". It is defined as one twelfth of the rest mass of an unbound atom of carbon-12 in its nuclear and electronic ground state, and has a value of  $1.660538782(83) \times 10^{-27}$  kg.

The following diagram displays the mass spectra of three simple gaseous compounds, carbon dioxide, propane and cyclopropane. The molecules of these compounds are similar in size,  $\text{CO}_2$  and  $\text{C}_3\text{H}_8$  both have a nominal mass of 44 Da, and  $\text{C}_3\text{H}_6$  has a mass of 42 Da. The molecular ion is the strongest ion in the spectra of  $\text{CO}_2$  and  $\text{C}_3\text{H}_6$ , and it is moderately strong in propane. The unit mass resolution is readily apparent in these spectra (note the separation of ions having  $m/z=39, 40, 41$  and  $42$  in the cyclopropane spectrum). Even though these compounds are very similar in size, it is a simple matter to identify them from their individual mass spectra. By clicking on each spectrum in turn, a partial fragmentation analysis and peak assignment will be displayed. Even with simple compounds like these, it should be noted that it is rarely possible to explain the origin of all the fragment ions in a spectrum. Also, the structure of most fragment ions is seldom known with certainty.

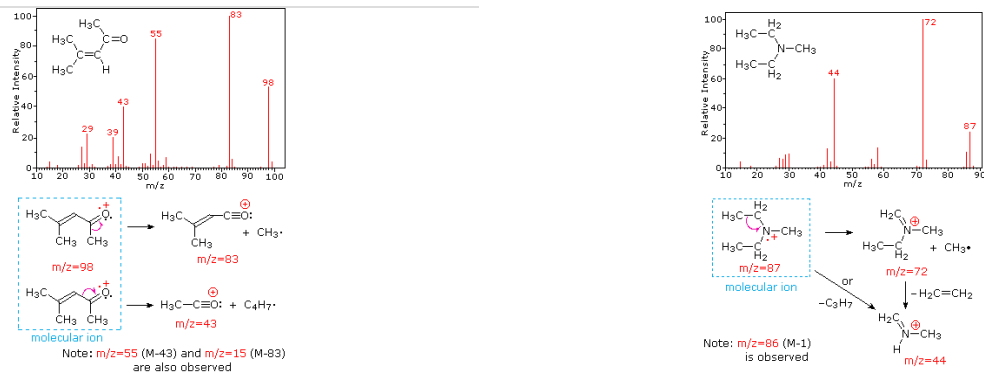


Since a molecule of carbon dioxide is composed of only three atoms, its mass spectrum is very simple. The molecular ion is also the base peak, and the only fragment ions are CO ( $m/z=28$ ) and O ( $m/z=16$ ). The molecular ion of propane also has  $m/z=44$ , but it is not the most abundant ion in the spectrum. Cleavage of a carbon-carbon bond gives methyl and ethyl fragments, one of which is a carbocation and the other a radical. Both distributions are observed, but the larger ethyl cation ( $m/z=29$ ) is the most abundant, possibly because its size affords greater charge dispersal. A similar bond cleavage in cyclopropane does not give two fragments, so the molecular ion is stronger than in propane, and is in fact responsible for the base peak. Loss of a hydrogen atom, either before or after ring opening, produces the stable allyl cation ( $m/z=41$ ). The third strongest ion in the spectrum has  $m/z=39$  ( $\text{C}_3\text{H}_3$ ). Its structure is uncertain, but two possibilities are shown in the diagram. The small  $m/z=39$  ion in propane and the absence of a  $m/z=29$  ion in cyclopropane are particularly significant in distinguishing these hydrocarbons.

Most stable organic compounds have an even number of total electrons, reflecting the fact that electrons occupy atomic and molecular orbitals in pairs. When a single electron is removed from a molecule to give an ion, the total electron count becomes an odd number, and we refer to such ions as **radical cations**. The molecular ion in a mass spectrum is always a radical cation, but the fragment ions may either be even-electron cations or odd-electron radical cations, depending on the neutral fragment lost. The simplest and most common fragmentations are bond cleavages producing a neutral radical (odd number of electrons) and a cation having an even number of electrons. A less common fragmentation, in which an even-electron neutral fragment is lost, produces an odd-electron radical cation fragment ion. Fragment ions themselves may fragment further. As a rule, odd-electron ions may fragment either to odd or even-electron ions, but even-electron ions fragment only to other even-electron ions. The masses of molecular and fragment ions also reflect the electron count, depending on the number of nitrogen atoms in the species.

Ions with no nitrogen or an even # N atoms	odd-electron ions even-number mass	even-electron ions odd-number mass
Ions having an odd # N atoms	odd-electron ions odd-number mass	even-electron ions even-number mass

This distinction is illustrated nicely by the following two examples. The unsaturated ketone, 4-methyl-3-pentene-2-one, on the left has no nitrogen so the mass of the molecular ion ( $m/z = 98$ ) is an even number. Most of the fragment ions have odd-numbered masses, and therefore are even-electron cations. Diethylmethylamine, on the other hand, has one nitrogen and its molecular mass ( $m/z = 87$ ) is an odd number. A majority of the fragment ions have even-numbered masses (ions at  $m/z = 30, 42, 56$  &  $58$  are not labeled), and are even-electron nitrogen cations. The weak even-electron ions at  $m/z=15$  and  $29$  are due to methyl and ethyl cations (no nitrogen atoms). The fragmentations leading to the chief fragment ions will be displayed by clicking on the appropriate spectrum. Repeated clicks will cycle the display.



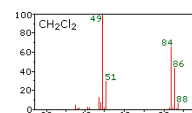
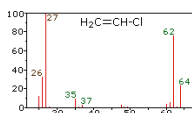
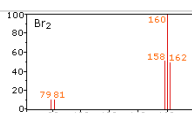
4-methyl-3-pentene-2-one | N,N-diethylmethylamine

When non-bonded electron pairs are present in a molecule (e.g. on N or O), fragmentation pathways may sometimes be explained by assuming the missing electron is partially localized on that atom. A few such mechanisms are shown above. Bond cleavage generates a radical and a cation, and both fragments often share these roles, albeit unequally.

### ISOTOPES

Since a mass spectrometer separates and detects ions of slightly different masses, it easily distinguishes different isotopes of a given element. This is manifested most dramatically for compounds containing bromine and chlorine, as illustrated by the following examples. Since molecules of bromine have only two atoms, the spectrum on the left will come as a surprise if a single atomic mass of 80 Da is assumed for Br. The five peaks in this spectrum demonstrate clearly that natural bromine consists of a nearly 50:50 mixture of isotopes having atomic masses of 79 and 81 Da respectively. Thus, the bromine molecule may be

composed of two  $^{79}\text{Br}$  atoms (mass 158 Da), two  $^{81}\text{Br}$  atoms (mass 162 Da) or the more probable combination of  $^{79}\text{Br}$ - $^{81}\text{Br}$  (mass 160 Da). Fragmentation of  $\text{Br}_2$  to a bromine cation then gives rise to equal sized ion peaks at 79 and 81 Da.



bromine

vinyl chloride

methylene chloride

The center and right hand spectra show that chlorine is also composed of two isotopes, the more abundant having a mass of 35 Da, and the minor isotope a mass 37 Da. The precise isotopic composition of chlorine and bromine is:

- **Chlorine:** 75.77%  $^{35}\text{Cl}$  and 24.23%  $^{37}\text{Cl}$
- **Bromine:** 50.50%  $^{79}\text{Br}$  and 49.50%  $^{81}\text{Br}$

The presence of chlorine or bromine in a molecule or ion is easily detected by noticing the intensity ratios of ions differing by 2 Da. In the case of methylene chloride, the molecular ion consists of three peaks at  $m/z=84$ , 86 & 88 Da, and their diminishing intensities may be calculated from the natural abundances given above. Loss of a chlorine atom gives two isotopic fragment ions at  $m/z=49$  & 51 Da, clearly incorporating a single chlorine atom. Fluorine and iodine, by contrast, are monoisotopic, having masses of 19 Da and 127 Da respectively. It should be noted that the presence of halogen atoms in a molecule or fragment ion does not change the odd-even mass rules given above.

To make use of a calculator that predicts the isotope clusters for different combinations of chlorine, bromine and other elements [Click Here](#). This application was developed at Colby College.

### ISOTOPIC ABUNDANCE CALCULATOR

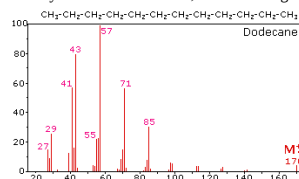
Calculator interface showing input fields for Molecular Ion (100%), M+1, and M+2.

Two other common elements having useful isotope signatures are carbon,  $^{13}\text{C}$  is 1.1% natural abundance, and sulfur,  $^{33}\text{S}$  and  $^{34}\text{S}$  are 0.76% and 4.22% natural abundance respectively. For example, the small  $m/z=99$  Da peak in the spectrum of 4-methyl-3-pentene-2-one (above) is due to the presence of a single  $^{13}\text{C}$  atom in the molecular ion. Although less important in this respect,  $^{15}\text{N}$  and  $^{18}\text{O}$  also make small contributions to higher mass satellites of molecular ions incorporating these elements.

The calculator on the right may be used to calculate the isotope contributions to ion abundances 1 and 2 Da greater than the molecular ion (M). Simply enter an appropriate subscript number to the right of each symbol, leaving those elements not present blank, and press the "Calculate" button. The numbers displayed in the M+1 and M+2 boxes are relative to M being set at 100%.

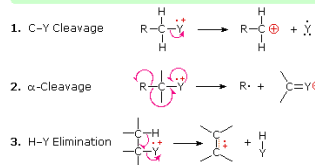
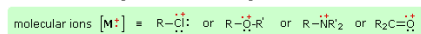
### FRAGMENTATION PATTERNS

The fragmentation of molecular ions into an assortment of fragment ions is a mixed blessing. The nature of the fragments often provides a clue to the molecular structure, but if the molecular ion has a lifetime of less than a few microseconds it will not survive long enough to be observed. Without a molecular ion peak as a reference, the difficulty of interpreting a mass spectrum increases markedly. Fortunately, most organic compounds give mass spectra that include a molecular ion, and those that do not often respond successfully to the use of milder ionization conditions. Among simple organic compounds, the most stable molecular ions are those from aromatic rings, other conjugated pi-electron systems and cycloalkanes. Alcohols, ethers and highly branched alkanes generally show the greatest tendency toward fragmentation.



The mass spectrum of dodecane on the right illustrates the behavior of an unbranched alkane. Since there are no heteroatoms in this molecule, there are no non-bonding valence shell electrons. Consequently, the radical cation character of the molecular ion ( $m/z = 170$ ) is delocalized over all the covalent bonds. Fragmentation of C-C bonds occurs because they are usually weaker than C-H bonds, and this produces a mixture of alkyl radicals and alkyl carbocations. The positive charge commonly resides on the smaller fragment, so we see a homologous series of hexyl ( $m/z = 85$ ), pentyl ( $m/z = 71$ ), butyl ( $m/z = 57$ ), propyl ( $m/z = 43$ ), ethyl ( $m/z = 29$ ) and methyl ( $m/z = 15$ ) cations. These are accompanied by a set of corresponding alkenyl carbocations (e.g.  $m/z = 55, 41$  & 27) formed by loss of 2 H. All of the significant fragment ions in this spectrum are even-electron ions. In most alkane spectra the propyl and butyl ions are the most abundant.

The presence of a functional group, particularly one having a heteroatom Y with non-bonding valence electrons (Y = N, O, S, X etc.), can dramatically alter the fragmentation pattern of a compound. This influence is thought to occur because of a "localization" of the radical cation component of the molecular ion on the heteroatom. After all, it is easier to remove (ionize) a non-bonding electron than one that is part of a covalent bond. By localizing the reactive moiety, certain fragmentation processes will be favored. These are summarized in the following diagram, where the green shaded box at the top displays examples of such "localized" molecular ions. The first two fragmentation paths lead to even-electron ions, and the elimination (path #3) gives an odd-electron ion. Note the use of different curved arrows to show single electron shifts compared with electron pair shifts.

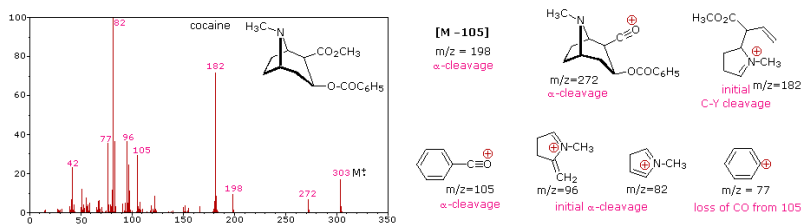


The charge distributions shown above are common, but for each cleavage process the charge may sometimes be carried by the other (neutral) species, and both fragment ions are observed. Of the three cleavage reactions described here, the  $\alpha$ -cleavage is generally favored for nitrogen, oxygen and sulfur compounds. Indeed, in the previously displayed spectra of 4-methyl-3-pentene-2-one and N,N-diethylmethanamine the major fragment ions come from  $\alpha$ -cleavages. Further examples of functional group influence on fragmentation are provided by a selection of compounds that may be examined by clicking the left button below. Useful tables of common fragment ions and neutral species may be viewed by clicking the right button.

Assigned Mass Spectra

View Fragment Tables

The complexity of fragmentation patterns has led to mass spectra being used as "fingerprints" for identifying compounds. Environmental pollutants, pesticide residues on food, and controlled substance identification are but a few examples of this application. Extremely small samples of an unknown substance (a microgram or less) are sufficient for such analysis. The following mass spectrum of cocaine demonstrates how a forensic laboratory might determine the nature of an unknown street drug. Even though extensive fragmentation has occurred, many of the more abundant ions (identified by magenta numbers) can be rationalized by the three mechanisms shown above. Plausible assignments may be seen by clicking on the spectrum, and it should be noted that all are even-electron ions. The  $m/z = 42$  ion might be any or all of the following:  $\text{C}_3\text{H}_6$ ,  $\text{C}_2\text{H}_2\text{O}$  or  $\text{C}_2\text{H}_4\text{N}$ . A precise assignment could be made from a high-resolution  $m/z$  value (next section).

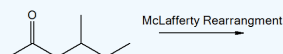
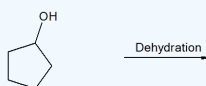
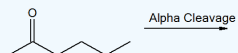


Odd-electron fragment ions are often formed by characteristic rearrangements in which stable neutral fragments are lost. Mechanisms for some of these rearrangements have been identified by following the course of isotopically labeled molecular ions. A few examples of these rearrangement mechanisms may be seen by clicking the following button.

Assorted Rearrangement Fragmentations

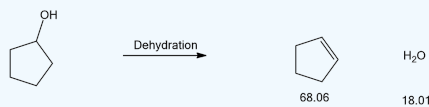
### Exercise

7. What are the masses of all the components in the following fragmentations?



Answer

7.



### CONTRIBUTORS AND ATTRIBUTIONS

#### CONTRIBUTORS

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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## 11.10: DETERMINATION OF THE MOLECULAR FORMULA BY HIGH RESOLUTION MASS SPECTROMETRY

### HIGH RESOLUTION MASS SPECTROMETRY

In assigning mass values to atoms and molecules, we have assumed integral values for isotopic masses. However, accurate measurements show that this is not strictly true. Because the strong nuclear forces that bind the components of an atomic nucleus together vary, the actual mass of a given isotope deviates from its nominal integer by a small but characteristic amount (remember  $E = mc^2$ ). Thus, relative to  $^{12}\text{C}$  at 12.0000, the isotopic mass of  $^{16}\text{O}$  is 15.9949 Da (not 16) and  $^{14}\text{N}$  is 14.0031 Da (not 14).

Formula	$\text{C}_6\text{H}_{12}$	$\text{C}_5\text{H}_8\text{O}$	$\text{C}_4\text{H}_8\text{N}_2$
Mass	84.0939	84.0575	84.0688

By designing mass spectrometers that can determine  $m/z$  values accurately to four decimal places, it is possible to distinguish different formulas having the same nominal mass. The table on the right illustrates this important feature, and a double-focusing high-resolution mass spectrometer easily distinguishes ions having these compositions. Mass spectrometry therefore not only provides a specific molecular mass value, but it may also establish the molecular formula of an unknown compound.

Tables of precise mass values for any molecule or ion are available in libraries; however, the mass calculator provided below serves the same purpose. Since a given nominal mass may correspond to several molecular formulas, lists of such possibilities are especially useful when evaluating the spectrum of an unknown compound. Composition tables are available for this purpose, and a particularly useful program for calculating all possible combinations of H, C, N & O that give a specific nominal mass has been written by Jef Rozenski. To use this calculator [Click Here](#).

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### CONTRIBUTORS

- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)

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