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**Teaching spectroscopy through the use of computer simulation**

**Pfister, Karen Louise, D.A.**

**Middle Tennessee State University, 1991**

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**TEACHING SPECTROSCOPY THROUGH THE USE  
OF COMPUTER SIMULATION**

**K. L. Pfister**

**A dissertation presented to the  
Graduate Faculty of Middle Tennessee State University  
in partial fulfillment of the requirements  
for the degree Doctor of Arts**

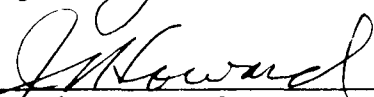
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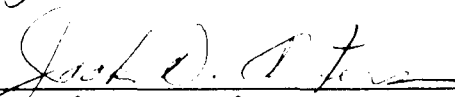
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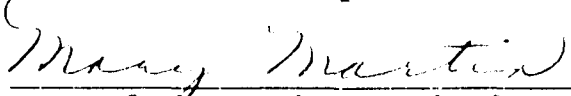
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## ABSTRACT

### TEACHING SPECTROSCOPY THROUGH THE USE OF COMPUTER SIMULATION

K. L. Pfister

Spectral analysis of hydrocarbons is an important part of teaching organic chemistry. This field has depended heavily upon infrared spectroscopy (IR) and proton nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR) with some emphasis placed on mass spectroscopy (mass spec) and carbon-13 nuclear magnetic resonance spectroscopy ( $^{13}\text{C}$  NMR). The main use of these concepts, while briefly covered during lecture, is in the identification of unknowns in qualitative organic laboratory sessions. The combination of "wet" qualitative chemical analysis and spectroscopic analysis of a compound makes positive identification of an unknown possible.

While some large universities have teaching laboratories equipped with an IR and an  $^1\text{H}$  NMR spectrometer, many schools do not have these facilities. Paul Schatz of the University of Wisconsin recognized this problem and designed a software package for computers which simulates two of the most common spectrometers; the Perkin Elmer 1310 IR and the Varian EM 360 NMR.

The primary purpose of this project was to design a

K. L. Pfister

workbook which includes an introduction to the spectroscopic methods, and contains appropriate instructions for using the Paul Schatz simulators. The workbook is structured primarily around proton NMR and IR simulators and written predominantly for institutions that do not have instrumentation available to organic students.

In addition to covering IR and proton NMR spectroscopy, the workbook also discusses  $^{13}\text{C}$  NMR and mass spectroscopy. Since the NMR simulator is not designed for  $^{13}\text{C}$  NMR and a mass spec simulator does not exist, the second part of this project involved simulating mass and  $^{13}\text{C}$  NMR spectra that complement the IR and proton NMR spectra available with the simulator software packages. The  $^{13}\text{C}$  NMR and mass spec spectra were saved on disks and accompany the workbook. These supplemental data disks should be especially beneficial to the instructor as mass and  $^{13}\text{C}$  NMR spectra are difficult to acquire.

After completing the workbook, the student should be able to identify all four types of spectra, and successfully operate the instrument simulators.



## ACKNOWLEDGMENTS

I would like to thank Dr. Walter Nelms, Dr. Douglas Tuech, Mr. Jim Chumney, Mr. Frank Dodson, and Mr. Van Veatch of Jackson State Community College without whose support this project would not have been possible. Thanks is also expressed to Dr. Dan Scott of the Department of Chemistry and Physics of Middle Tennessee State University, for his continued encouragement. Special appreciation is extended to other Middle Tennessee State faculty, Dr. James Howard, Dr. Martin Stewart, and Dr. Jack Arters. Their example and commitment to excellence has left a lasting impression. Most importantly, I would like to thank the chairman of my committee, Dr. Roy Clark, for his understanding and patient direction.

There are some very special people that must be mentioned. Without their inspiration, this project would have never been more than an idea. Those people are students, past and present, that have not only encouraged their teacher, but played an instrumental role in the creation and completion of this project. Appreciation is expressed to Ms. Tonya Middleton Kirby, Mr. Eddie Moody, and Ms. Laurie Young for reviewing parts of the workbook. Special thanks is given to Mr. Jesse Salmon for his time and patience in solving software and hardware problems.

I would like to thank Mr. Brent Veatch and Mr. Ed Carey

for their time and efforts, especially when it came to dealing with computers. Special gratitude is extended to friends, Ms. Angla Hinson and Ms. Marie Sheeks for their support during this time. Last, but not least, once again, I thank you, Mom and Dad, for all that you have helped me to become.

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## CHAPTER 1

### INTRODUCTION

Spectral analysis of hydrocarbons is an important aspect in the teaching of organic chemistry. For years, the backbone of analysis has rested upon infrared spectroscopy (IR) and nuclear magnetic resonance spectroscopy (NMR), primarily proton ( $^1\text{H}$  NMR). Some emphasis was placed on mass spectroscopy (mass spec). Recently, carbon-13 nuclear magnetic resonance spectroscopy ( $^{13}\text{C}$  NMR) has been added to the topics covered in the undergraduate course (1,2). These concepts, while covered briefly in a lecture course, are many times supplemented in a laboratory session, and later applied to qualitative organic analysis in the identification of unknowns. Information obtained from the spectra indicate the presence of particular functional groups as well as the carbon structure of the molecule. The combination of "wet" qualitative chemical analysis and spectroscopic analysis of a compound makes positive identification of an unknown possible.

Well-equipped teaching laboratories have an IR and an NMR spectrometer available for student use. In some instances, larger universities limit student usage of these instruments to upper level courses or research, thus the undergraduate organic student never becomes familiar with an actual spectrometer. Equipment is very expensive,

therefore many smaller institutions cannot afford even the most inexpensive instruments. In both of these situations, the student experience in spectroscopy is limited to text-book examples of spectral interpretation. If organic qualitative analysis is incorporated into the laboratory schedule, the instructor must provide each student with photocopied spectra of their unknown to compensate for the lack of appropriate instrumentation. While this method works fine in helping determine the identity of the unknown, the student lacks practical knowledge and skill that is acquired only by operating an actual spectrometer.

Paul Schatz of the University of Wisconsin has addressed this situation by designing computer software (available from Queue, Inc. Bridgeport, CT) that simulate two commonly used spectrometers, a Perkin Elmer 1310 IR (3) and a Varian EM 360 NMR (4). The computer monitor displays a control panel which resembles that of the actual instrument. By following a series of instructions, the student operates the simulator either from the keyboard or by using a mouse. A sample is chosen from a directory of prerecorded spectra that have been saved on disk. After the proper instrumental adjustments have been made, a spectrum is obtained which may then be plotted or printed on a dot-matrix printer.

In conjunction with the basic software packages, additional data disks may be purchased which contain a variety of spectra. These spectra make favorable choices for



qualitative unknowns or may be used by an instructor as lecture supplements or examination questions. The complete setup; computer, simulator software and additional data disks containing spectra for both instruments will cost approximately two thousand dollars. If an appropriate computer is already available, the cost drops to four hundred dollars. In either case, the price is much less than the amount needed to purchase even the least expensive spectrometers.

In several instances, the simulators have been successfully used as tutorials (5-7). That is, the student practices with the simulator until he or she feels confident enough to operate the actual spectrometer. This gives a student time to learn at their own rate and correct many of the common mistakes that can be made before running an expensive piece of equipment.

One significant handicap associated with the simulator software packages is that only one user's manual is provided. Directions in these manuals, especially the NMR one, are not "student friendly" and the time needed to read and understand the directions is costly to both student and instructor. Institutions that have already used the simulators report that they have written their own instruction sets and distributed them to the students (5-7).

Another problem associated with spectral analysis in the identification of an unknown lies in the interpretation of

the spectra themselves. While most organic textbooks cover these subjects in the detail appropriate for a beginner (8-15), instructors may or may not discuss the topics sufficiently in lecture courses. The projected material to be covered in such a course is tremendous and many times overwhelms the student. The student may seek the aid of tutorial software that deals with these topics (16-21) if the institution has the appropriate facilities. If necessary, a student may refer to one of the many books that deal exclusively with spectroscopic methods (22-83) and interpretation of spectra (84-96) for help. This seems a reasonable approach, however, the majority of these books are written for upper level courses or researchers, thus the benefit to an introductory student is minimal. Several instrument companies have designed suitable workbooks that discuss the fundamental theories associated with a particular instrument (97). Unfortunately, these are not published textbooks, and may be obtained legally only when one attends a workshop (98-99), or purchases the instrument.

Since no workbook is available which (1) addresses spectroscopy on an introductory level, (2) utilizes the PC and simulated spectra, and (3) contains directions for using the Paul Schatz simulators, the primary purpose of this project was to design such a workbook. The workbook, which is suitable for publication, is intended to be used predominantly in institutions that do not have instrumentation available

to organic students. It is structured around the proton NMR and IR simulators, but also can be applied in a course which does not use the simulators.

In addition to covering IR and proton NMR spectroscopy,  $^{13}\text{C}$  NMR and mass spectroscopy are also discussed in the workbook. As the NMR simulator is not designed for  $^{13}\text{C}$  NMR, and a suitable simulation of a mass spectrometer does not exist (100-102), the second part of this project involved simulating mass and carbon-13 NMR spectra. These spectra are provided on data disks that accompany the workbook. A list of the names of the spectra is included in the appendix. These spectra complement many of the IR and NMR spectra already available from Queue. Combining the spectra obtained from the simulators with those from the  $^{13}\text{C}$  NMR and mass spec data disks, makes it possible for a student to have an IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and mass spectrum of their unknown. The supplementary data disks should be especially beneficial to the instructor as mass and  $^{13}\text{C}$  NMR spectra are much more difficult to acquire than IR and  $^1\text{H}$  NMR.

After completing the workbook, the student should have an understanding of the four types of spectroscopy, be able to interpret spectra, and operate not only the simulators, but be able to obtain spectra from the actual spectrometers as well.

## CHAPTER 2

### METHODS AND MATERIALS

#### The Workbook

Each topic addressed in the workbook briefly describes the theory associated with the spectroscopic method, and the fundamental principles needed for spectral interpretation. As this is an introductory workbook, many concepts such as NMR  $J$  constants are not even mentioned. Since learning is facilitated by writing (103-104) and problem solving, various concepts are reinforced by appropriate exercises that lead the student through interpretation of spectra. These exercises may be checked or graded by the instructor who then notes the progress a student has made in understanding the material presented. In addition to the exercises, specific learning objectives are outlined so that the student is aware of the concepts they must master upon completion of each chapter. Spectroscopy can be a very intimidating subject to a student, therefore this workbook tries to relate ideas to the student in an enjoyable, non-threatening fashion. The student workbook, entitled, Spectroscopy: Step-by-Step, addresses the following topics:

The Electromagnetic Spectrum  
Infrared Spectroscopy  
Operation of IR Simulator  
Nuclear Magnetic Spectroscopy

$^1\text{H}$  NMR

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

Operation of NMR Simulator

Mass Spectroscopy

As this workbook deals specifically with instrumental simulators, rather than incorporating spectra from the traditional references, Sadtler (105-106) or Aldrich (107-108), the spectra in the workbook were generated by either the NMR or IR simulator, or are mass spec or  $^{13}\text{C}$  NMR spectra that were produced as part of this project. In addition to incorporating simulated spectra into the workbook, many of the exercises require a student to actually obtain one or more spectra that must be interpreted for compound identification. The student workbook is included in chapter four of this dissertation. Because this chapter encompasses an entire book, it has been further subdivided into separate chapters. Chapter one of the workbook discusses the electromagnetic spectrum; chapter two, infrared spectroscopy; chapter three, nuclear magnetic spectroscopy; chapter four deals with mass spectroscopy. The figures in chapter four of the dissertation are labelled Figure 1.1, Figure 2.1, and so on. In this manner they can be differentiated from Figure 1 and Figure 2 found in chapter two of the dissertation. As the workbook is included within the text of the dissertation, the pages are numbered accordingly.

### Mass and $^{13}\text{C}$ NMR Spectra

Mass spec data were adapted from the Wiley/NBS Registry of Mass Spectral Data (109). (Before publication, proper copyright permission will be obtained from Wiley.) To produce the simulated mass spectra, a problem-solver graphics program, TK Solver (110) was used. This particular program was chosen because it not only generated bar graphs that mocked an actual mass spectrum, but graph data saved on disk with specific TK Driver (a sub-program of TK Solver) commands could be displayed on the computer monitor or printed without the aid of the main program. This feature is especially advantageous because it allows an instructor to use the data disks that accompany the workbook without having to purchase the TK Solver software. A template data disk named "massspec" was prepared by entering into the list sheet of the program, x coordinate values relating to mass units from zero to two hundred. The y coordinate values corresponded to relative intensity. On the template, zeroes were entered for all intensity values. A write protect tab was placed on the data disk to protect it from being written over. To produce a simulated spectrum, the template was called up from TK Solver and the relative intensities of the peaks entered at the specific mass units. The spectrum was then given an appropriate code name that corresponded to the NMR and IR spectra already assigned by Paul Schatz. For example, the spectrum for the compound propanoic acid is called

up by highlighting PMR2 or IR2. The mass spectrum therefore was named ms2 (in this situation the use of upper or lower case letters is irrelevant to the computer). After naming the spectrum, it was saved on a data disk separate from the template. The appropriate TK Driver sub-programs were then installed and saved with the data to make it possible to either view the simulated spectral files on the computer monitor or print them. This procedure was followed to generate spectra for twenty-five compounds. An example of such a mass spectrum is shown in Figure 1.

Proton decoupled carbon-13 NMR spectra for the twenty-five compounds were obtained using a Bruker AC-200 Fourier transform (FT) NMR spectrometer. All compounds used were reagent grade. The samples were prepared as either twenty percent by volume or by weight solutions in deuterated chloroform.

The spectrum of each sample was plotted and the data saved on the hard disk drive of the Bruker and backed-up on eight-inch floppies. Peak picking values were printed. These values corresponded to the parts per million (ppm) and relative intensity of each peak in the spectrum.

To generate the simulated spectra, several modifications had to be made in the way TK Solver was used. Unlike mass spectra, carbon-13 spectra are not bar type-graphs, but appear as narrow peaks. Another variation is found in the x coordinate scale which refer to the ppm values. The values

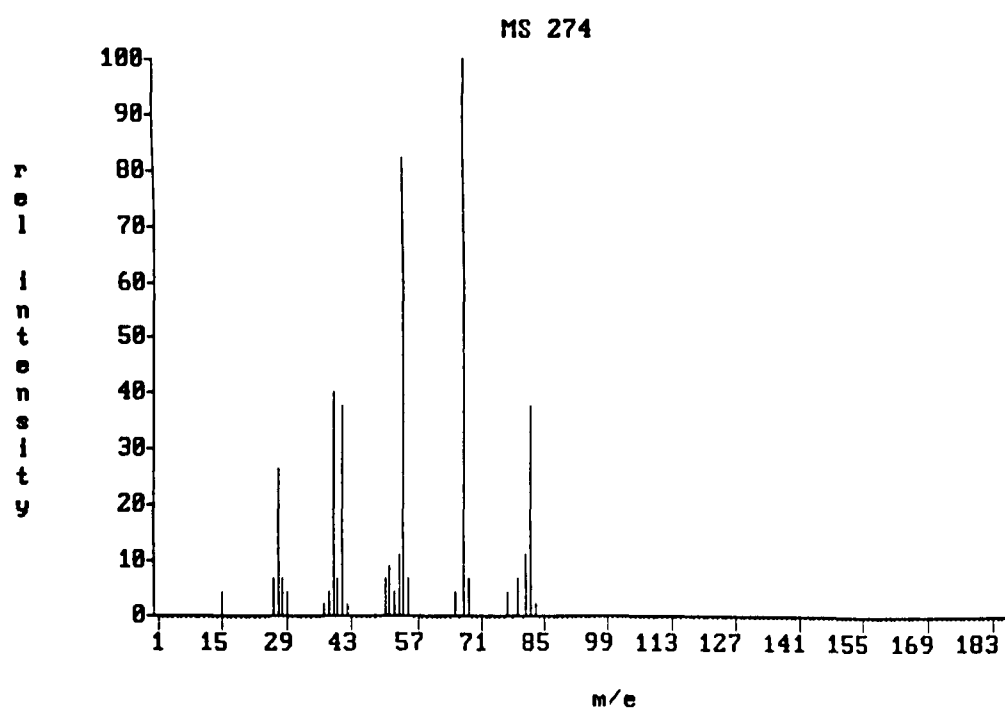


Figure 1 Mass Spectrum of Cyclohexene, ms274.

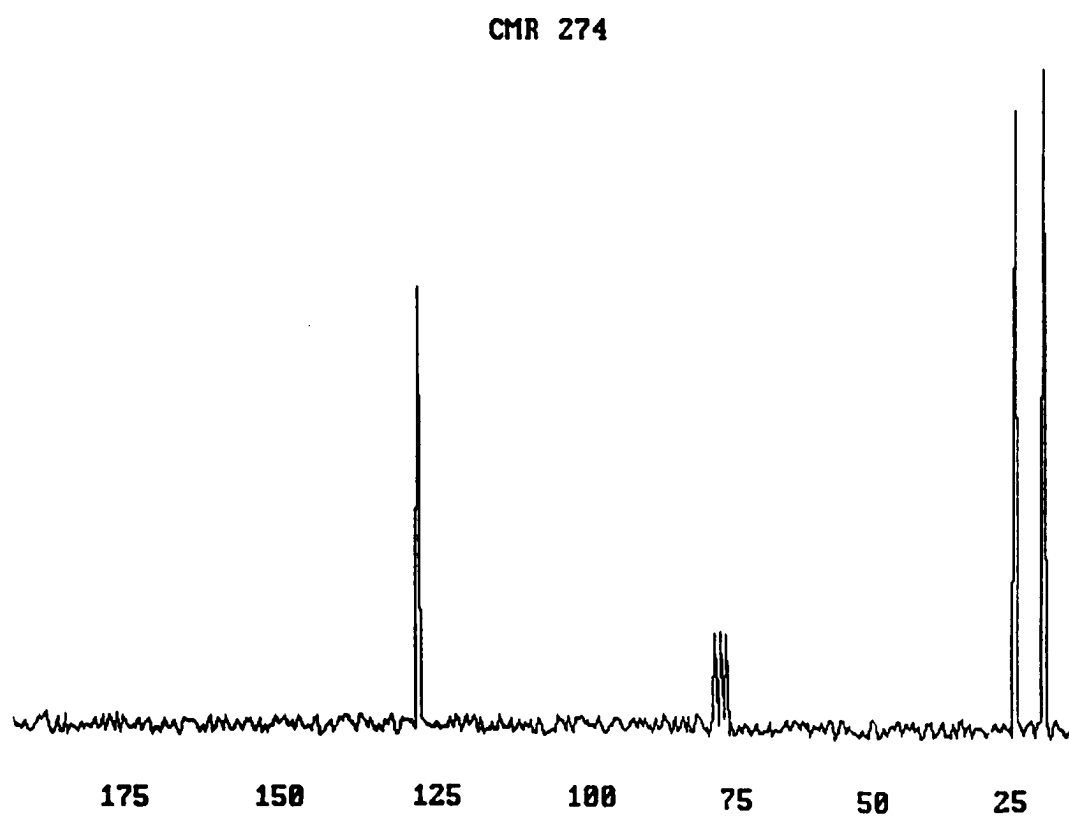


of larger magnitude are located at the left-hand side of the spectrum while zero ppm is found on the right-hand side. Also, carbon-13 NMR is very sensitive and the spectra normally show significant noise. Noise levels of the spectra vary depending upon the sample and its concentration.

Peaks were produced by using the line graph instead of the bar graph. As the line graph plotted numbers that increased from left to right, the negative ppm values were entered into the list sheet for the x coordinates. These numbers ranged from -440 to 0 producing a spectrum that spanned 220 to 0 ppm. Doubling the actual ppm values made smaller increments on the graph thus forming the necessary narrow peaks. The x axis label was not printed (it would have recorded -440 to 0) but another one which began at 220 and decreased in increments of 25 was made.

To solve the noise problem, a random number generator produced a series of 440 numbers with a value less than one. The upper-end values were varied to make three different noise levels. These numbers were inserted into the list sheet of TK Solver as the intensity value y coordinates. Three different templates called c13n1, c13n2 and c13n3 were created and a write-protect tab placed on the disk. To produce a simulated spectrum, a template was chosen that appropriately reflected the noise level of the actual spectrum. By doubling the peak picking ppm values and entering their magnitudes in the intensity list, a suitable

simulation was made. Each compound was named in a similar manner as its mass spectrum, this time the prefix cmr was used. Figure 2 displays an example of a simulated carbon-13 spectrum.



**Figure 2 Carbon-13 Spectrum of Cyclohexene, cmr274.**

## CHAPTER 3

### RESULTS AND DISCUSSION

#### Computer Hardware and Software

The simulators run from an IBM-PC, PC-XT, or PC-AT with a minimum of 256 random access memory (3,4). The computer must be equipped with an IBM Color/Graphics adapter (CGA) or the IBM Enhanced Graphics adapter (EGA). A monitor compatible with the graphics adapter is essential. The PC Disk Operating System (DOS) must be 2.0 or greater. The minimum printer requirements will be satisfied by an Epson MX or FX dot-matrix printer. Other options include an IBM Graphics Plotter (Models 7371 or 7372) or Hewlett Packard Graphics Plotter (Models 7470A or 7475A). Either of these plotters must have a serial adapter installed in the computer. A Sweet-P Model 100 Plotter with an installed parallel adapter may also be used. Another option, that is not necessary to run the simulator, is a mouse. Either the Microsoft Mouse or Mouse Systems Mouse which has a serial adapter installed is suitable. The Bus Version of a Microsoft Mouse having its own adapter card can also be used by the simulator.

To obtain the simulated Carbon-13 NMR or mass spectra, the computer hardware requirements (excluding the mouse) are essentially the same as for the simulators. An IBM computer or compatible, with a CGA, EGA, or VGA card and corresponding color monitor are necessary. An Epson MX or FX printer

is also required.

The simulator software must be purchased from Queue Inc. The  $^{13}\text{C}$  NMR and mass spectra accompany the workbook and therefore do not have to be purchased separately.

#### Limitations of NMR and IR Simulator Software

The simulator software provides an excellent package, however, there are some things of which to be aware. The instructions in the manual direct the installation of DOS onto the program disks. If one is confident that the software will not be used on another computer, this is definitely beneficial. If, however, one may wish to use this software on different IBM or compatible computers, especially those with hard-disk drives, there may be some problems with DOS compatibility. It is advisable therefore not to install the DOS onto the program disk. The computers with two disk drives will have to be booted up each time, but the inconvenience may save money and frustration at a later date. Once the computer is booted, direct the student to type MOCKNMR or MOCKIR and press Return, and the simulator will appear on the screen.

The simulators may be operated either by using a mouse or the keyboard. If a mouse has been installed, typing KEYS is supposed to activate the keyboard and deactivate the mouse. To avoid confusion, it is best to decide if a mouse is to be used or not before starting the program, thus the student will become familiar with one method. There are

advantages to either method of operation. Using a mouse makes the simulator "feel" more like operating the actual instrument; i.e., the mouse cursor is represented by a hand on the computer screen. The operator moves the mouse control and places the hand on the button or knob that is either to be turned on or off, much like one would do to actually turn on and off the control buttons. If the simulator is being used as a tutorial in preparation for operating either a Varian 360 NMR or a Perkin Elmer IR 1310, it will prove advantageous to equip the computer with a mouse option.

New instruments today are almost exclusively computer interfaced and much of the operation is done from a computer keyboard. For example, a JEOL GX-270 FT-NMR appears to be nothing more than a computer. There are no knobs or buttons to push or turn. The instrument is completely operated from a computer keyboard. As instrumentation becomes more dependent on computer operation, future chemists will probably need to be more comfortable with a keyboard than with button pushing and knob turning. For this reason, it is believed that, even though students will not gain the same sense of "button control" a mouse option offers, they will still benefit, in the long run, from learning to operate the simulators from the keyboard of a computer.

Another thing to be aware of when using the simulators involves the NMR sweeptime and the IR scantime. Both of

these features may be adjusted on the simulated spectrometers; however, neither the actual time needed to acquire a spectrum, nor the resolution of the spectrum changes. Varying the NMR radiofrequency (rf) and making gain adjustments on the IR does affect the spectrum. The instructor may want to change these settings drastically in order to give a student practice in making the proper corrections necessary to obtain a good spectrum.

When using the IR simulator, pressing the Alt and F2 keys simultaneously allows the name of the sample to be shown on the screen. This feature has been omitted in the student workbook so that the samples remain unknown if the instructor has not prepared a separate data disk. (Preparation of data disks as unknowns is outlined in the manual that accompanies the software.)

#### Limitations of $^{13}\text{C}$ NMR and Mass Spec Data Disks

There are some limitations associated with the mass spec and  $^{13}\text{C}$  NMR data disks which are saved in TK Driver files. These files are set up to run on a computer that has a color monitor and therefore some problems may be encountered if a monochrome monitor is used. One will just have to try the computer set-up out in order to see if it will work properly. The simulated spectra may be either viewed on the computer terminal or printed; i.e., it is not possible to view and print the spectrum simultaneously. To view a spectrum, one would first insert the spectra data disk into the com-

puter and type `dir/w` and hit the Return or Enter key. This command displays a directory of the filenames of the spectra. Notice that each filename has a descriptive name followed by a three-letter "extent". For example, a filename might be `MS8.EGA`. This means that this is a file of mass spectrum 8 that can be viewed on an EGA (or VGA) screen. To view it, type `SHOW MS8.EGA` (remember that the use of capital letters is not essential in entering the command). If one is using a CGA monitor, then typing `SHOW MS8.CGA` will display the spectrum on the screen. To print the spectrum, clear the monitor by pressing any key and at the computer prompt, type `SHOW MS8.PRT` and the spectrum will be printed on an Epson printer.

An unusual problem was encountered in producing the mass spectra. The bar graph option was chosen because it produced thin lines instead of bars when the two hundred mass units were entered into the list sheet. After entering the intensity values and a spectrum was plotted, it was discovered that the software decided upon the mass unit scale. This scale was not in normal increments of five, ten or twenty but in increments of fourteen. It was decided to keep this unconventional scale, however, because 15, 29, 43, 57, and 71 are printed on the spectrum and represent very important fragments in mass spectrometry.

#### Teaching With Simulators

In 1987, I ordered the NMR simulator software from Com-



press (now owned by Queue). At the time, it was possible to order a teaching package (which is no longer available) containing four simulator program and four data disks. This appeared to be ideal as it would be virtually impossible to teach a class with only one program disk, and the package was much cheaper than the four individual sets. While I was impressed with the capabilities of the simulator, it became very clear to me that the software was not necessarily "student friendly" and while the package had four program disks, only one user's manual accompanied the software. In addition, the instructions in the manual were difficult to follow. A beginner, with no previous NMR experience would waste a great deal of time just trying to interpret the manual.

As a result, I wrote a series of directions necessary to obtain a spectrum and integrate it. At the time I was directing a sophomore research project, and decided to have the student test the directions before they were given to the organic class. I was informed by the student that the directions were not effective. "They explained too much." The student took them and rewrote a new set of directions in the step 1, step 2, step 3, format. A corrected version of these directions is included in the NMR chapter of Chapter 4. Exercises for obtaining additional spectra from the data disks were also added to the directions.

A sufficient number of computers with the appropriate

hardware specifications were found and approximately three students assigned to each computer. Instead of using a computer monitor, I used a liquid crystal display (LCD) with an overhead projector to display the control panel of the simulator. In this fashion, the students could observe on the overhead projection what should actually be happening in the event that they became confused while operating the computer at their station. There was one handicap to overcome, however, the buttons on the LCD appeared dark when operative and light when inoperative. This is exactly reversed from what the students observed on the computer monitor.

While the students followed the directions, and successfully obtained spectra independently, I was never sure if they truly understood the concept of using the software to learn how to operate an actual instrument. I had the impression that most of them viewed the session as one on how to use a computer and that this was some type of computer game. Unfortunately, time was against us and the computer simulator was left to cover other material.

The following year, I ordered the IR simulator package. The IR instructions were much clearer than the NMR ones and therefore were photocopied for the students to use. The previously written NMR directions were given to each student. They were required to obtain both IR and NMR spectra. The students seemed to understand the IR better (it is a

much simpler instrument to operate); however, to my disappointment, I felt the same way I had the previous year, namely, that this was more of a computer lesson than an instrumental one. This is when the concept of preparing a comprehensive workbook on spectroscopy that incorporated the use of the simulators became an apparent necessity. It is hoped that by the time a student completes the workbook, he or she will not only understand spectroscopy but the importance of these computer simulators from an instrumental perspective.

**CHAPTER 4**  
**THE WORKBOOK**

**SPECTROSCOPY: STEP-BY-STEP**

**K. L. Pfister**

**Jackson State Community College**

**Jackson, Tennessee**

Dedicated To:  
Mr. Frank Boller,  
Judy and Maria Koonce

## PREFACE

Unlike most books that cover spectral analysis, Spectroscopy: Step-by-Step, is written for a first year organic chemistry student. It is assumed that the student knows little more than the fundamental concepts of organic chemistry, and is familiar with the functional groups. Each topic addressed in the workbook briefly describes the theory associated with the spectroscopic method, and the fundamental principles needed for spectral analysis. As this is an introductory workbook, many concepts, though covered in an organic textbook, are not even mentioned. The student is not only advised, but encouraged, to refer to the textbook whenever necessary.

Exercises have been designed to help the student master specific concepts. This is a workbook, and it is expected that students should feel free to write in the margins, underline, write questions, and work out the solutions to the exercises.

In addition to introducing spectroscopic methods, this workbook also includes directions necessary to use the IR and NMR computer simulators designed by Paul Schatz of the University of Wisconsin. (These software packages are available from Queue.) This should be especially beneficial to those students, who for whatever reason, are not able to experience operating the actual spectrometers.

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CHAPTER 1  
THE ELECTROMAGNETIC SPECTRUM

OBJECTIVES

Upon completion of chapter one, you should:

1. Understand the following terms:

electromagnetic radiation

electromagnetic spectrum

wavelength

frequency

inverse relationship

speed of light

nanometer

hertz

Planck's constant

Joules

spectroscopy

molecular structure

2. Be able to successfully calculate wavelength, frequency, and energy from the appropriate equations.
3. Know the relationship between wavelength and frequency, frequency and energy, and wavelength and energy.
4. Give the names of the types of spectroscopy mentioned in this chapter. Briefly describe what information is obtained from each spectroscopic method.



## INTRODUCTION

Every day our lives are touched and affected by various forms of electromagnetic radiation. Examples include the microwaves that cook food, television and radio waves broadcasting the latest events and entertainment, ultra-violet rays absorbed from a tanning bed or at the beach, and x-rays that heal cancer patients as well as provide valuable medical information. These, and several less common forms of electromagnetic radiation are categorized into what is referred to as the electromagnetic spectrum. This spectrum is shown in Figure 1.1.

Each form of radiation is characterized by a range of specific wavelengths and frequencies. Wavelength, denoted by the symbol  $\lambda$ , refers to the distance between nodes of a wave whereas frequency,  $\nu$ , relates to the number of times the node of a wave passes a point in a given amount of time. These values are inversely proportional to each other; i.e., the smaller the wavelength, the greater the frequency or number of times a wave passes a point in a specific amount of time. Figure 1.2 describes this inverse relationship which is also written mathematically as:

$$(1.1) \quad \lambda \propto \frac{1}{\nu}$$

Any form of electromagnetic radiation whether it is a microwave, sunbeam, radiowave, or a cosmic ray, travels at a specific rate or velocity known as the speed of light. The

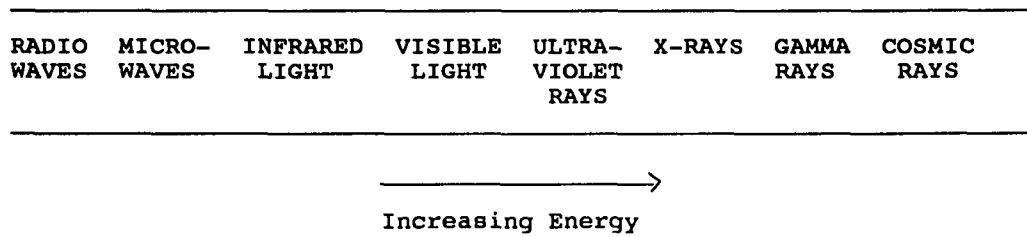


Figure 1.1 Energy Components of the Electromagnetic Spectrum.

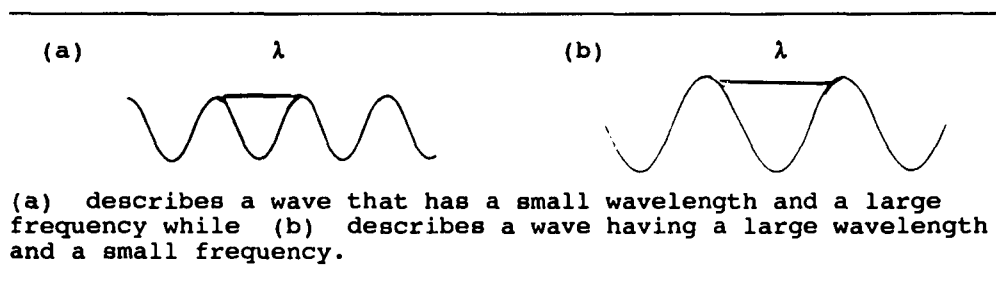


Figure 1.2 Inverse Relationship of  $\lambda$  and  $\nu$ .

speed of light is denoted as  $c$ , and has a value of  $3.00 \times 10^8$  m/s. Relating this information to the mathematical expression in (1.1), an equation, (1.2), is established. By using equation (1.2), the frequency or wavelength of a wave may be calculated when the other value is given.

$$(1.2) \quad c = \lambda \nu$$

where  $c$  = speed of light,  $3.00 \times 10^8$  m/s

$\lambda$  = wavelength in meters, m

$\nu$  = frequency in Hertz, Hz, (cycles/s) or  $s^{-1}$

=====

#### Example 1

Many times wavelength is expressed not in meters but in nanometers,  $1.0 \times 10^{-9}$  m. Determine the wavelength in nanometers, associated with the emission of red light from a traffic signal. The frequency of this light is  $4.62 \times 10^{14} s^{-1}$ .

(a) To calculate wavelength:

$$c = \lambda \nu$$

$$\lambda = c / \nu$$

$$= \frac{3.00 \times 10^8 \text{ m/s}}{4.62 \times 10^{14} s^{-1}}$$

$$= 6.49 \times 10^{-7} \text{ m}$$

(b) To convert to nanometers, nm:

$$\text{nm} = \left( 6.49 \times 10^{-7} \cancel{\text{m}} \right) \left( \frac{1.00 \times 10^9 \text{ nm}}{1.00 \cancel{\text{m}}} \right)$$

$$= 649 \text{ nm}$$

The inverse relationship of frequency and wavelength is shown in this example as frequency is a large number and wavelength is not a large number.

=====

Figure 1.3 lists the characteristic wavelengths and frequencies associated with radiant energy of the electromagnetic spectrum.

Exercise 1: Find the wavelength of a radio wave that has a frequency of  $1.5 \times 10^8$  Hz.

Exercise 2: What wavelengths are associated with the visible region of the electromagnetic spectrum?

Exercise 3: What range of frequencies relate to the infrared region of the spectrum?

Two theories are used to describe the properties of light. The first theory which we have already discussed, refers to light as having the characteristics of a wave. The second theory explains light as containing little packages of energy called photons. The energy of a photon of electromagnetic radiation may be calculated from its frequency by using equation (1.3):

$$(1.3) \quad E = h\nu$$

where  $E$  = energy in Joules, J

$h$  = Planck's constant,  $6.63 \times 10^{-34}$  J·s

$\nu$  = frequency in Hz.

It is easy to see from this mathematical relationship that frequency and energy are directly related; i.e., an

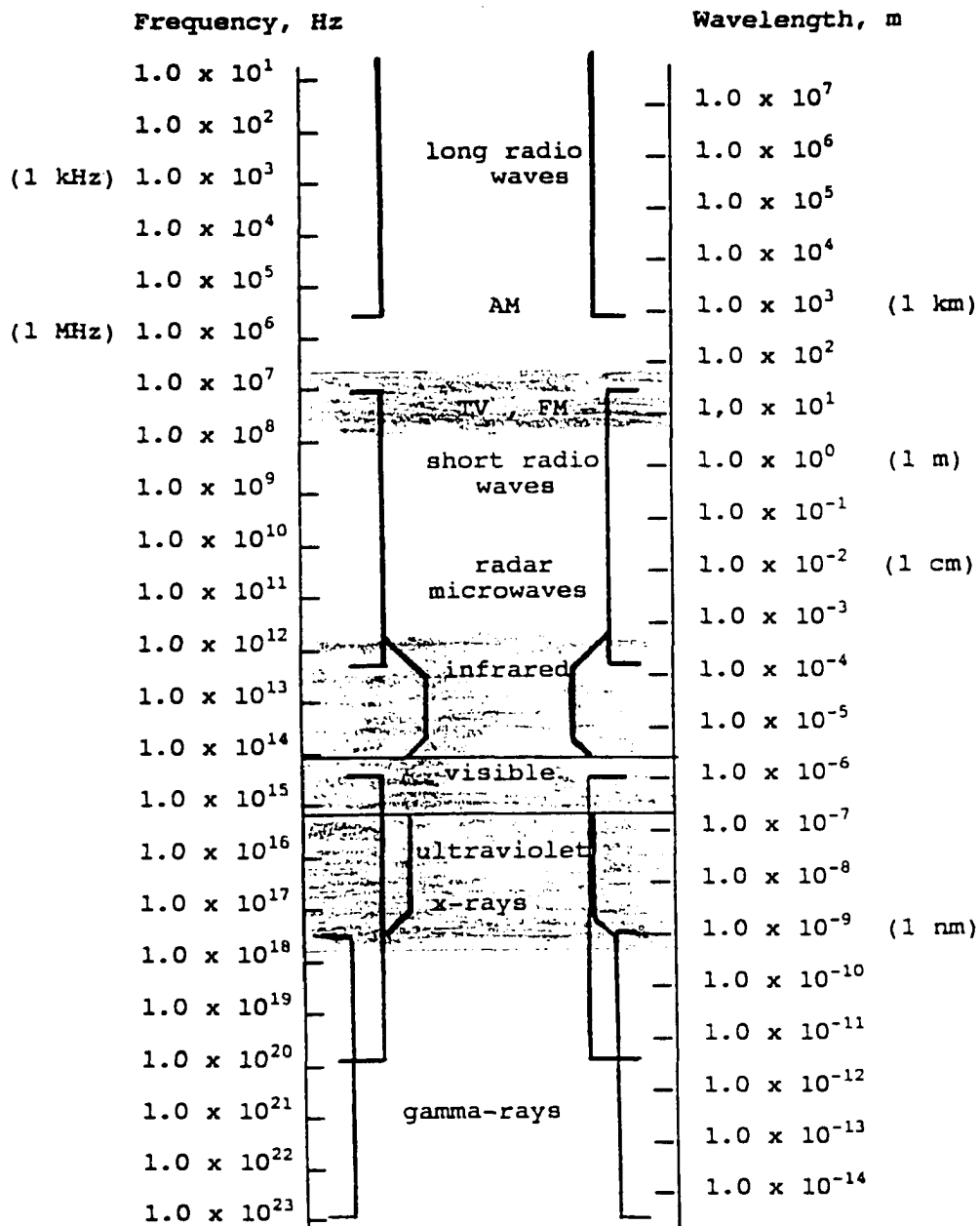


Figure 1.3 Wavelengths (m) and Frequencies (Hz) of The Electromagnetic Spectrum.

increase in frequency indicates an increase in energy and vice versa.

=====

### Example 2

What energy is associated with the emission of blue light having a wavelength of 475 nm?

(a) To convert nm to m:

$$\begin{aligned} m &= \left( 475 \text{ nm} \right) \left( \frac{1.00 \text{ m}}{1.00 \times 10^9 \text{ nm}} \right) \\ &= 4.75 \times 10^{-7} \text{ m} \end{aligned}$$

(b) To determine frequency:

$$\begin{aligned} \nu &= c/\lambda \\ &= \frac{3.00 \times 10^8 \text{ m s}^{-1}}{4.75 \times 10^{-7} \text{ m}} \\ &= 6.32 \times 10^{14} \text{ s}^{-1} \end{aligned}$$

(c) To calculate the energy per photon:

$$\begin{aligned} E &= h\nu \\ &= (6.63 \times 10^{-34} \text{ J s}) (6.32 \times 10^{14} \text{ s}^{-1}) \\ &= 4.19 \times 10^{-19} \text{ J} \end{aligned}$$

=====

**Exercise 4:** Determine the energy per photon of a cosmic ray that has a wavelength of  $3.00 \times 10^{-6} \text{ nm}$ ?

**Exercise 5:** What wavelength is associated with an x-ray that has an energy per photon of  $7.0 \times 10^{-17} \text{ J}$ ?

**Exercise 6:** Name the type of electromagnetic radiation that has a frequency of 1000 kHz? What energy and wavelength relate to this frequency? (Refer to Figure 1.3.)

**Exercise 7:** Find the energy range associated with infrared radiation.

**Exercise 8:** Which region is higher in energy, the infrared or the ultraviolet?

**Exercise 9:** Which part of the spectrum is lower in frequency, the gamma ray or the radiowave?

#### SPECTROSCOPY AND THE ELECTROMAGNETIC SPECTRUM

The application of several forms of electromagnetic radiation are very useful to the organic chemist and have been incorporated into what is known as the field of spectroscopy. The word spectroscopy is derived from the Latin word spectros which means light, and the Greek scopy which means to study. Therefore the word spectroscopy literally means; the study of light in reference to the electromagnetic spectrum. In Figure 1.3, these specific energy forms have been indicated by the shaded areas.

**Exercise 10:** Name the types of electromagnetic radiation indicated on the electromagnetic spectrum.

While spectroscopy is useful in many areas of chemistry and physics, an organic chemist primarily depends upon various forms of spectroscopy to aid in the determination of the molecular structure of a compound. Different spectroscopic methods provide unique information concerning carbon structure of a molecule as well as the presence of functional groups. Three of these methods will be presented and discussed in the following chapters. They include infrared (IR), nuclear magnetic resonance (NMR), and mass spectroscopy (mass spec). Infrared spectroscopy aids an organic chemist predominately in identifying the functional groups contained in the molecule. Nuclear magnetic resonance spectroscopy provides information concerning the structural arrangement of atoms in a molecule. Two forms of nuclear magnetic resonance spectroscopy are especially important in organic chemistry, proton, and carbon-13,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR, respectively. Both NMR methods are discussed in chapter three. Last but certainly not least, mass spectroscopy provides valuable information concerning the molecular weight and carbon structure of a molecule.

Combining information obtained from these spectroscopic methods makes absolute identification of a compound possible. The chapters to come will address each method individually with emphasis placed on interpretation of the results. When you approach interpretation of each of the forms of spectroscopy, view it as a jigsaw puzzle. You will obtain



pieces of information that must be juggled and fit into the proper place. If you become frustrated, remember, many great chemists have suffered the same challenges before you and are much better for their experiences. When you finally get all the pieces properly situated, and your compound has been properly identified, you should feel a deep sense of pride and accomplishment. Good luck! Are you ready?

CHAPTER 2  
INFRARED SPECTROSCOPY

OBJECTIVES

1. Before you attempt this chapter, you should review the following terms:
  - infrared radiation
  - frequency
  - wavelength
  - molecular vibrations
  - dipole moment
  - bond angle
2. Upon completion of this chapter, you should understand and be able to define the following terms:
  - absorption spectroscopy
  - spectrometer
  - absorption bands
  - molecular energy absorptions
  - percent transmittance
  - monochrometer
  - reference beam
  - microns, micrometers
  - wavenumber
  - stretching vibrations
  - symmetrical
  - unsymmetrical
  - bending vibrations

in-plane bending

out-of-plane bending

infrared active

infrared inactive

fingerprint region

3. Briefly describe the function of the infrared spectrometer. Why is a reference beam and cell used?
4. Convert from wavelength to wavenumbers.
5. Be familiar with the region of wavelengths that an infrared spectrometer scans.
6. Why do the peaks in an infrared spectrum appear "upside-down?"
7. Discuss stretching and bending vibrations in infrared spectroscopy.
8. Be able to locate stretching and bending vibrations on an infrared spectrum.
9. Given an infrared spectrum, be able to identify the functional groups that are present in a molecule.
10. Use the fingerprint region of an infrared spectrum to identify disubstituted benzenes.
11. Successfully obtain an infrared spectrum by using the IR Simulator.

## INTRODUCTION

Infrared (IR) spectroscopy is a form of absorption spectroscopy. That is, a molecule absorbs radiation which, in this case, is in the infrared region of the electromagnetic spectrum. The amount of light absorbed by the molecule as the instrument scans the various wavelengths is detected in the spectrometer (instrument), and recorded graphically as a spectrum. The absorption bands or peaks in a spectrum occur at those wavelengths that correspond to molecular energy transitions. The areas of the spectrum lacking peaks point out wavelengths where the molecule does not absorb radiation. An infrared spectrometer records 100% transmittance (i.e., all the light is detected; none is absorbed) at the top of the spectrum, 0% transmittance (all light is absorbed; none is detected) at the bottom. This explains why the graph appears to be "upside-down" (see Figure 2.1, 2.2, and 2.3).

## INSTRUMENTATION

An infrared spectrometer is a fairly simple instrument. It consists of a light source that emits all wavelengths of infrared energy. The light is split by mirrors into two separate beams, a reference beam and a sample beam. The reference beam passes through a cell which is empty if the sample is a pure substance, or contains the solvent if the sample is in solution. The different wavelengths of both beams are sorted in a monochromator (device that separates

radiation into individual wavelengths) and then directed to a detector. Since absorbances of both the sample and reference cells are noted by the detector, possible solvent interferences may be eliminated. The resulting signal is then sent from the detector to the recorder which in turn, produces a spectrum. A simple block diagram of the infrared spectrometer is illustrated in Figure 2.1.

#### INFRARED WAVELENGTHS AND WAVENUMBERS

Refer back to the electromagnetic spectrum, Figure 1.3. Note that wavelengths of  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-4}$  m characterize the IR region. These correspond to  $1.0 \times 10^3$  to  $1.0 \times 10^5$  nm. Organic molecules, however, absorb energy primarily between  $2.5 \times 10^3$  to  $20 \times 10^3$  nm. Therefore, the spectrometer does not scan the complete infrared region but only part of it.

Originally, wavelengths in infrared spectroscopy were expressed as microns ( $\mu$ ), or micrometers ( $\mu\text{m}$ ), either of which equals  $1.0 \times 10^{-6}$  m or  $1.0 \times 10^3$  nm. This means that the absorption bands in a spectrum range from 2.5 to 20  $\mu$  or  $\mu\text{m}$ . A more recent convention, however, has been to express the absorption bands as wavenumbers,  $\bar{\nu}$ , the reciprocal of the wavelength in cm. Wavenumbers are therefore expressed as  $\text{cm}^{-1}$ . (I realize this may be confusing, but hang in there.) Equation 2.1 is used to make the simple calculation between a wavelength and a wavenumber.

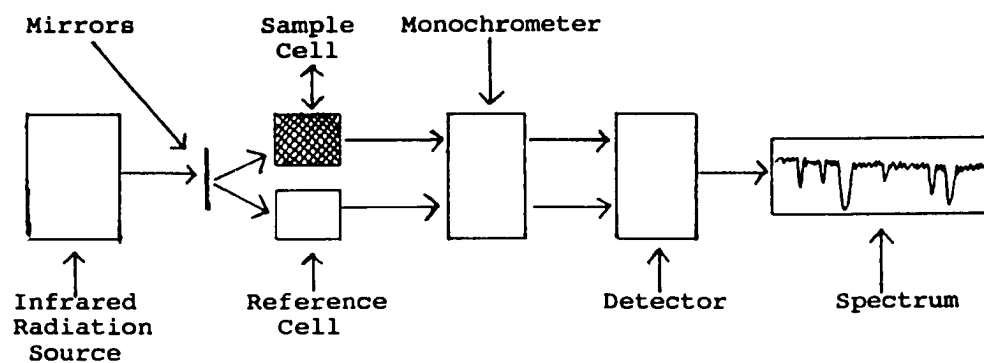


Figure 2.1 Block Diagram of an Infrared Spectrometer.

$$(2.1) \quad \bar{\nu} = \frac{1}{\lambda}$$

where  $\bar{\nu}$  = wavenumber in  $\text{cm}^{-1}$

$\lambda$  = wavelength in cm

=====

### Example 1

What wavenumber is associated with a wavelength of  $1.6 \times 10^{-5}$  m?

- (a) Since the unit associated with wavenumbers is  $\text{cm}^{-1}$ , a conversion must first be made from m to cm.

$$\text{cm} = (1.6 \times 10^{-5} \text{ m}) \left( \frac{100 \text{ cm}}{1 \text{ m}} \right)$$

$$= 1.6 \times 10^{-3} \text{ cm}$$

- (b) To determine wavenumber:

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

$$= \frac{1}{1.6 \times 10^{-3} \text{ cm}}$$

$$= 625 \text{ cm}^{-1}$$

=====

Exercise 1: Calculate  $\bar{\nu}$  at  $3.3 \mu$ .

Exercise 2: What wavelength, in nm, relates to  $1250 \text{ cm}^{-1}$ ?

Exercise 3: Calculate the range of wavenumbers that an infrared spectrometer will scan in order to obtain a spectrum of an organic compound.

Since  $\bar{\nu}$  is an inverse function of wavelength as is frequency, many times wavenumbers are referred to as frequencies. For example, an absorbance recorded at  $2000\text{ cm}^{-1}$  could be called either a wavenumber of 2000 or a frequency of 2000. Also, the higher frequencies correspond to absorbencies of higher energy; lower frequencies, lower energy.

**Exercise 4:** What frequency or wavenumber will have the highest energy on an infrared spectrum?  
The lowest?

Figure 2.2 shows an infrared spectrum of the organic hydrocarbon, hexane, while Figure 2.3 is an infrared spectrum of benzoic acid. Percent transmittance is plotted on the vertical axis. Wavenumbers are recorded on the horizontal axis. Sometimes the opposite horizontal axis is also plotted in wavelengths. Either way, the necessary absorption bands may be easily identified by wavenumbers and occasionally by wavelengths.

#### MOLECULAR VIBRATIONS AND INFRARED SPECTROSCOPY

Now that you have seen an infrared spectrum, let us discuss what information can be determined from the absorption bands or peaks. Recall that molecules are in constant motion and therefore experience molecular vibrations. Two major types of vibrations exist, the stretch and the bend. A stretch results when the bond length between atoms increases or decreases, in essence, the bond stretches as you



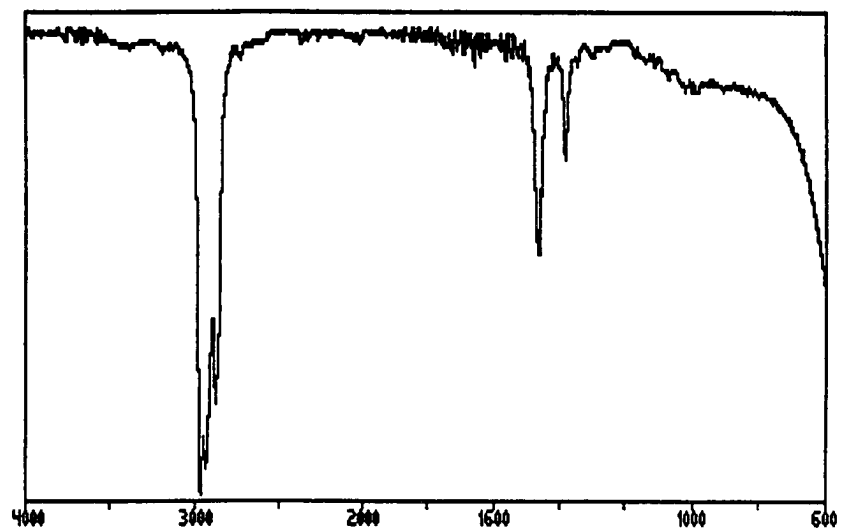


Figure 2.2 Infrared Spectrum of Hexane.

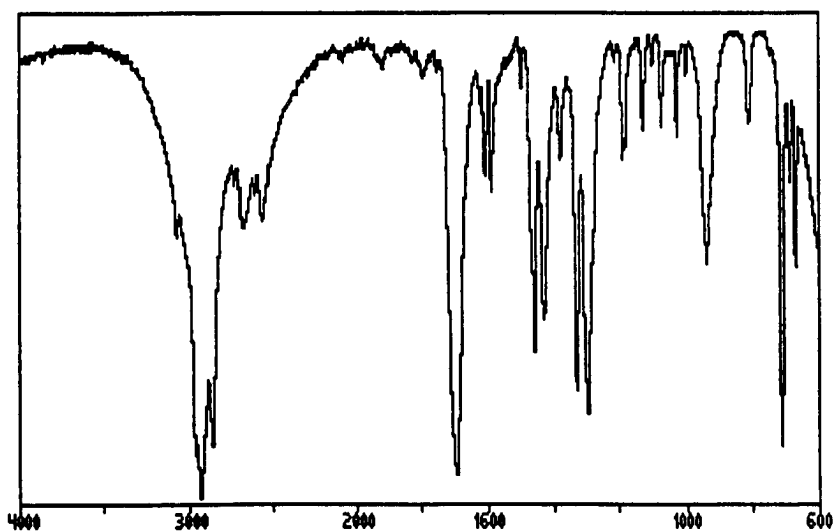


Figure 2.3 Infrared Spectrum of Benzoic Acid.

might stretch. Those stretches that change the dipole moment of the bond are termed unsymmetrical and are infrared active. That means that these vibrations may appear as peaks in an infrared spectrum. Symmetrical stretches on the other hand, do not change the dipole moment of a molecule and being infrared inactive will not produce peaks in a spectrum. To summarize, a stretch must change the dipole moment of a bond in order to be infrared active and thereby produce a peak in a spectrum. Figure 2.4 illustrates both the symmetrical and unsymmetrical stretches.

A bend, on the other hand, occurs if the bond angle between atoms changes. Both in-plane and out-of-plane bending exist, each of which have symmetrical and unsymmetrical vibrations. Unlike the stretches however, the symmetrical bends may be infrared active. Figure 2.5 depicts possible bending vibrations.

#### RELATIVE POSITIONS AND INTENSITIES OF MOLECULAR VIBRATIONS

As a rule, a molecule expends more energy shifting the dipole moment than changing a bond angle, thus stretches are associated with higher energies, higher frequencies (usually above  $1300\text{ cm}^{-1}$ ), and bending vibrations with lower energies, lower frequencies (below  $1400\text{ cm}^{-1}$ ). There is a region from approximately  $1450 - 1000\text{ cm}^{-1}$  where stretching and bending vibrations may overlap. (This is not an overly important fact, just something for you to remember when you

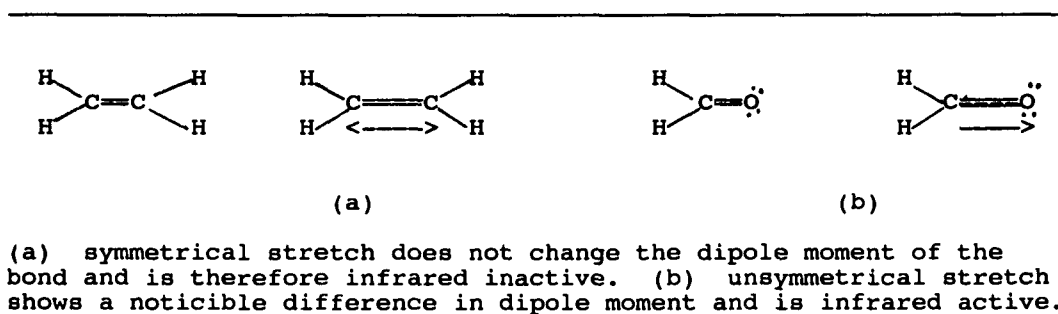


Figure 2.4 Symmetric and Unsymmetric Stretching Vibrations.

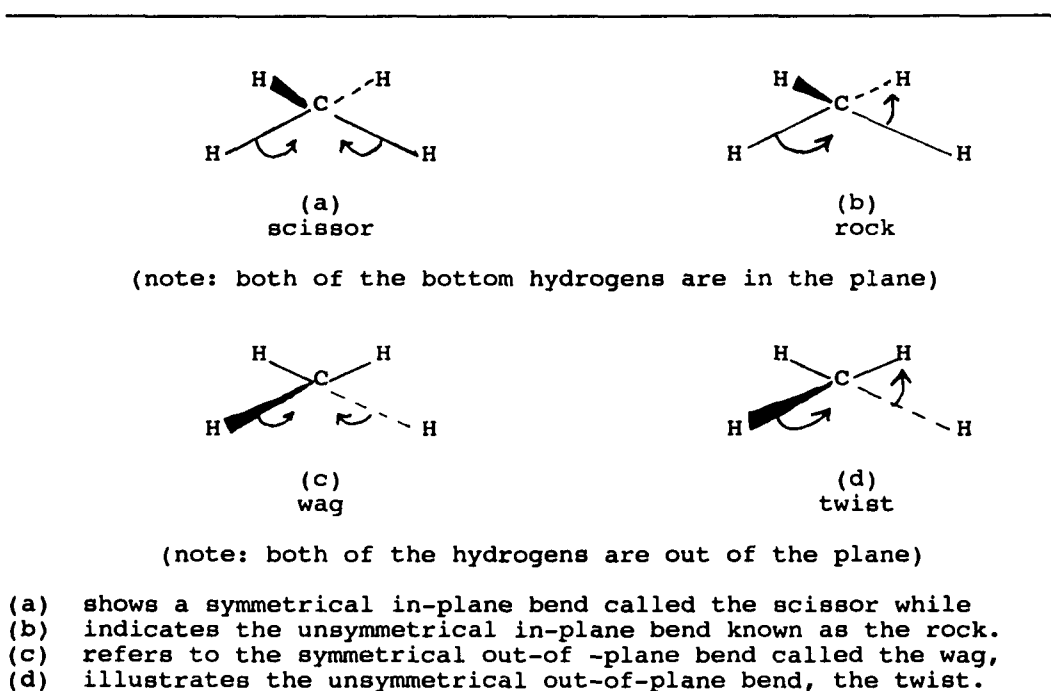


Figure 2.5 Symmetric and Unsymmetric Bending Vibrations.

are having a bad day!) Also, in an infrared spectrum, stretching absorptions may result in producing peaks of greater intensity than bending vibrations.

Stronger bonds experience vibrations of higher energy than do weaker bonds. The C-H stretch of an alkyne has an absorption frequency of approximately  $3300\text{ cm}^{-1}$ , whereas the C-H stretch of an alkane absorbs around  $2900\text{ cm}^{-1}$  (recall that triple bonds are stronger than single bonds). The C=O stretch of a carbonyl group is found in the vicinity of  $1700\text{ cm}^{-1}$ , while the C-O stretch of an alcohol is located around  $1100\text{ cm}^{-1}$ .

**Exercise 5:** In the spectrum of hexane would the absorption peak at  $3000\text{ cm}^{-1}$  be classified as a stretch or a bend? At  $1400\text{ cm}^{-1}$ ?

**Exercise 6:** Give the frequencies associated with two stretches in the spectrum of benzoic acid found in Figure 2.3. Indicate the wavenumber of a bend found in the same spectrum.

Why are stretches and bends recorded as peaks on an infrared spectrum? Recall that a sample is placed in a spectrometer and irradiated with infrared energy. The instrument then scans a range of frequencies from  $4000\text{ cm}^{-1}$  to  $600\text{ cm}^{-1}$  (refer to Exercise 3). During the scan, if the frequency of the radiation matches a stretching or bending

vibration frequency of the molecule, the molecule will absorb some of the light energy causing an absorbance band to be recorded on the spectrum. The more energy absorbed by the molecule, the greater the intensity of the peak, the less energy absorbed, the weaker the peak. On the other hand, if the radiation frequency does not coincide with a vibration, then energy is not absorbed by the molecule and a peak does not appear in the spectrum.

Exercise 7: Refer to the spectrum of hexane. Which peak shows the greatest intensity, the one located at approximately  $1400\text{ cm}^{-1}$  or the one at  $3000\text{ cm}^{-1}$ ? Would you predict this peak to be a stretch or a bend?

#### SPECTRAL ANALYSIS

Table I lists the common vibration frequencies and their relative intensities. Carefully review this list and become familiar with the wavenumbers associated with the various functional groups. Familiarity with this information will be a tremendous help to you in faster identification of infrared spectra. Be patient, the good part, putting the puzzle pieces together, is about to come.

Exercise 8: What wavenumbers correspond to the stretch of a carbonyl  $\text{C}=\text{O}$  bond? Refer to Table I.

Table I. Characteristic Infrared Absorption Frequencies

bond		stretching, $\text{cm}^{-1}$	bending, $\text{cm}^{-1}$
C-H	alkane	2850-2960 (s)	1350-1470 (s)
	methyl		1430-1470
	isopropyl		1375
	tert-butyl		1370, 1385*
C-H	alkenes	3020-3080 (m)	1170
	$\text{RC}=\text{CH}_2$		1370 (s), 1395 (m)
	$\text{R}_2\text{C}=\text{CH}_2$		675-1000 (s)
	cis-RCH=CHR		910-920 (s)
	trans-RCH=CHR		990-1000 (s)
C-H	aromatic	3000-3010 (v)	880-900 (s)
	monosubstituted		675-730 (v)
	m-disubstituted		965-975 (s)
	o-disubstituted		675-870 (v)
	p-disubstituted		690-710
C-H	alkynes	3300 (s)	730-770
C-H	aldehyde	2900, 2900 (m)	690-710
C=C	alkenes	1620-1680 (v)	750-810
C≡C	alkynes	2100-2260 (v)	735-770
C≡N	nitriles	2220-2260 (v)	810-840
C=O	carbonyls	1690-1760 (s)	
	aldehydes	1720-1740 (s)	
	ketones	1705-1725 (s)	
	esters	1735-1750 (s)	
	acids	1700-1725 (s)	
	amides	1650-1690 (s)	
C-O	alcohols	1000-1300 (s)	
	ethers		
	esters		
	acids		
O-H	alcohols	2500-3590 (s)	
	phenols		
	acids		
	nonhydrogen-bonded alcohols	3590-3650 (v)	
	hydrogen-bonded alcohols	3200-3600 (s, broad)	
N-H	amines	3300-3500 (m)	1590-1620 (v)
	amides	3350-3500 (m)	1510-1655 (s)
C-N	amines, aliphatic	1020-1220 (w)	
	amines, aromatic	1250-1360 (s)	
NO <sub>2</sub>	nitro compounds	1515-1560 (s)	
		1345-1385 (s)	

- between wavenumbers indicates the region of the spectrum the absorption bands may be located.

, between wavenumbers means that multiple peaks (usually doublets) are present.

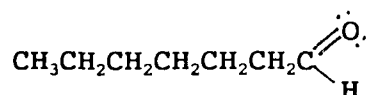
\* represents a symmetrical doublet.

(s) indicates strong; (m) moderate; (w) weak; and (v) variable absorption band.

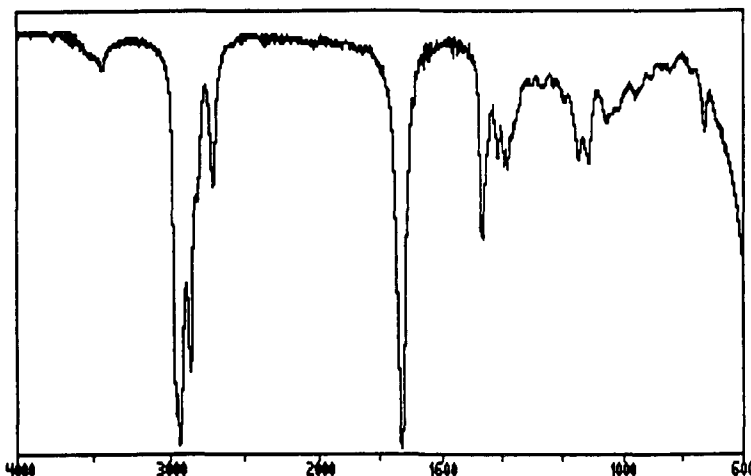
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Example 2:

Consider the molecule heptanal,  $\text{CH}_3(\text{CH}_2)_5\text{CHO}$ . Use Table 2.1 to predict and properly identify the important peaks present in the spectrum. Heptanal is an aliphatic aldehyde having a structural formula of:



You can see from the formula that this molecule has alkane character and therefore we would expect the spectrum to have C-H stretching around  $2900\text{ cm}^{-1}$  (refer to the table). Since the compound contains a carbonyl group, specifically an aldehyde, a strong C=O stretch at  $1730\text{ cm}^{-1}$  is expected. C-H stretches indicating the presence of an aldehyde should also be present at  $2700$  and  $2900\text{ cm}^{-1}$ . It should be noted here that the second stretch at  $2900$  may be "hidden" by the C-H stretch of the alkane. Below is the actual spectrum for heptanal.



Notice that the important absorbance bands predicted from the table are present in the spectrum. (See that the aldehyde  $2900\text{ cm}^{-1}$  peak was not masked by the alkane C-H stretch.) It is also apparent that all of the peaks in the spectrum have not been identified. Do not be concerned about this, many times it is not possible to assign all of the absorption bands, especially if you are a beginner. Just concentrate on identifying the common peaks indicated in Table 2.1.

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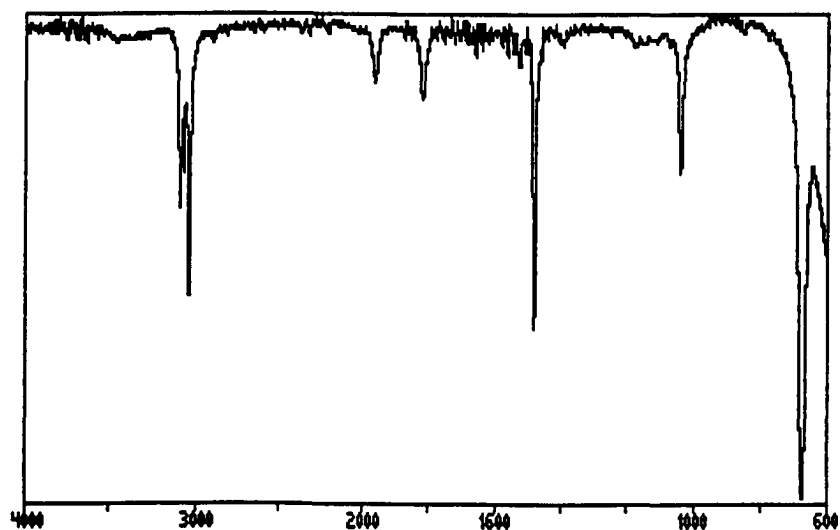
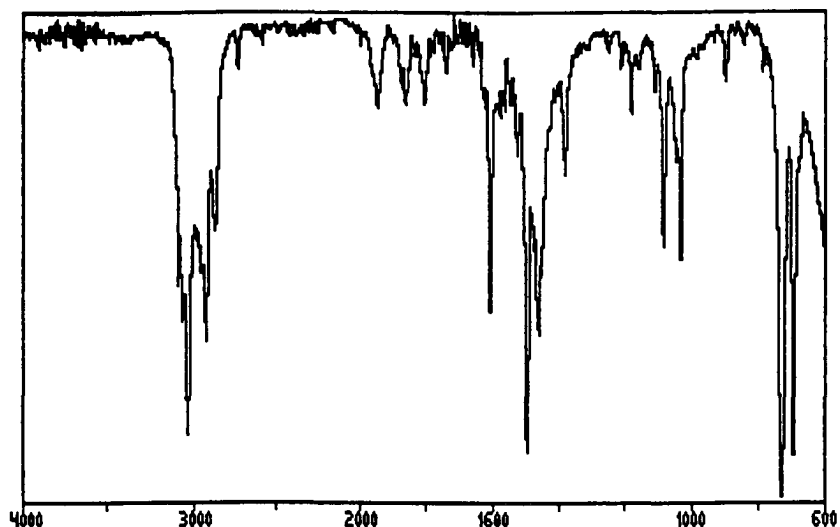
**Exercise 9:** How could you differentiate between 1-hexene and 1-hexyne in an infrared spectrum?

**Exercise 10:** Predict the important peaks that would appear in the spectrum of n-heptyl amine.

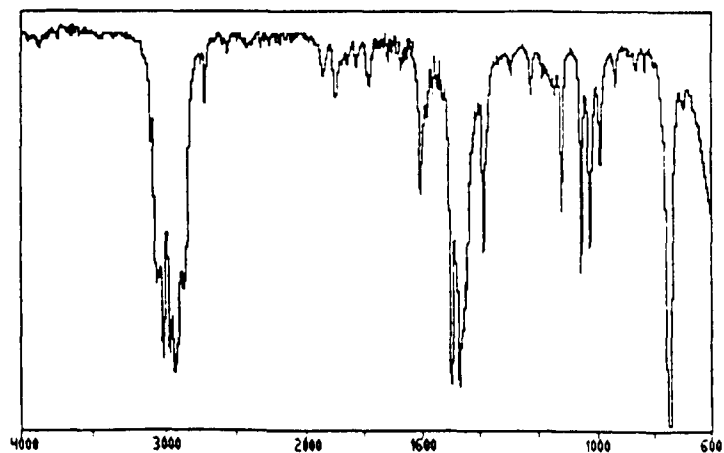
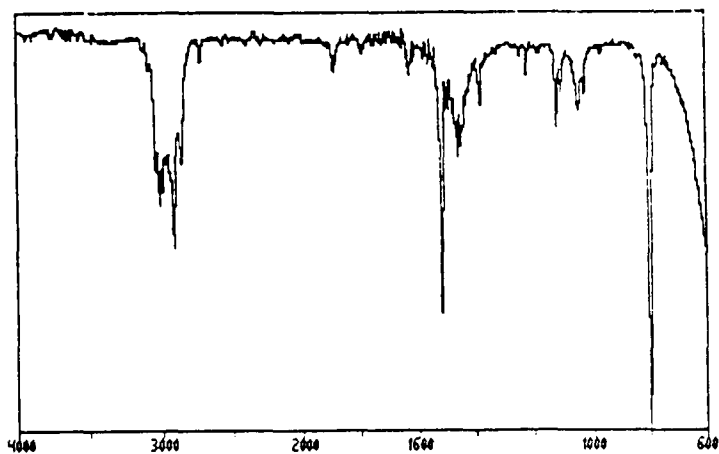
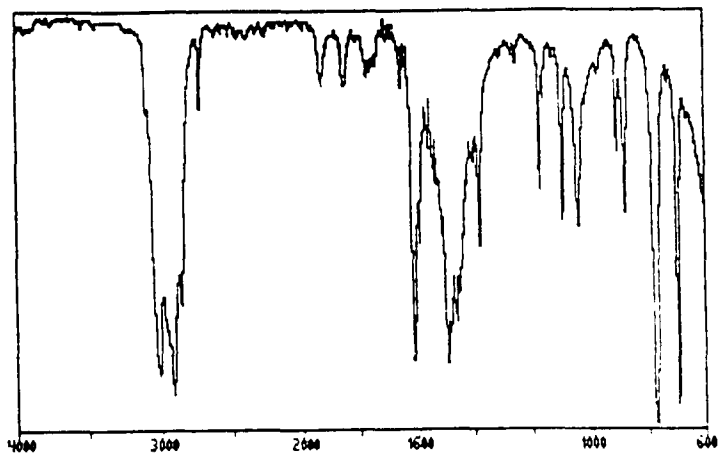
**Exercise 11:** Repeat the same procedure for 1-heptanol.



**Exercise 12:** Below are the spectra (plural of spectrum) of benzene and toluene. Identify the major absorption bands in the spectra and thereby identify each compound. (Hint: a look at the lower end of the spectrum where the C-H bends are located will probably be helpful in making this identification.)



**Exercise 13:** The spectra of o, p and m disubstituted xylenes are given below. Use the wavenumbers in the lower end of the spectrum to correctly identify each compound.



In Exercise 13, the spectra of the molecules are almost identical. Apparent variations occur in the lower frequencies of each spectrum. This area is called the fingerprint region of an infrared spectrum, and like a human fingerprint, is unique for each compound. So while some peaks (found in the higher wavenumbers) might be identical to those found in a spectrum of a similar compound, variations will occur in the fingerprint region of the spectra. In general, the fingerprint region extends from approximately  $1400 - 600 \text{ cm}^{-1}$ . Another example of similar compounds, 1-bromooctane and 2-bromooctane, are shown in Figure 2.6. Compare the upper frequencies of the spectra and note that differences arise only in the fingerprint region of each spectrum. Positive identification of a compound can be made by comparing the unknown spectrum to a published one found in a reference handbook such as the Aldrich Library of Infrared Spectra (107) or the Sadtler Indices (105).

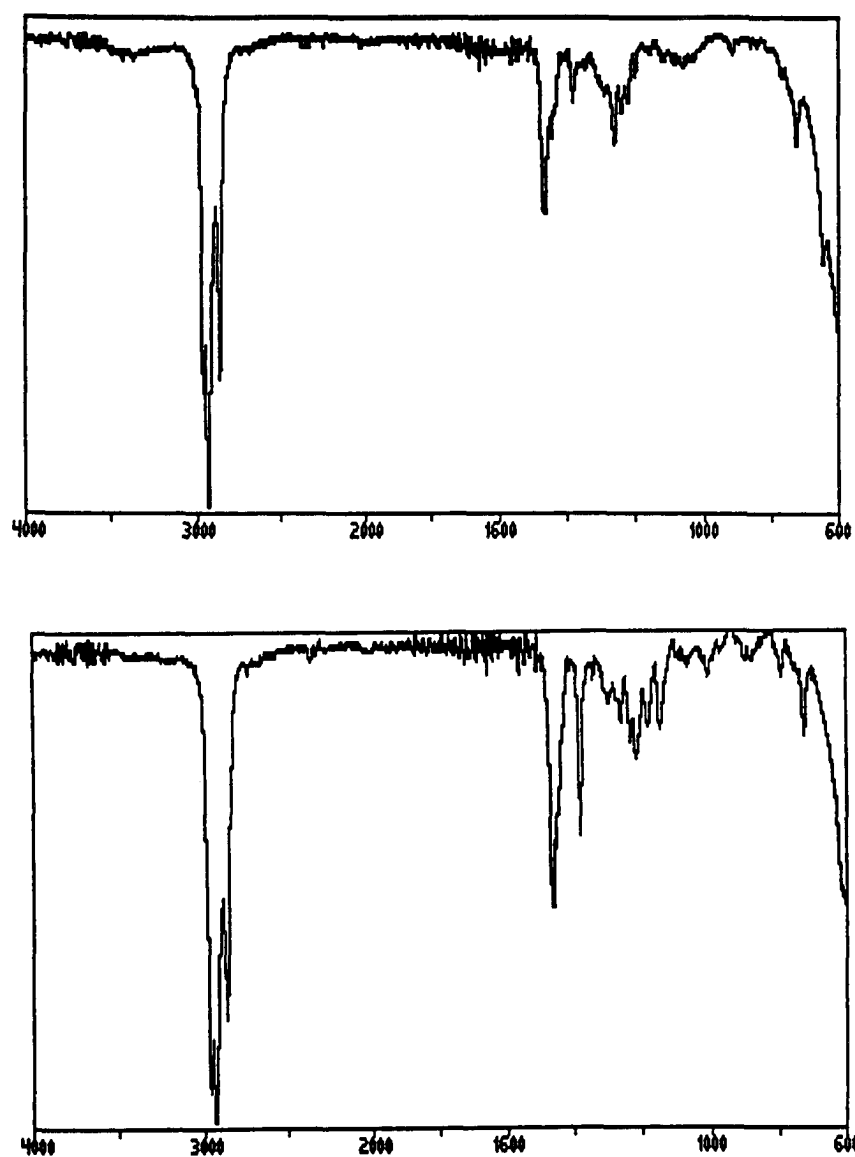
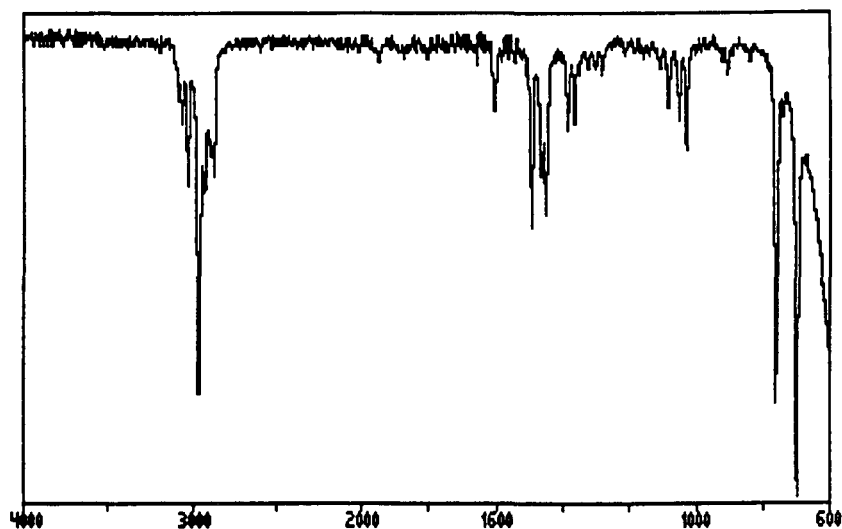
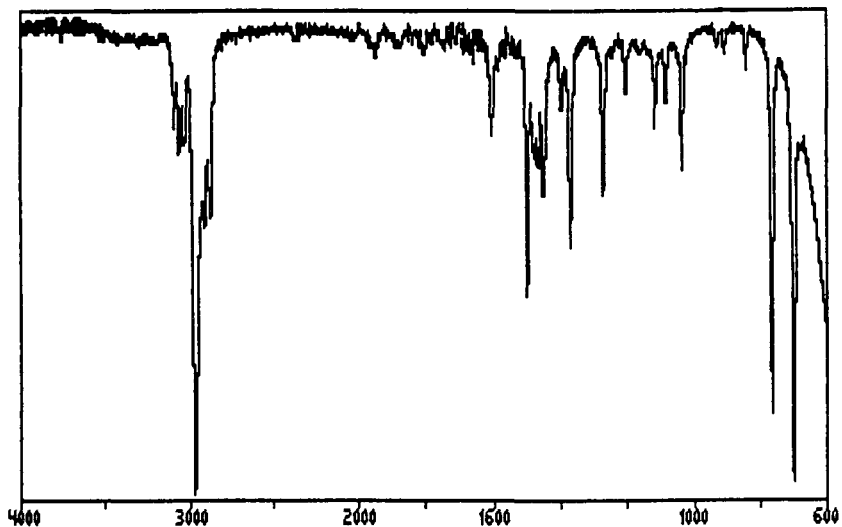
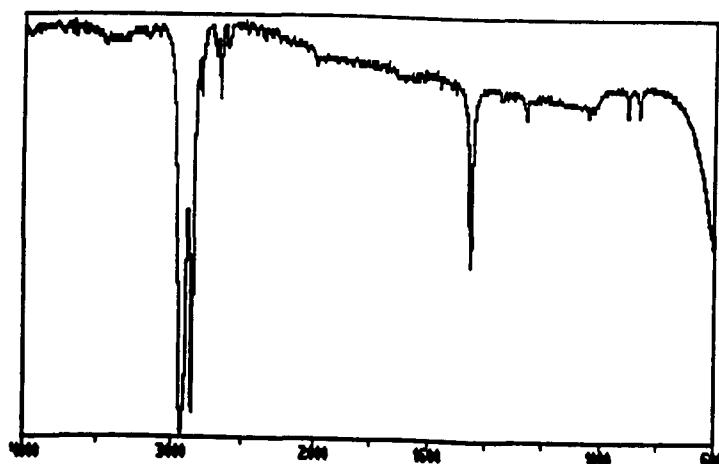
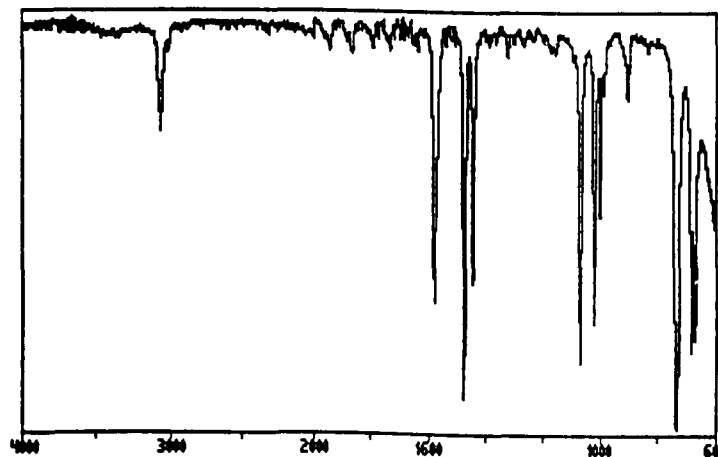
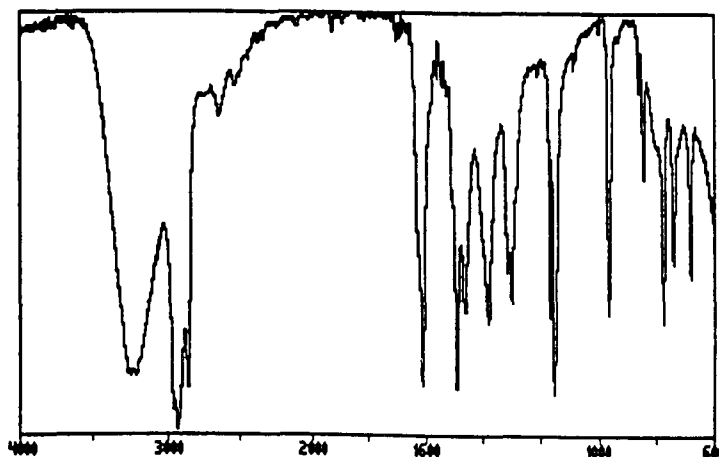


Figure 2.6 Infrared Spectra of 1-Bromooctane (top) and 2-Bromooctane (bottom).

**Exercise 14:** If one of the mentioned infrared indices or another one is available for your use, identify the following spectra. One of the compounds is isopropyl benzene, the other, t-butylbenzene. Even if these books are not available, use Table I to identify major structural differences in the molecules.



**Exercise 15:** The spectra of 1-bromobutane, resorcinol, and cyclohexane are given below. Identify peaks of significance in each spectrum and identify the compounds.



**Exercise 16:** Compare the spectra of benzene (Exercise 12) and cyclohexane (Exercise 15). Note any differences.

**Exercise 17:** What differences would you expect to see in the spectra of isopropyl alcohol and of acetone?

## OBTAINING AN IR SPECTRUM FROM THE SIMULATOR

## INTRODUCTION

Interpreting an infrared spectrum takes on a completely new meaning when one actually acquires it from a spectrometer rather than a reference book. Many times chemists anxiously anticipate the results obtained from infrared spectroscopy. Were they able to successfully convert that alcohol into an aldehyde? How would they know? Inspection of the spectrum around  $3200\text{ cm}^{-1}$  would show the presence of O-H stretching of the alcohol. Is it gone? Does a strong C=O stretch exist around  $1700\text{ cm}^{-1}$ ? If so, then an aldehyde has indeed been produced. What a relief, all that hard work, hours in the laboratory, has not been in vain.

Ideally, an organic laboratory should be equipped with an infrared spectrometer. These instruments are fairly easy to operate and produce results quickly. Unfortunately, it is not always possible to equip laboratories with these instruments. If this is the case, an infrared spectrum of a compound may be obtained from a data base of spectra by using a computer simulated Perkin Elmer 1310 infrared spectrometer (3). The control panel that appears on the computer screen replicates that of the actual instrument. The series of instructions used to produce an infrared spectrum from the simulator is essentially identical to that followed to obtain a spectrum from a spectrometer. If one becomes proficient using the simulator, there should be little difficulty operating an



actual Perkin Elmer 1310 spectrometer, or for that matter, most other IR spectrometers.

The user's manual that accompanies the software includes instructions that describe the function and operation of the simulator (3). These instructions have been outlined in this workbook for you. If you are operating the simulator from a keyboard and not a mouse, a diagram of the keystrokes needed to operate the instrument simulator is provided. Brief definitions of the functions of the control buttons have also been included in Figure 2.7.

In order to obtain an infrared spectrum the following procedures must be followed:

1. Place a sample in the spectrometer (when using the simulator this means loading a data file from disk).
2. Check the settings to make sure they are correct
3. Adjust %T, the pen should register between 95 - 90%.
4. Check gain and adjust if necessary.
5. Record spectrum.
6. Interpret spectrum.
7. Show your lab partner.

Ready?

## CONTROL PANEL OF IR SIMULATOR

wave- number	scan	
chart expansion		
0.5 #7	1 #8	
scantime/slit program		
wide 3 #4	narrow 12 #5	
chart #1	wave- number #2	gain check #3
parameter adjust		
Ins Del		

## OTHER KEYSTROKES:

Return or Enter - starts and stops SCAN.

Shift Q - allows you to quit.

F - allows you to a) obtain a file by pressing the ? key and indicating if the data file will come from drive A, B, or C.

When the choices appear on the screen, press the space bar until the sample to be read is highlighted and then press Return or Enter.

b) print a spectrum on Epson printer by pressing P

c) plot a spectrum on a graphics plotter by pressing G

d) cancel by pressing the Esc key.

N - allows you to erase the printed spectrum and record another.

T - adjusts the percent transmittance (%T). Pressing T alone moves the pen down, shift T moves the pen up. Normally the baseline (position of pen) should be about 95 - 90 %.

Control button is on if the light appears in left hand corner.

Figure 2.7 Control Panel of IR Simulator.

## IR SIMULATOR CONTROL FUNCTIONS

1. WAVENUMBER - displays the wavenumber being scanned.  
Usually a spectrum begins at 4000.
2. SCAN - begins and ends scan. This is controlled by the Enter or Return key on the keyboard.
3. CHART EXPANSION - allows one to choose a regular or condensed spectrum. One is the normal setting.
4. SCANTIME - determines the length of time the spectrometer will scan a sample. (A longer scantime sometimes increases the quality of the spectrum.)  
Normal setting is 3 minutes. (On the simulator, the time does not change when this setting varies.)
5. CHART - allows the chart paper to be moved in or out of the spectrometer.
6. WAVENUMBER - changes the wavenumber of the spectrometer, allows a specific area of the spectrum to be scanned.
7. GAIN CHECK - when turned on should deflect the pen by only 10%. This control must be turned off in order to obtain a spectrum. If the gain is not properly set, the simulator will not operate.
8. PARAMETER ADJUST - makes the proper gain adjustments.  
If the pen deflects less than 10% when the GAIN CHECK button is depressed, the gain must be turned down. If the pen moves more than 10%, the gain must be increased.

## STARTING THE COMPUTER

### Using the Mouse

The infrared simulator program may be used with or without a mouse depending upon the type of computer setup that is available. If the computer is equipped with a mouse, first, boot up the computer, and then type MOUSE if it is a Microsoft Mouse or MMOUSE for a Mouse Systems Mouse and then pressing the Return or Enter key at the > prompt. When the mouse is engaged, the keyboard is inoperative. To gain keyboard control, type KEYS and press Return or Enter at the > prompt.

### Using Two-Drive System

If you are using a two-drive system, insert the program disk (that has DOS installed on it) into drive A and turn on the computer. The control panel should appear on the screen. If DOS has not been installed, insert the systems disk, turn on the computer, wait for the true prompt, enter the time, hit Return, enter the date, hit Return, then remove the systems disk and replace it with the IR program disk. Type MOCKIR and press Return. The control panel should now be displayed.

### Hard Disk Drive

If you are using a hard disk drive, turn on the computer and wait for the computer to boot. Install the mouse if appropriate, (follow directions in first paragraph). Place the program disk into drive A or B (ask instructor which

drive you are using) and type MOCKIR followed by pressing Return.

#### OPERATING THE IR SIMULATOR

1. a) If you are using the keyboard, refer to the diagram of the control panel and follow the necessary commands.  
b) If a mouse is available, place the mouse cursor over a particular button on the control panel or a command at the top of the computer screen. Click the mouse on to activate the control.
2. Place sample into instrument.
  - a) Keyboard:
    - Type F and hit Return.
    - Press the ? key to load a sample.
    - Choose Drive A, B, or C.
    - Press the space bar until the sample to be loaded is highlighted (highlight MORE SAMPLES if the one to be loaded does not appear on the list).
    - Hit Return. The sample has now been loaded.
  - b) Mouse:
    - Place mouse on FILE and click on.
    - Click on LOAD SAMPLE.
    - Choose Drive A, B, or C.
    - Click the mouse to highlight the name of the sample to be read. (Click on MORE SAMPLES if the one to be loaded does not appear on the list).

-Load the highlighted data file by placing the mouse on LOAD DATA FILE and click it on.

3. Check instrument settings.

- a) Place new paper in spectrometer.
- b) Check the SCANTIME and CHART EXPANSION. The current settings will have a dot in the left hand corner of the button. Change them if necessary.
- c) Check %T and adjust if necessary. The baseline (position of the pen) should be somewhere between 95 - 90%.
- d) Check the GAIN SETTING. When the GAIN CHECK button is engaged, the pen should deflect only 10%. If it moves less than 10% the gain should be decreased (use the down arrow (PARAMETER ADJUST)). If more than 10%, it should be increased (the up arrow PARAMETER ADJUST). Turn off the GAIN CHECK and SCAN the spectrum. If the gain has not been properly set, the instrument will not start. The gain must be readjusted. Continue this procedure until the simulator will run in the SCAN mode.
- e) Turn the instrument off by disengaging the SCAN mode.
- f) Print or Plot your spectrum. (Keyboard users press the F key and then hit Return. Choose P for printer, G for graphics plotter).
- g) Start your infrared spectrum collection.

**Exercise 1:** All spectrometers must be referenced periodically to assure proper calibration. In infrared spectroscopy, the reference sample is polystyrene, a thin film of plastic. The film is placed in the sample cell of the spectrometer and a spectrum obtained. A close examination of the location of the peaks associated with the obtained spectrum with the standard reference spectrum, allows an operator to judge if the instrument is properly calibrated or not. Obtain a spectrum of polystyrene which is the first sample on the program disk. Why do you think polystyrene was chosen as a standard reference?

**Exercise 2:** Call up sample 24 on the program disk and obtain the infrared spectrum of the compound. Try to identify the important absorption bands.

**Exercise 3:** At approximately 97% T, record the infrared spectrum of sample 315 found on data disk 2. Repeat the same procedure for 94% T. Compare the two spectra. What slight differences can be noted?

**Exercise 4:** Review quiz! Demonstrate (yes, that means you must get up) the symmetrical and unsymmetrical stretching associated with infrared vibrations. For extra credit, try the wag, the rock, the scissor and the twist.

**Exercise 5:** Most samples are placed between two sodium chloride windows and then inserted into the sample holder of the infrared spectrometer. Since light must pass through the sample, the majority of liquids may be scanned quite easily. A pure liquid is referred to as a neat sample. Solid samples, which will not allow the passage of light must be prepared specially. Two methods are preferred, one a KBr pellet and the other a mull. The pellet is prepared when KBr is carefully ground with the sample in a mortar. The mixture is then pressed with pressure until a transparent window through which light can pass results. The mull is prepared by adding a drop of oil, either Nujol or Fluorolube to the solid and carefully grinding in the mortar. A transparent paste results. One problem associated with the mull process is that both oils contain hydrocarbons which absorb IR radiation. One oil absorbs predominately in the upper wavenumbers, the other in the fingerprint region. Since a spectrum should always indicate the type of sample preparation, one would know to mentally subtract out those absorbencies associated with the specific oil used.

Now, finally, to your exercise. Obtain the IR spectra for Nujol (number 135 on data disk 1), and Fluorolube (129 on data disk 1). Which one absorbs in the fingerprint region?

Why do you think two oils are used to prepare different mulls of the same sample? Refer to Figure 2.3, the spectrum of benzoic. Remember benzoic acid is a solid. Which oil do you think was used to prepare this sample? Why?



CHAPTER 3  
NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

OBJECTIVES

1. Before you attempt this chapter, review the following terms:

- electromagnetic spectrum
- radiofrequency
- induction
- nonpolar covalent bond
- polar covalent bond

2. Upon completion of this chapter you should be able to define and understand the following terms:

- Nuclear Magnetic Resonance
- $^1\text{H}$  NMR
- $^{13}\text{C}$  NMR
- chemical shift
- nuclear spin
- induced or applied field
- resonance
- resonance lines
- ppm
- upfield
- downfield
- shielding
- deshielding
- TMS

electronic environment

equivalent and nonequivalent protons, carbons

integration

spin-spin coupling

singlet

doublet

triplet

quartet

multiplet

CW NMR

FT-NMR

3. Determine the types of protons or carbons in a molecule from the chemical shifts of the signals.
4. From the integration of a proton spectrum, determine the number of protons in a particular electronic environment
5. List the information that can be obtained from a  $^1\text{H}$  NMR spectrum.
6. Identify an unknown compound from its  $^1\text{H}$  NMR spectrum.
7. List the differences and similarities of  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR.
8. Given the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra, be able to determine the identity of a compound.
9. Describe the function of an NMR spectrometer.
10. Successfully obtain from the simulator and integrate a proton NMR spectrum.

## INTRODUCTION

Nuclear magnetic resonance (NMR) is another form of absorption spectroscopy. In NMR, the nuclei of certain atoms resonate (vibrate) when simultaneously placed in a magnetic field and irradiated with radiofrequency energy. The absorption of energy by the nuclei (called resonance) is detected by the spectrometer and recorded as a signal in a spectrum. The specific locations of signals or peaks in a spectrum, referred to as chemical shifts, indicate the electronic or chemical environment of the nuclei in the molecule.

One criterion necessary for nuclear magnetic resonance to occur is that some of the nuclei in a molecule have a property known as spin. Not all nuclei have spin, only those having an odd atomic number or mass number. Two such nuclei are very important to the organic chemist, proton,  $^1\text{H}$  and  $^{13}\text{C}$  ( $^{12}\text{C}$ , which has an even number of both protons and neutrons, does not have a spin). Since every hydrocarbon contains both hydrogen and carbon atoms, these two separate forms of nuclear magnetic resonance spectroscopy,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR, provide valuable information concerning the structural make-up of any organic compound.

## INSTRUMENTATION

Essentially, an NMR spectrometer is equipped with a magnet which provides an applied magnetic field referred to as  $H_0$ . An NMR tube, which contains the sample, is placed

between the poles of a magnet of the spectrometer and spun to average field homogeneity. As the sample spins in the magnetic field, it is also irradiated with radiofrequency energy. In some instruments, the frequency is held constant while sweep coils slightly vary the field of the magnet. Different nuclei in a molecule will absorb the radiofrequency as the field strength changes thus separate signals are recorded on a spectrum. See Figure 3.1 for a simplified illustration of an NMR spectrometer.

Exercise 1: Differentiate between the instrumentation in IR and NMR spectroscopy. What energy source is used in each method? In IR does the spectrometer scan various frequencies or is the frequency held constant? In NMR does the frequency change or is it held constant?

#### NUCLEAR SPIN AND RESONANCE

Certain atomic nuclei have magnetic properties which cause them to behave as tiny bar magnets. When placed in a magnetic field, symbolized by  $H_0$ , the nucleus (or "magnet") will spin and align in one of two ways, (1) with the applied magnetic field or (2) against the applied field. (A nucleus that does not have a spin such as carbon-12 will be unaffected by the presence of the magnetic field.) Those nuclei that line up with the field are "strengthened" by the field

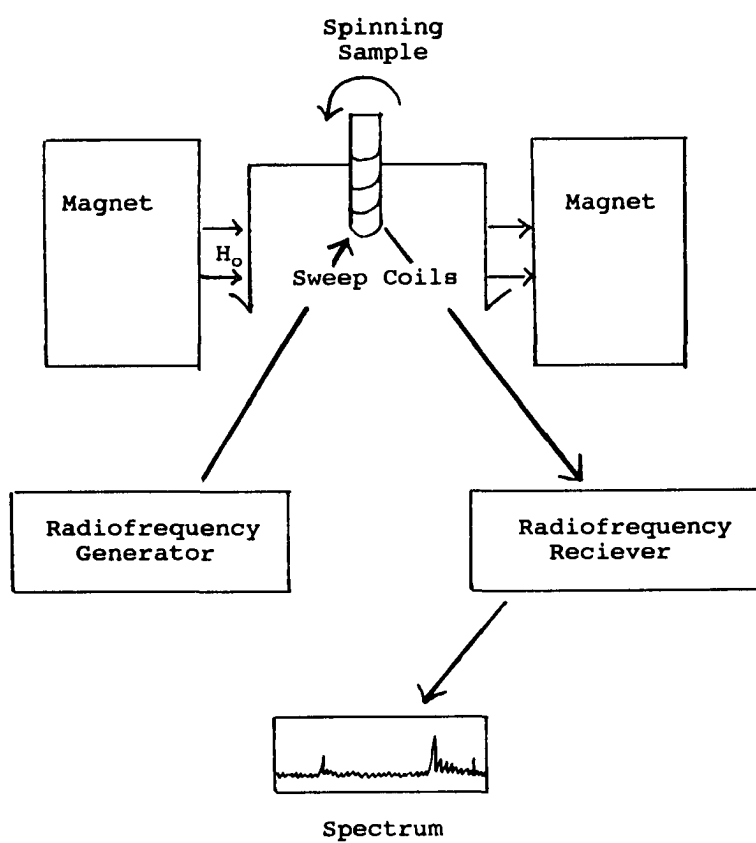


Figure 3.1 Simple Diagram of an NMR Spectrometer.

and are therefore in a lower energy state than those that line up against the field. (Think of two people riding bicycles, one with the wind and the other against the wind. Obviously, the one riding with the wind expends less energy, will be in a lower energy state, while the one riding against the wind will expend more energy, and be in a higher energy state.) Nuclei in the lower energy state are designated by having a spin of  $+1/2$  whereas those in the higher energy state are indicated by a spin of  $-1/2$ . (Some nuclei may have spins other than  $+$  or  $- 1/2$ , but for the sake of simplicity, these will not be discussed here.)

In the magnetic field, an energy difference ( $\Delta E$ ) exists between the nuclei of spin  $+1/2$  and those of spin  $-1/2$ . Now, if the sample is irradiated with radiofrequency energy that corresponds exactly to  $\Delta E$ , some of the nuclei in the lower state will absorb the energy and "flip" to the higher energy state. This flip of the nuclei causes resonance, a signal that is recorded on a spectrum.

Before we continue, please examine closely Figure 3.2. Hopefully these concepts will become clearer with the illustration.

**Exercise 2:** In your own words, explain the difference between the behavior of a nucleus with spin placed in a magnetic field and one that does not have a spin also placed in a field. When nuclei with spin are placed in a magnetic field and irradiated with the radiofrequency equal to  $\Delta E$ , what happens?

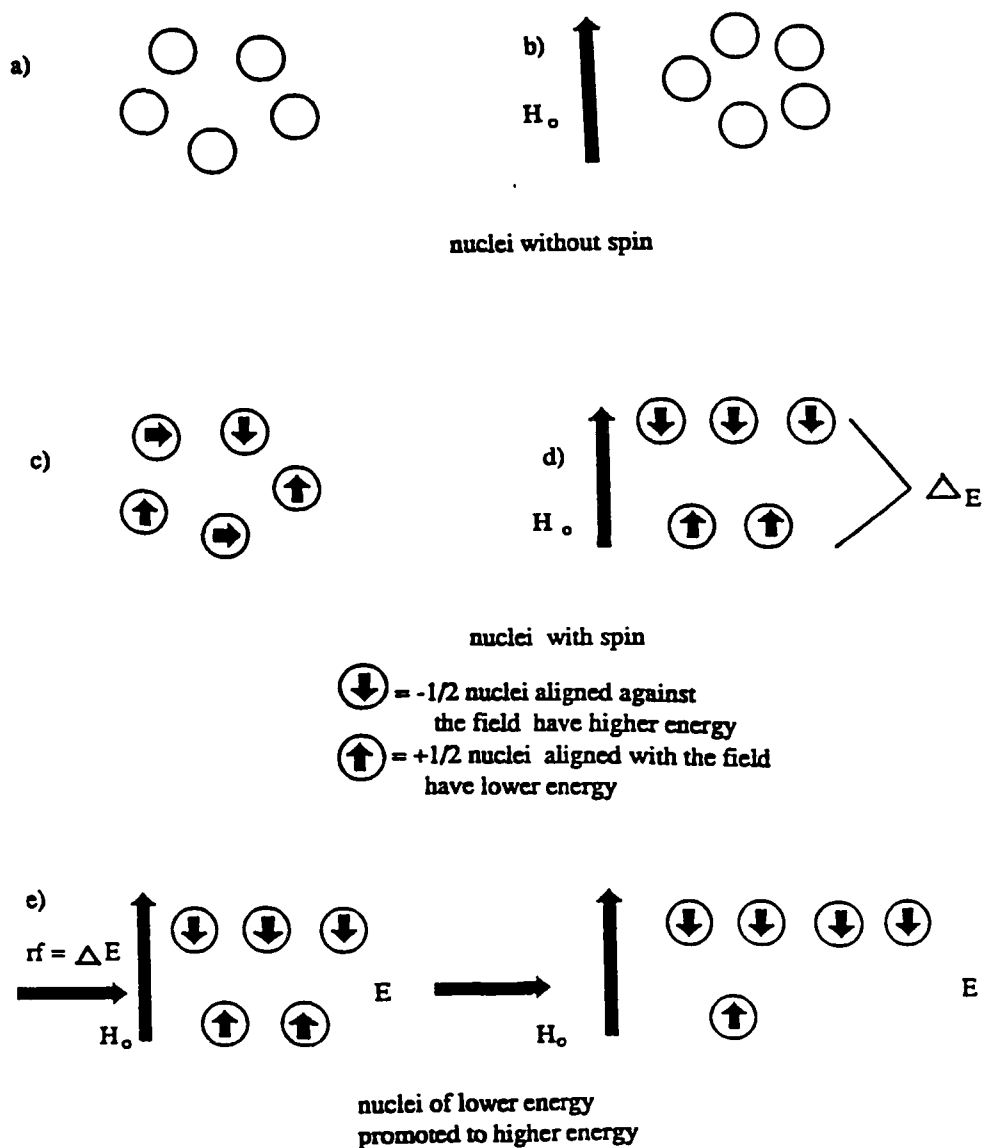
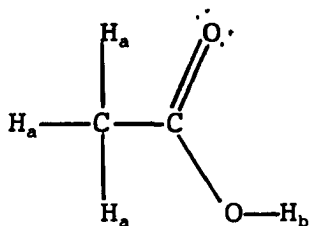


Figure 3.2 (a) and (b) illustrate nuclei without spin align randomly with or without the magnetic field, (c) shows that in the absence of a magnetic field spin nuclei behave similarly to those nuclei without spin; however, in (d) the spin nuclei in a magnetic field align either with or against the field, whereas nuclei in (e) when irradiated with radiofrequency equal to  $\Delta E$ , are promoted to higher energy from lower energy.

## ELECTRONIC ENVIRONMENTS

Let us now expand upon the idea of nuclear spin and obtaining resonance lines in a proton spectrum (the same ideas can be applied later to carbon-13). An organic molecule contains many hydrogen atoms. The nucleus of hydrogen known as the proton, is immersed in an electron environment that varies depending upon the other atoms to which the hydrogen atom is bonded. Simply stated, atoms bonded to the hydrogen electronically affect the hydrogen nucleus. If protons are not found in similar electronic environments, they are electronically and chemically nonequivalent. A familiar example to help distinguish between equivalent and nonequivalent hydrogens is illustrated in the molecule, acetic acid. The hydrogens associated with the alkyl group experience the warm security of nonpolar covalent bonds. These protons are referred to as being equivalent; i.e., when the C-C sigma bond is rotated, one hydrogen can not be distinguished from another. The hydrogen bonded to the electronegative oxygen of the carboxyl group however, is acidic due to its polar bond, and therefore ionizes easily. It is not equivalent with the other three protons. These are examples of hydrogen atoms that exist in two separate electronic environments. In an  $^1\text{H}$  NMR spectrum, there will be two separate signals (not four) one representing each unique electronic environment.





- (a) The three alkyl hydrogens are electronically identical while  
 (b) the carboxyl hydrogen is in a different environment.

**Exercise 3:** Draw out the structure for the following molecules and indicate those hydrogens you expect to be electronically equivalent, electronically different. (Hint: To differentiate, box, circle, or put a triangle around the identical ones.) Indicate the number of signals you would expect in each spectrum.  
 (a) acetone, (b) formaldehyde, (c) propane,  
 (d) 1-propanol, and (e) 2-heptanone.

### SHIELDING AND DESHIELDING

Let us return to the discussion concerning the effect electronic environment has upon the spin of the proton. In a molecule, the proton is bonded to an adjacent atom. When placed in a magnetic field, the electrons involved in the

bonding circulate about the proton, thus protecting it somewhat from the induced magnetic field. This protection is called shielding and compared to a naked proton, a shielded hydrogen will require more energy to flip to the higher energy state. Various atoms and types of bonding have different shielding effects on a proton.

View the NMR spectrum shown in Figure 3.3. Note that the numbers are on the bottom of the spectrum, and that zero is located on the right, ten on the left side. These units are called delta units,  $\delta$ , or parts per million, ppm. This scale is used in identifying chemical shifts. A peak that is located closer to the zero represents a proton that is more shielded, harder to flip. This proton is said to be shifted upfield. Alkyl groups usually contain mostly shielded protons. The peaks found closer to ten ppm, indicate hydrogens that are deshielded, easier to flip, and are shifted downfield. Protons bonded to an electronegative element such as a halogen or an oxygen or protons involved in pi bonding are deshielded. Aromatic hydrogens are especially deshielded, the protons associated with the carboxyl groups, even more so. (Many times the ppm scale must be expanded to eleven or twelve ppm in order to record the carboxyl hydrogen.) Table II lists the chemical shifts of several of the functional groups. Remember that chemical shifts are relative and may be affected by the presence of other atoms.

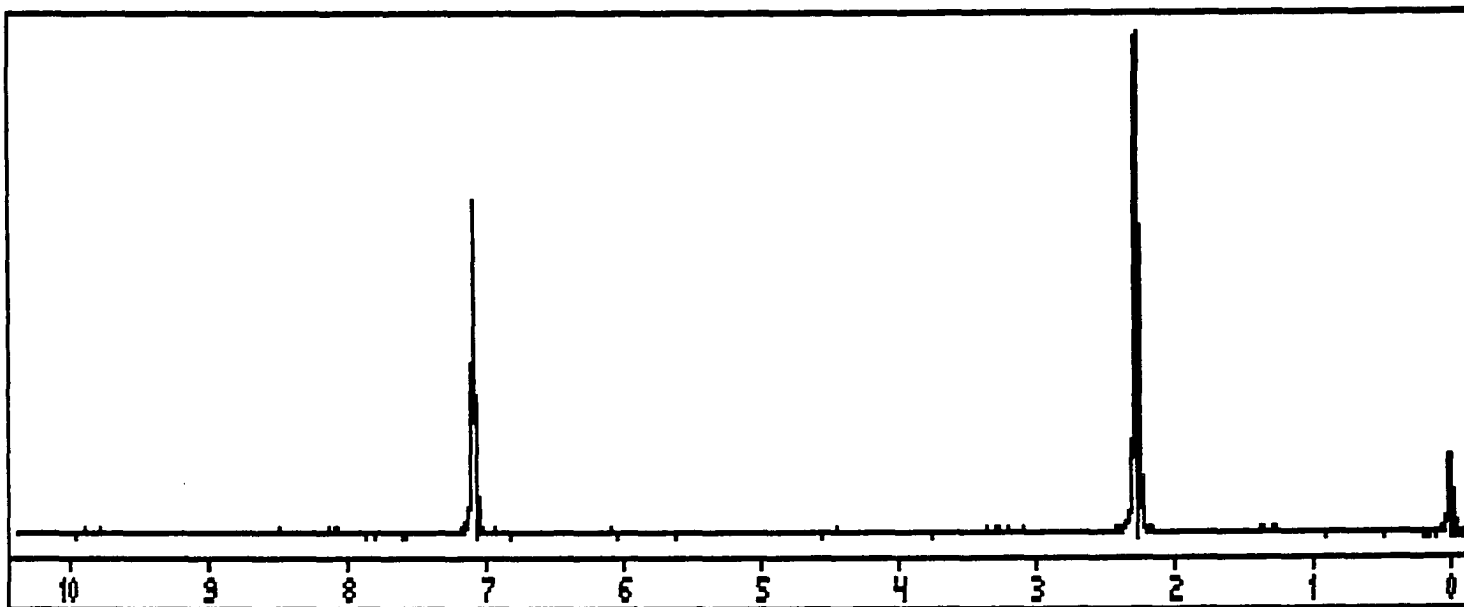
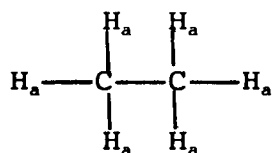


Figure 3.3 Proton Spectrum of Compound A. This compound has a molecular formula of  $C_8H_{10}$ . It can be noted from the spectrum that there are two separate types of protons in the molecule, one set that is shielded, the other, deshielded.

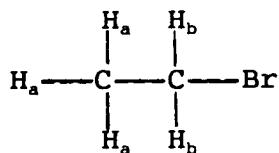
Table II. Proton Chemical Shifts

type of proton		chemical shift, ppm
$\text{RCH}_3$	(primary)	0.8 - 1.2
$\text{R}_2\text{CH}_2$	(secondary)	1.1 - 1.5
$\text{R}_3\text{CH}$	(tertiary)	1.5
$\text{ArH}$	(aromatic)	6.0 - 8.0
$\text{ArCH}_3$	(benzylic)	2.2 - 2.5
$\text{C}=\text{CH}$	(vinylic)	4.9 - 5.9
$\text{C}=\text{C}-\text{CH}_3$	(allylic)	1.7
$\text{C}\equiv\text{CH}$	(acetylenic)	2.3 - 2.9
$\text{FCH}$		4.0 - 4.5
$\text{ClCH}$		3.0 - 4.0
$\text{BrCH}$		2.5 - 4.0
$\text{ICH}$		2.0 - 4.0
$\text{ROH}$		1.5 - 6.0
$\text{ArOH}$		6.0 - 8.0
$\text{RC}-\text{CH}$   O		2.0 - 2.7
$\text{HC}=\text{O}$		9.0 - 10.0
$\text{RCOOH}$		10.0 - 12.0
$\text{HCCOOR}$		2.1
$\text{RCOOCH}$		3.8
$\text{RCOCH}$		3.2 - 4.3
$\text{RNH}_2$		1.0 - 3.0
$\text{R}_2\text{NH}$		2.0 - 4.0
$\text{RCNRH}$   O		5.0 - 9.0
$\text{ArNH}$		3.0 - 5.0

For example, let us consider the molecules ethane and bromoethane. By examining the structure of ethane, it is apparent that all of the hydrogens are equivalent. Therefore we would expect to see one peak in the spectrum, and by using Table II, note that it should be located around 1.0 ppm. Bromoethane, on the other hand, does not contain all equivalent protons. The three on the methyl group are identical to each other and the two on the other carbon are equivalent, thus two different signals are expected in its spectrum. Bromine, being electronegative, withdraws electrons by induction thereby deshielding not only the hydrogens bonded to the same carbon, but, to a slighter degree, the hydrogens bonded to the adjacent carbon as well. This causes the chemical shifts of both peaks in bromoethane to be somewhat deshielded when compared to ethane.



ethane



bromoethane

#### REFERENCING THE SPECTRUM

Shielding and deshielding are relative concepts. In order to be more specific in measurement, a reference standard must be added to the sample. Several are available, but the most popular for proton use is tetramethylsilane,  $(\text{CH}_3)_4\text{Si}$ , better known as TMS. The protons in TMS are

extremely shielded, consequently other protons are deshielded when compared to TMS. The TMS peak is therefore placed at zero ppm and all other peaks are referenced to it.

Exercise 4: Refer to the spectrum in Figure 3.3. Note the position of the reference peak. What is the chemical shift, in ppm, of the most shielded protons? The most deshielded?

### INTEGRATION

Let us summarize what has been covered so far. A sample is placed in an NMR and irradiated with a constant radiofrequency. As the magnetic field changes, different protons are brought into resonance which are recorded as peaks on a spectrum. The position of the peaks, known as chemical shifts, indicate the protons in different electronic environments. A standard, usually TMS, is added to the sample for reference purposes. Signals located near the reference peak are shielded and appear upfield on the spectrum. Those peaks at the other end of the spectrum are said to be shifted downfield because they are deshielded.

Believe it or not, even more information can be obtained from an NMR spectrum. Refer to the spectrum in Figure 3.4. Actually, this is the same spectrum as found in Figure 3.3, only this time some extra "lines" have been added. These lines represent integration from which a ratio of the number

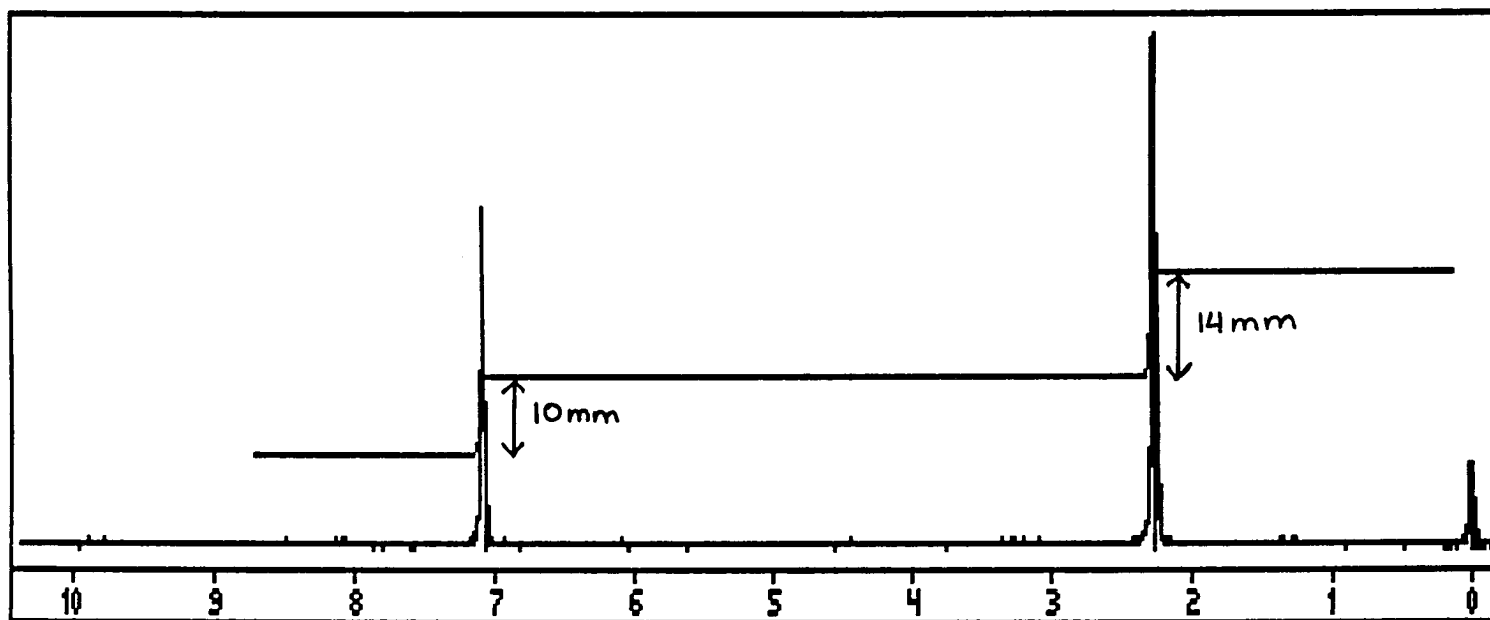


Figure 3.4 Integrated Spectrum of Compound A in Figure 3.3. Notice the integral line is slightly larger for the signal of greater intensity located at 2.2 ppm.

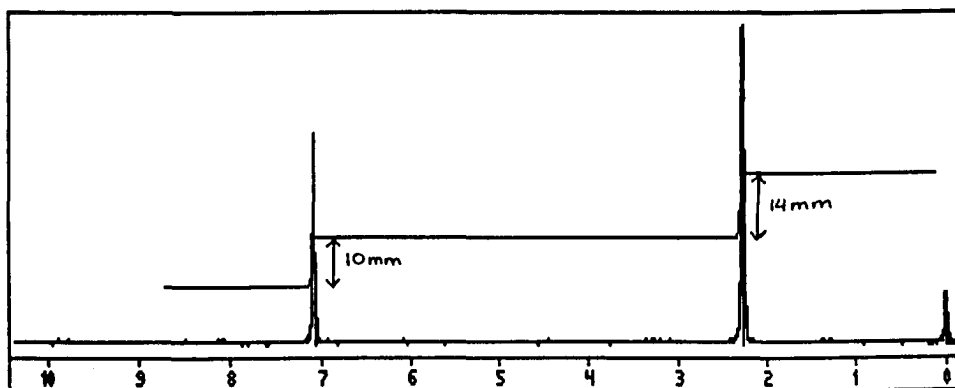
of identical protons in each of the electronic environments may be determined. Notice that the integration line appears to be greater for the larger peak. This is to be expected, as the number of hydrogens present in a particular environment is proportional to the area under the peak. As you will see, this feature of  $^1\text{H}$  NMR is a tremendous aid in structural determination of a compound.

=====

### Example 1

Determine the structural formula and identity of Compound A from the integrated spectrum found in Figure 3.4. The molecular formula of this unknown was given in Figure 3.3 as  $\text{C}_8\text{H}_{10}$ .

The spectrum has been reproduced here for convenience. Notice that lines have been drawn on the spectrum, and the distances from the bottom of the integration lines to the top have been measured in mm.\* Take out a ruler and measure Figure 3.4 for yourself.



The area under signal (a) is 14 mm and under signal (b) is 10 mm. This gives a total area of 24 mm.

Next, take the number of protons given in the formula and divide by the total area of the integrated signals. This provides the number of protons per mm.



$$\frac{10 \text{ protons}}{24 \text{ mm}} = 0.42 \text{ protons/mm}$$

To determine the number of protons that produce signal (a) and (b), multiply the mm under each signal by your ratio:

$$\begin{aligned} \text{(a)} \quad (14 \text{ mm}) \left( \frac{0.42 \text{ protons}}{\text{mm}} \right) \\ = 5.88 \text{ protons} \\ = 6 \text{ protons} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad (10 \text{ mm}) \left( \frac{0.42 \text{ protons}}{\text{mm}} \right) \\ = 4.2 \text{ protons} \\ = 4 \text{ protons} \end{aligned}$$

Since there must be a whole number of protons, (a) rounds to 6 protons and (b) to 4 protons. This gives a total of 10 hydrogens as is indicated by the molecular formula.

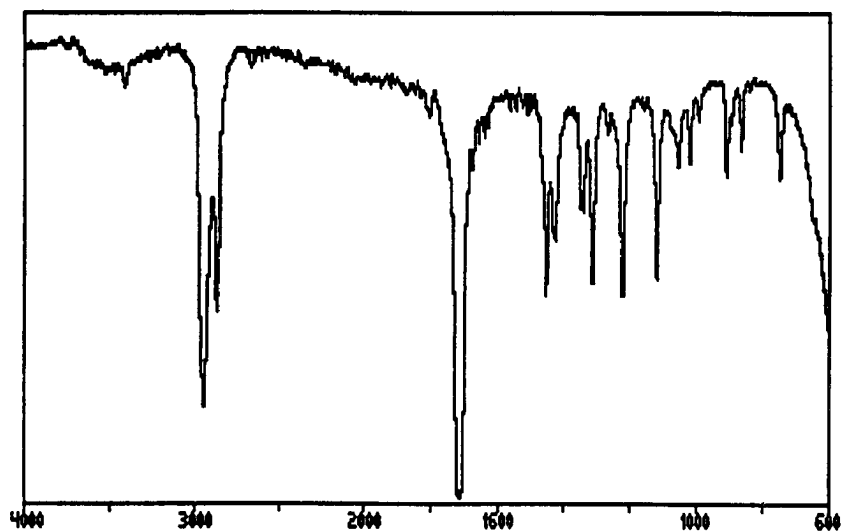
This information indicates that there are four deshielded protons in the molecule, and six that are more shielded. By using Table 3.1, the chemical shifts of these protons infer that an aromatic is present (7.2 ppm) and alkyl groups probably deshielded by the aromatic ring (2.2 ppm). An "educated" guess to make at this time would be to indicate that the molecule is probably para-disubstituted (having methyl groups in identical chemical environments). There are no other atoms besides carbon or hydrogen, therefore the likely choice is p-xylene.

As a word of encouragement, recall that sometimes positive identification of a molecule is possible only from the combined information of several types of spectroscopy. For example, para substitution would be confirmed in the fingerprint region of the IR spectrum. So if, at this point, you might have chosen ortho substitution instead of para for Compound A, without any more information, this would have been an acceptable attempt.

\* Some spectra are plotted on chart paper. In this situation, the blocks are counted and measuring is unnecessary.

=====

Exercise 5: Determine the identity of the compound whose proton and IR spectra are given below. The molecular formula for this molecule is  $C_6H_{10}O$ .



### SPLITTING PATTERNS

In addition to determining the different electronic environments and protons in those environments, a  $^1\text{H}$  NMR spectrum also provides information concerning the protons located on adjacent carbons. Refer back to the spectrum of Figure 3.4. We have already discussed the chemical shifts and integration of the peaks. Each signal has just one peak which is referred to as a singlet. Now look at the spectrum in Figure 3.5. Notice the chemical shifts and integration. Even though there are similarities, a major difference arises between this spectrum and the one viewed previously. Instead of individual singlets, two of these signals are split into multiple peaks. If a signal is split into two peaks, it is called a doublet, three peaks a triplet, and for a chance at the grand prize, what are four peaks called? Yes, yes, you are a winner! The correct answer is, a quartet. (See, you really do understand the finer details of chemistry!) Signals containing more than four peaks are usually referred to as multiplets. This splitting of signals into multiple peaks is called spin-spin coupling.

What does this information, the number of peaks in a signal, provide about a compound? In a nutshell, spin-spin coupling results from the interaction of protons on adjacent carbon atoms with the protons in the particular environment being considered. If a signal contains multiple peaks, it is said to be split by the neighboring protons. The number

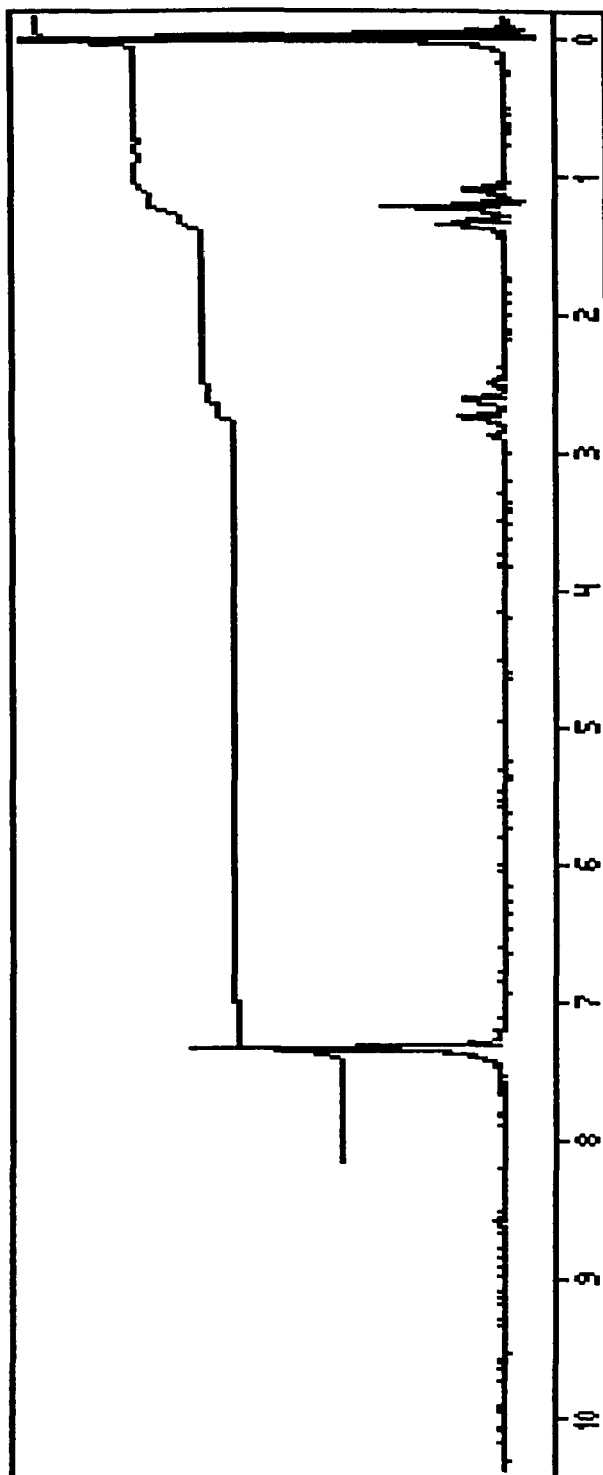


Figure 3.5 Proton Spectrum of Compound B. Molecular formula for the compound is  $C_8H_{10}$ .

of neighboring protons can be determined by counting the number of peaks present in the signal and then applying the  $n+1$  rule. The variable,  $n$ , represents the number of adjacent protons. For example, if a signal is a triplet, the equation becomes;  $n+1=3$ , where the number three indicates the triplet. The variable  $n$ , therefore, equals two. If the signal is a singlet, this usually infers that there are not any electronically different protons adjacent to the nucleus or nuclei responsible for the appearance of the signal.

Again refer back to Example 1 and closely examine the structure of the molecule. Notice that the aromatic hydrogens are all identical and have no protons on adjacent carbons that are in electronically different environments. The same situation holds true for the aliphatic protons. Since neither set of protons are affected by other hydrogen nuclei, the signals are singlets. If you are experiencing slight confusion at this point, be patient, maybe the concept will become clearer in the next example.

**Exercise 6:** List and explain three very important pieces of information that can be deduced from a proton NMR spectrum.

=====

### Example 2

Determine the structure of compound B in Figure 3.5.  
The molecular formula is  $C_8H_{10}$ .

Even though the formulas are the same for both compound A and B, a quick glance at each spectrum shows that they do not represent the same molecule.

The chemical shifts of compound B indicate, once again, an aromatic set of hydrogens and two aliphatic sets of protons. The integration (follow the same steps outlined in Example 1) provides a ratio of:

4.95 : 1.65 : 3.33.

When rounded, 5 protons : 2 protons : 3 protons for a total of the needed 10.

It can be deduced from the lack of splitting, that the aromatic protons are identical and are isolated from other protons.

The alkyl groups are different however. The middle set of peaks, the quartet, has a ratio of 2. Translated, this means that two hydrogens "see" three other hydrogens. (Applying the  $n+1$  rule, three protons would cause a quartet.)

The last set of peaks, the triplet, has a ratio of three. This indicates that three hydrogens (from the ratio) "see" two other protons (from the triplet).

Let us assimilate this information:

- 5 aromatic protons
- 2 aliphatic protons that "see" 3 other protons
- 3 aliphatic protons that "see" 2 other protons.

By now you have probably already identified the molecule! Yes, pat yourself on the back, it's ethylbenzene!

=====

**Exercise 7:** Determine the splitting patterns for the following molecules: (a) acetone, (b) bromoethane, and (c) 1-chloropropane (this one is tricky, remember, the center carbon, and it's hydrogens, have not one, but two neighboring sets of protons).

It should be noted here that this description of spin-spin splitting is brief and therefore does not include many factors that effect spin-spin coupling. These concepts will be left for discussion in a more detailed study of NMR spectroscopy.

**Exercise 8:** Without the spectra, take the following data and determine the structure of Unknown X which has a molecular formula of  $C_4H_9Br$ .

IR - strong absorbance at  $2900\text{ cm}^{-1}$   
NMR -doublet at 3.33 ppm has a ratio of 2  
          multiplet at 1.95 ppm has a ratio of 1  
          doublet at 1.04 ppm has a ratio of 2

## FOURIER TRANSFORM NMR

The type of spectrometer described in the last section is called continuous wave (cw) NMR. That is, the instrument scans the full spectrum while constantly irradiating the sample with the radiofrequency. This method works very well for obtaining the proton spectrum, but loses sensitivity when dealing with carbon-13. Why is this the case? The element carbon exists predominately as the carbon-12 isotope. Only one percent represents carbon-13. As a result, very few of the carbon atoms in a molecule are actually the necessary C-13 isotope, therefore the spectrometer must be extremely sensitive in order to detect the signals. In recent years, another method of NMR, Fourier transform (FT), which has a greater sensitivity than the cw method, has become a popular form of instrumentation. This method, referred to as FT-NMR, is used to obtain both proton and carbon spectra (as well as spectra for many other nuclei that are not mentioned here). FT-NMR instrumentation differs from cw NMR. In FT, the sample is pulsed with the radiofrequency, while in the cw method, the sample is continuously irradiated with the radiofrequency as the magnetic field is varied. At any rate, spectral analysis essentially remains the same.

## <sup>13</sup>C NMR SPECTROSCOPY

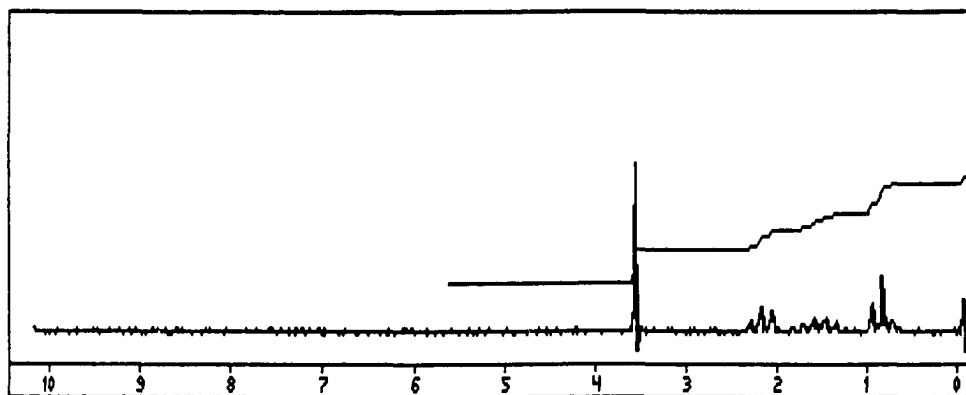
Most of the concepts covered in <sup>1</sup>H NMR can be applied to <sup>13</sup>C NMR, however several differences exist between the two



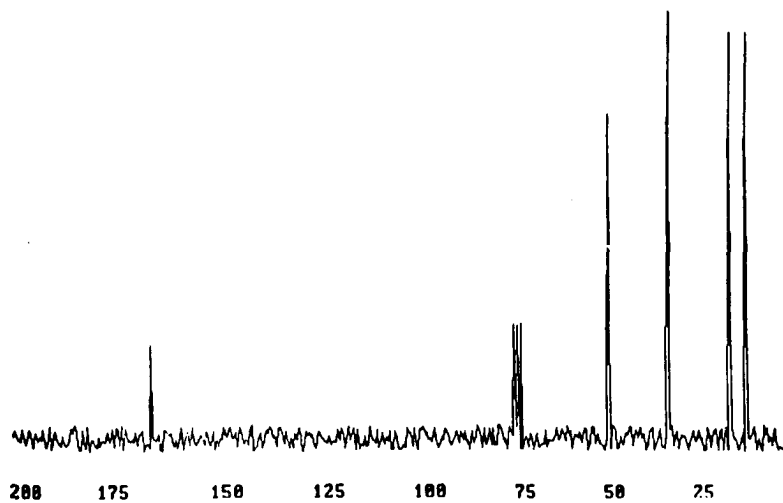
forms of nuclear magnetic resonance. These differences will be discussed now.

#### THE $^{13}\text{C}$ NMR SPECTRUM

Several major differences can be noted when the proton spectrum of a compound is compared to its carbon-13 spectrum. Figure 3.6 shows the proton and carbon-13 spectra of methyl butyrate. The carbon spectrum contains singlet peaks whereas the proton spectrum shows multiplets. (An exception must be noted here. At 77 ppm on the carbon-13 spectrum a triplet has been recorded. This triplet belongs to the solvent  $\text{CDCl}_3$ , which has been used as a reference standard in the C-13 spectra used in this workbook.) The number of signals in a C-13 spectrum, disregarding impurities, solvent or reference peaks, should equal the number of different carbons in the molecule. Each signal is recorded as a singlet and not as a multiplet. There are two reasons for the singlet signal. The first deals with the relative abundance of the carbon-13 isotope. Since carbon-13 comprises only one percent of carbon, the chances of one C-13 nucleus being adjacent to another carbon-13 nucleus in the molecule are slim. This all but eliminates the carbon-13 carbon-13 splitting problem. Splitting problems do arise however, from adjacent protons. This phenomenon is overcome by what is known as proton decoupling. A carbon spectrum that has not been decoupled does indeed demonstrate splitting patterns. While coupled spectra can be very confusing,



(a)



(b)

Figure 3.6 (a)  $^1\text{H}$  NMR Spectrum of Methyl Butyrate. (b)  $^{13}\text{C}$  NMR Spectrum of Methyl Butyrate.

they provide information concerning the number of hydrogen atoms bonded to the carbon in question. To avoid undue confusion, the  $^{13}\text{C}$  NMR spectra used in this workbook have been decoupled. Another difference between the proton and carbon spectra is found on the ppm scale. Proton spectra usually span zero to ten ppm. Carbon-13 spectra extend from zero to at least two hundred ppm. Since the number of signals in  $^{13}\text{C}$  NMR reflect the number of identical carbons in a molecule, these spectra are not integrated.

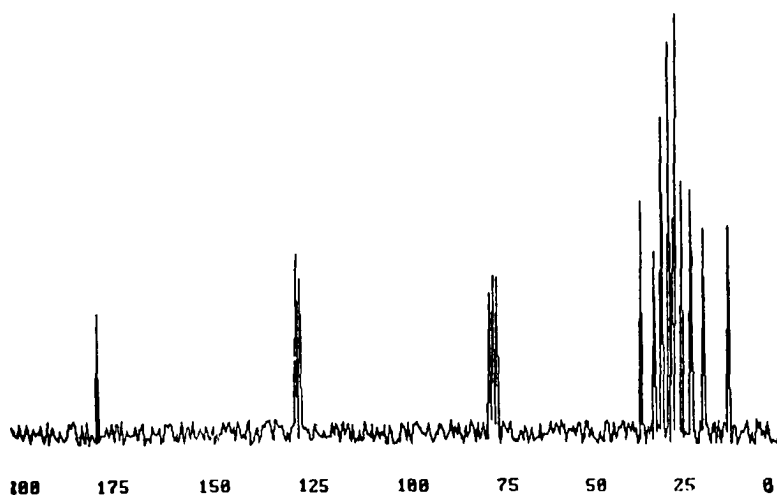
Table III lists the chemical shifts associated with carbon-13 nuclei. Note that like the proton chemical shifts, the alkyl carbons are shielded, aromatic carbons and those bonded to electronegative elements are deshielded. Particularly interesting is the extreme deshielding of the carbonyl carbons associated with aldehydes and ketones. What chemical shifts relate to the presence of these carbons?

Exercise 9: Predict the number of signals you would expect to see in a  $^{13}\text{C}$  NMR spectrum of  
(a) 2-heptanone, (b) 3-pentanone,  
(c) p-chlorobenzoic acid, and  
(d) 3-fluoropentane.

Table III. Carbon-13 Chemical Shifts

type of carbon		ppm
$\text{RCH}_3$	(primary)	13.0 - 15.0
$\text{R}_2\text{CH}_2$	(secondary)	16.0 - 25.0
$\text{R}_3\text{CH}$	(tertiary)	25.0 - 40.0
$\text{ArH}$	(aromatic)	125.0 - 150.0
$\text{RCH}=\text{CH}_2$	(vinylic)	115.0 - 140.0
$\text{RC}\equiv\text{CH}$	(acetylenic)	65.0 - 85.0
$\text{RCH}_2\text{Cl}$		40.0 - 45.0
$\text{RCH}_2\text{Br}$		28.0 - 35.0
$\text{RC}\equiv\text{N}$		117.0 - 125.0
$\text{RCH}$   O		190.0 - 200.0
$\text{RCR}$   O		205.0 - 210.0
$\text{RCOR}$   O		160.0 - 175.0
$\text{RCOOH}$		170.0 - 185.0
$\text{RCH}_2\text{OH}$		50.0 - 65.0
$\text{RCH}_2\text{NH}_2$		35.0 - 45.0

**Exercise 10:** Below is the  $^{13}\text{C}$  NMR spectrum of oleic acid. How many signals are there in the spectrum? From what you can determine from the structure of the acid, explain the number of peaks in the spectrum. As well as you can, identify these peaks.



**Exercise 11:** Refer to Figure 3.6 and integrate the proton spectrum. Identify the protons associated with each signal in the spectrum. By using Table III, identify the signals found on the C-13 spectrum of methyl butyrate.

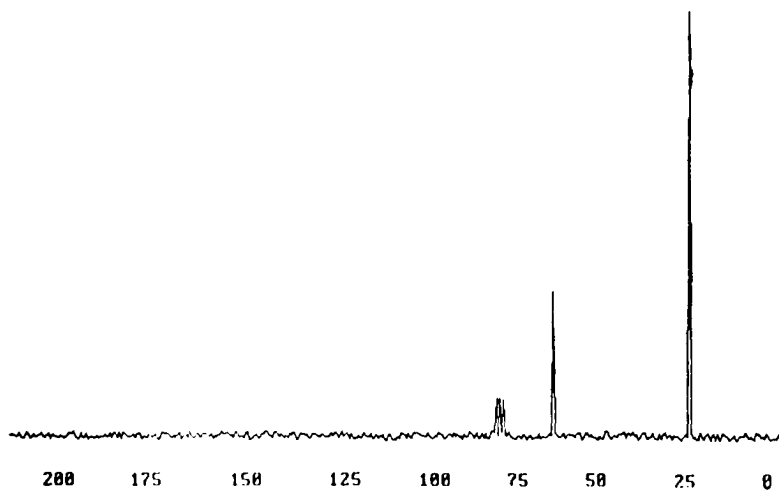
**Exercise 12:** Consider the molecules 1-butanol and butanoic acid. How could you distinguish between these compounds (a) by their infrared spectrum, (b) by their  $^1\text{H}$  NMR spectrum, and (c) their  $^{13}\text{C}$  NMR spectrum.

**Exercise 13:** On a  $^{13}\text{C}$  NMR spectrum, how could you distinguish between pentanoic acid and ethyl propanoate, both of which have five carbon atoms?

**Exercise 14:** If you were given a proton NMR of 2-heptanone and of heptanal, how could you tell, in a moments glance, which spectrum belonged to the aldehyde?

**Exercise 15:** How many signals would you expect to find in a  $^{13}\text{C}$  NMR of benzyl alcohol?

Exercise 16: From the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra below, identify the compound. Elemental analysis shows the presence of oxygen and a molecular formula of 40.0 g/mol.



**Exercise 17:** Unknown organic compound, UOC, has in its proton NMR spectrum two singlets at 1.42 and 2.00 ppm. Their proton ratio is 3:1. The C-13 spectrum has peaks at approximately 22, 28, 80, and 170 ppm. Important IR bands are located at 1740, 1255, and 1175 wavenumbers. Predict the structure of this compound.



## OBTAINING AN NMR SPECTRUM FROM THE SIMULATOR

### INTRODUCTION

Now that you know how to interpret an NMR spectrum, it is time to acquire one for yourself. As with the IR, you will be using a simulated computer program instead of operating an actual spectrometer. The control panel that appears on the screen of your computer looks like the panel found on a Varian EM 360 continuous wave NMR. As you use this program, keep in mind that the basic directions you follow are the same procedures used in obtaining a spectrum from a spectrometer. Therefore, if you ever have an opportunity to use a Varian, the procedures are virtually the same. Provided in the user's manual and available on the HELP screens are guidelines describing the operation of the simulator (4). For your convenience, these have been outlined in this workbook.

To obtain an NMR spectrum:

1. Place the sample in the spectrometer  
(When using the simulator this means loading a data file from a disk).
2. Align the TMS signal on 0 ppm.
3. Set the spectrum width (usually 10 ppm).
4. Set the offset or the end of sweep (usually 0 ppm).
5. Find the largest peak in the spectrum and adjust the amplitude.

6. Record the spectrum.
7. Integrate the spectrum.
8. Evaluate and interpret the spectrum.
9. If it is your first spectrum, or one that you are especially proud of, take it home and put it on the refrigerator.

To accomplish these steps, a series of directions have been provided. If you are using a keyboard and not a mouse, a diagram (Figure 3.7) indicating the keystrokes necessary to operate the control buttons has been designed for your referral. This figure is included in the section that contains the directions necessary for obtaining a spectrum from the simulator. Brief definitions of the functions of the control buttons are also included. Well, there is nothing left to do but get started. Are you ready to run your first spectrum? I thought so. Did you clear off a special place on the 'fridge before you left the house this morning?

## NMR SIMULATOR CONTROL FUNCTIONS

## 1. SWEEP CONTROLS

- A. Sweep Width - determines the range of ppm to be scanned. Normal setting is 10 ppm.
- B. End of Sweep - determines the end of the spectrum relative to the TMS signal. Most spectra scan 10 ppm, therefore this setting is usually set at 0.
- C. Sweep Time - setting reflects the time needed to scan a spectrum. A longer sweep time usually increases the resolution ("quality") of the spectrum. Normal setting is 5 minutes. Changing the sweep time on the simulator however does not effect the time or spectrum.
- D. Sweep Zero - control used to align the TMS signal with zero ppm.

## 2. SPECTRUM AMPLITUDE

- A. Course - increases or decreases the height of the signals by 10, 100 or 1000 times.
- B. Fine - increases or decreases the height of the signals by much smaller increments.
- C. Filter - Increasing the filter can reduce high frequency noise. A noisy spectrum has a lot of smaller "signals" in the baseline. A good spectrum has little noise or a high signal to noise ratio. Normal setting is 0.1.

### 3. RF FIELD

- A. Power - determines the amount of radiofrequency energy that irradiates the sample. Increasing the power can increase the signal to noise ratio. Normal setting is 0.05.
- B. Phase - adjusts the signal shape. Control is not functional on the simulator.

### 4. RESOLUTION

- A. Y and Curvature - adjusts the homogeneity of the magnetic field. Controls are not functional on the simulator.

### 5. INTEGRATION

- A. Balance - keeps the integral line from drifting.
- B. Reset - moves the pen to the baseline.
- C. Hold - used to adjust the integral height.

### 6. RECORDER

- A. On/Off - turns the recorder on and off. Recorder must be off to load sample.
- B. Reverse - moves the carriage backward.
- C. Forward - moves carriage forward.
- D. Stop - stops carriage at the end of a scan. Must be engaged whenever the carriage is moved without first depressing the forward or reverse button.
- E. Pen Auto - engages pen for recording purposes.
- F. Pen Up - lifts pen so it will not record as the carriage is moved.

- G. Normal - must be engaged when running a spectrum.
- H. Integrate - must be engaged when integrating.
- I. Baseline - moves the position of the pen up or down.

### OPERATING THE NMR SIMULATOR

Follow the same directions for starting the computer that are outlined in the IR chapter. If you did not boot the computer with the program disk (the simulator will not appear on the screen) type MOCKNMR at the > and hit Return or Enter. If you are using the keyboard, refer to the diagram of the NMR control panel found in Figure 3.7. This will indicate the proper keystrokes needed to operate the controls. The control settings are written across the top of the monitor screen.

If you are using a mouse, moving the mouse up increases the values on the knobs, down decreases them. Normal settings can be viewed when the mouse is placed over the button on the simulator and simultaneously clicking the mouse. Also, the carriage may be moved faster forward and backward by using the mouse.

#### Obtaining A Spectrum

1. Turn on the computer and study the control panel.
2. Make sure recorder is off. (The button will appear black.)

<div style="display: flex; justify-content: space-around; margin-bottom: 5px;"> <span>Balance</span> <span>Reset</span> <span>Hold</span> </div> <div style="display: flex; justify-content: space-around; text-align: center;"> <div></div> <div></div> <div></div> </div> <div style="display: flex; justify-content: space-around; margin-top: 5px;"> <span>Spectrum Amplitude</span> </div> <div style="display: flex; justify-content: space-around; text-align: center;"> <div></div> <div></div> <div></div> </div> <div style="display: flex; justify-content: space-around; font-size: small;"> <span>Course</span> <span>Fine</span> <span>Filter</span> </div>	<div style="text-align: center; margin-bottom: 5px;">Sweep Controls</div> <div style="display: flex; justify-content: space-around; text-align: center;"> <div> Sweep Width</div> <div> End of Sweep</div> </div> <div style="display: flex; justify-content: space-around; text-align: center; margin-top: 10px;"> <div> Sweep Time</div> <div> Sweep Zero</div> </div>	<div style="text-align: center; margin-bottom: 5px;">RF Field</div> <div style="display: flex; justify-content: space-around; text-align: center;"> <div> Power</div> <div></div> </div> <div style="text-align: center; margin-top: 5px;">Phase</div> <hr/> <div style="text-align: center; margin-bottom: 5px;">Resolution</div> <div style="display: flex; justify-content: space-around; text-align: center;"> <div></div> <div></div> </div> <div style="display: flex; justify-content: space-around; font-size: small;"> <span>Y</span> <span>Curvature</span> </div>																																
<ol style="list-style-type: none"> <li>1. Normal NMR settings have a box around them, they are written across the top of the screen on the simulator.</li> <li>2. Letters on knobs indicate the keys to use on the keyboard.</li> <li>3. Depressing the shift with the letter key will increase the value needed; without the shift, the value will decrease.</li> <li>4.  indicates buttons that are inoperative on simulator.</li> <li>5.  indicates push buttons, all the rest are knobs that turn.</li> <li>6. ← key erases spectrum and places new chart paper on recorder.</li> <li>7. ? key loads new sample from data disk to simulator; recorder must be off to do this.</li> <li>8. The Num Lock key will move carriage quickly to the left; depressing skift key moves the carriage faster.</li> <li>9. The Scroll Lock key moves the carriage to right.</li> <li>10. ESC - quits program</li> </ol>																																		
<div style="display: flex; justify-content: space-between; align-items: flex-start;"> <div style="width: 45%;"> <p>Baseline Position</p> <div style="display: flex; align-items: center; margin-top: 10px;"> <div style="width: 15px; height: 30px; background-color: black; margin-right: 5px;"></div> <div style="display: flex; flex-direction: column; align-items: center;"> <div>↑ 8</div> <div>↓ 2</div> </div> </div> </div> <div style="width: 50%;"> <table style="width: 100%; border-collapse: collapse; font-size: small;"> <thead> <tr> <th style="width: 20%;"></th> <th style="width: 10%; text-align: center;">Mode</th> <th style="width: 10%; text-align: center;">Scan</th> <th style="width: 60%;"></th> </tr> </thead> <tbody> <tr> <td>Parking Lock</td> <td style="text-align: center;"></td> <td style="text-align: center;">9</td> <td>Reverse</td> </tr> <tr> <td>Resolution Adjust</td> <td style="text-align: center;"></td> <td style="text-align: center;">6</td> <td>Stop</td> </tr> <tr> <td>Amplitude</td> <td style="text-align: center;">7</td> <td style="text-align: center;">3</td> <td>Forward</td> </tr> <tr> <td>Set Normal</td> <td style="text-align: center;">4</td> <td></td> <td>Recorder</td> </tr> <tr> <td>Integrate</td> <td style="text-align: center;">1</td> <td style="text-align: center;">Return/Enter</td> <td>On/Off</td> </tr> <tr> <td></td> <td style="text-align: center;"></td> <td style="text-align: center;">-</td> <td>Pen Auto</td> </tr> <tr> <td></td> <td style="text-align: center;"></td> <td style="text-align: center;">+</td> <td>Pen Up</td> </tr> </tbody> </table> </div> </div>				Mode	Scan		Parking Lock		9	Reverse	Resolution Adjust		6	Stop	Amplitude	7	3	Forward	Set Normal	4		Recorder	Integrate	1	Return/Enter	On/Off			-	Pen Auto			+	Pen Up
	Mode	Scan																																
Parking Lock		9	Reverse																															
Resolution Adjust		6	Stop																															
Amplitude	7	3	Forward																															
Set Normal	4		Recorder																															
Integrate	1	Return/Enter	On/Off																															
		-	Pen Auto																															
		+	Pen Up																															

Figure 3.7 Control Panel of NMR Simulator.

3. Load a sample by pressing the ? key. (Keyboard command)
4. Choose sample by following directions on screen.
5. Turn on recorder by pushing the Return button. (Control Settings will appear at top of screen.)
6. Locate SWEEP CONTROLS and make the following adjustments:
  - A. Set SWEEP WIDTH on 10 and END OF SWEEP on 0.
  - B. Set SWEEP TIME; usually on 5 for normal spectrum.
  - C. Use SWEEP ZERO to align TMS with 0 ppm.
    1. Make sure PEN UP button is on (white).
    2. Press STOP.
    3. Move carriage to left with REVERSE key watching for vibrations. Adjust the SWEEP ZERO to align signal with 0 ppm. (Adjust SWEEP ZERO and move carriage from right to left until signal aligns.)
7. Make sure baseline is close to bottom of chart recorder. If adjustment is needed use keys 8 (up) and 2 (down).
8. Move carriage to left and watch for signals. Then return pen to highest peak.
9. Adjust SPECTRUM AMPLITUDE with the COURSE and FINE controls until highest peak fills the chart but does not go off the paper.
10. To Record a Spectrum:
  1. Move carriage to 10 ppm.

2. Press PEN AUTO.
3. Press FORWARD.
11. If spectrum is not acceptable, readjust controls as described previously. Then replace chart paper by pressing the left hand arrow, and continue with Recording a Spectrum.

#### Integration

1. Complete spectrum as previously described.
2. Make sure PEN UP is on (white).
3. Scan Mode should be on STOP.
4. Adjust baseline, probably up, so that it does not coincide with the spectrum baseline. (Use up (8) and down (2) keys.)
5. Set Control Panel for Integral Mode.
6. Move the carriage to a place where there is not a peak.
7. Adjust the baseline so that it does not drift. This is done by:
  - A. Press the INTEGRATOR RESET button.
  - B. If pen drifts (up or down), use BALANCE button to move as needed.
  - C. Alternate pressing the RESET and making BALANCE adjustments until there is no drift when RESET is pressed.
8. Adjust the magnitude by:
  - A. Moving the carriage to the left and pressing the RESET.



- B. Scan the spectrum with the PEN UP and watch the integration line as it crosses the largest peak.
  - C. If largest peak went off scale, press STOP.
  - D. Move carriage back to that area, push RESET, adjust the SPECTRUM AMPLITUDE, and rescan the area.  
(Alternate the procedure until a satisfactory integration curve is attained.)
  - E. When the carriage reaches the right side of the recorder, press STOP, and HOLD.
- 9. Disengage the HOLD and move the carriage to the left of the recorder.
  - 10. Press RESET and turn on PEN AUTO.
  - 11. Now move the carriage with the FORWARD button, when the carriage reaches the right press STOP.
  - 12. Print the integrated spectrum. (Use the Alt F1 key)

#### Expanding Spectrum Scale

Expanded scale is used when a routine spectrum does not give enough detail about a specific region of a spectrum. This technique allows us to enlarge portions of a spectrum.

- 1. Record a routine spectrum.
- 2. Locate the portion to be expanded.
- 3. Decide on what SWEEP WIDTH should be used (2 ppm is a good choice).
- 4. Now position pattern on paper with the END OF SWEEP control. This should be set so that the pen will scan the part of the spectrum needed. To do this, set

the END OF SWEEP on the number to the right of the region of the spectrum to be scanned.

5. Move baseline up slightly by using BASE LINE CONTROL.
6. Adjust the FINE SPECTRUM AMPLITUDE control so that the largest signal is on scale.
7. Position pen in the middle of chart recorder range and press the FORWARD button. This will record the expanded scale.

#### Obtaining Offsets

Some organic compounds have signals that appear outside the usual range (0 - 10 ppm). To obtain a spectrum of these signals, one must increase the range or obtain an offset on a regular spectrum. Increasing the scale is done by setting the SWEEP WIDTH on 20 ppm instead of 10 ppm, and following the instructions for a regular spectrum. Obtaining an offset is completed by following these directions:

1. Obtaining a normal spectrum.
2. Reset the END OF SWEEP control to allow the peak to be traced on a blank part of the spectrum.
3. Follow the normal spectrum instructions to print the offset.

**Exercise 1:** Follow the above procedures and obtain an integrated spectrum of Example 1 on the simulator program disk. Determine the relative number of protons in each environment. From the chemical shifts, determine what type of protons exist in the molecule.

- Exercise 2:** Obtain and integrate a normal spectrum of Example 2. Use the offsets to expand the region from 7-8 ppm. What did you observe from expanding the offsets?
- Exercise 3:** Obtain and integrate a normal spectrum for Example 3. This time, expand the sweep width to 20 ppm. Why do you think it was necessary to expand the scale? What did you notice about the ppm scale after you expanded it and printed out the spectrum?
- Exercise 4:** Stand up, stretch, look at the spectra you have already accumulated, congratulate yourself, and prepare to do another one.
- Exercise 5:** If the data disks are available, load from set four, diskette C sample number 86. This sample has a low signal to noise ratio, therefore adjustments might have to be made with the filter and/or rf power. Try several combinations to produce the best spectrum, change the settings, raise the baseline, and record part of that spectrum. Continue this procedure until the best spectrum is attained. What is the identity of this compound.

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CHAPTER 4  
MASS SPECTROSCOPY

OBJECTIVES

1. Before attempting this chapter, review the following:
  - radical
  - cation
  - pi bond
  - thermodynamic stability
  - stability of the carbocation
  - stability of the free radical
  - homolytic bond cleavage
  - heterolytic bond cleavage
  - resonance (do not confuse with NMR resonance)
2. Upon completion of this chapter, you should understand and be able to define the following terms:
  - radical cation
  - fragments
  - molecular ion
  - parent ion
  - mass/charge ratio,  $m/e$
  - base peak
  - acylium ion
3. Describe the function of a mass spectrometer.
4. Be familiar with the different fragmentation patterns of various functional groups.
5. Be able to identify the base peak and the molecular ion

peak in a mass spectrum.

6. What fragments will "show up" in a mass spectrum?  
Which fragments will not be recorded by a mass spectrometer?
7. Be able to show the resonance structures for a carbonyl radical cation.
8. Differentiate between the resonance in NMR spectroscopy and the resonance in number 7.
9. Be familiar with the M+1 and M+2 peaks of specific isotopes.
10. Know how to interpret a mass spectrum and thereby identify a compound, especially if other spectra (such as IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR are provided).

## INTRODUCTION

Mass spectroscopy, unlike the other forms of spectroscopy we have studied so far, does not absorb radiation emitted from the electromagnetic spectrum. Instead, a compound is vaporized under low pressure in the spectrometer, and then bombarded by a stream of high-energy electrons. This bombardment causes the ejection of an electron from the molecule producing, what is termed as, a radical cation. Because of the instability of the cation, it quickly splits into smaller pieces called fragments. Even though this may seem a bit drastic, hitting a molecule with such force, the fragmentation of the molecules surprisingly generates reproducible patterns. The study of these patterns is of great benefit to an organic chemist in determining the structure of an unknown molecule. In addition to providing structural information, a mass spectrum may also indicate the molecular weight of the compound.

## INSTRUMENTATION AND RECORDING OF DATA

A simple diagram of a mass spectrometer is shown in Figure 4.1. A small amount of sample is introduced into the instrument and vaporized. The sample concentration is kept low to minimize collisions between gas molecules and or fragments. (Recall that collisions between molecules may result in a chemical reaction which obviously must be avoided.) The vaporized molecules are then fed into a stream of high-energy electrons (usually 70 electron volts).

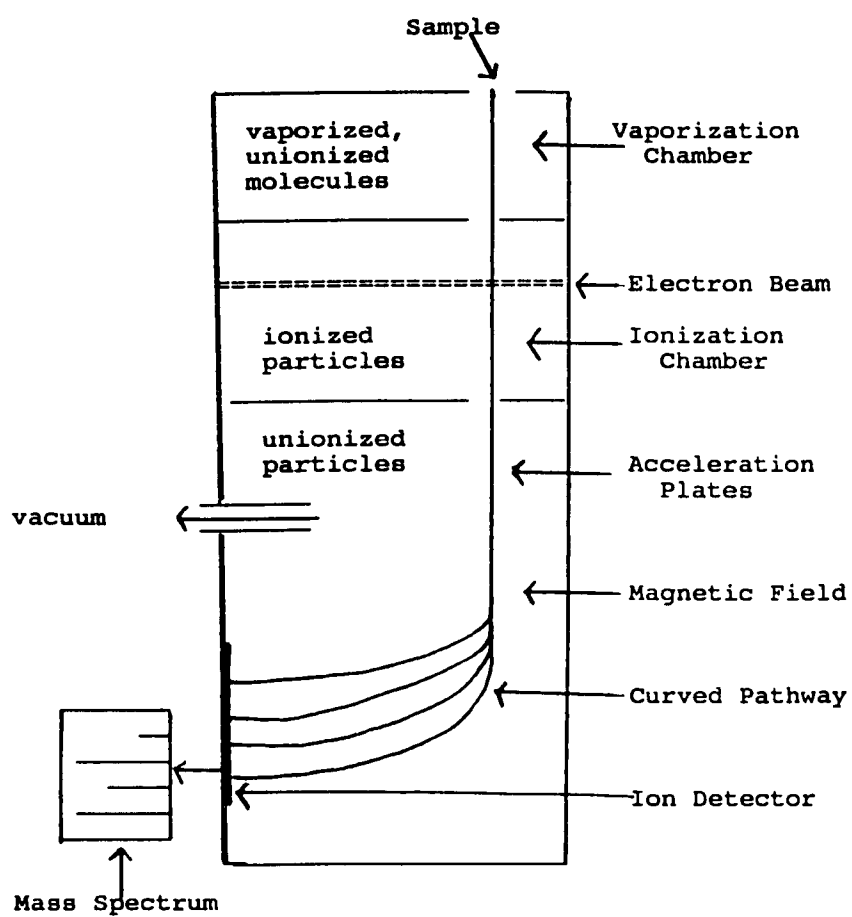


Figure 4.1 Simple Diagram of a Mass Spectrometer.

This stream of electrons causes the ejection of an electron from a molecule thus producing the initial radical cation. This radical cation is called the molecular ion ( $M^+$ ) or parent ion ( $P^+$ ). After the molecular ion has been formed, it may continue to fragment into other cations, free radicals and even neutral molecules.

The ions and fragments produced by the bombardment are then passed through an electric field which accelerates the cations. The uncharged radicals and neutral particles are not affected by the field and are therefore "washed" out by the vacuum. Next, the charged particles enter a magnetic field that curves their path according to their mass/charge ratio ( $m/e$ ). (Recall that moving charged particles in a magnetic field will behave as a magnet and be deflected.) As a rule, the lighter fragments are detected by the spectrometer and recorded in a spectrum first, the heavier ones last. A mass spectrum is a plot of the relative abundance (vertical axis) versus the  $m/e$  ratio (horizontal axis) of fragments. Usually the molecular ion ( $M^+$ ) is one of the last ions to be detected (as it is one of the heaviest particles) and is therefore located at the right end of the spectrum. Since most of the molecular ions fragment to gain stability, the  $M^+$  peak is sometimes small or may even be absent. Figure 4.2 shows a mass spectrum of octane. Note the low intensity of the  $M^+$  peak located at a  $m/e$  ratio of 114.



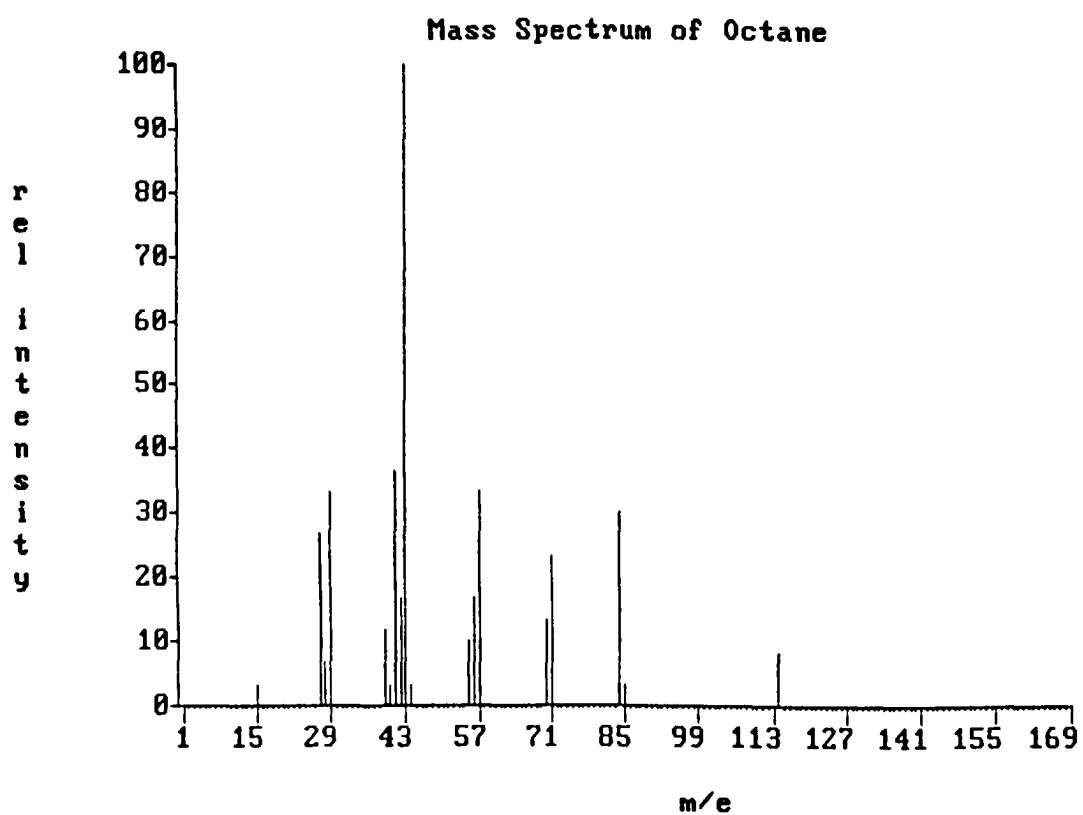
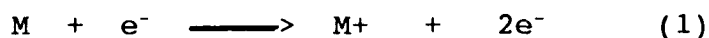


Figure 4.2 Mass Spectrum of Octane. (Adapted from NBS/Wiley Registry of Mass Spectral Data).

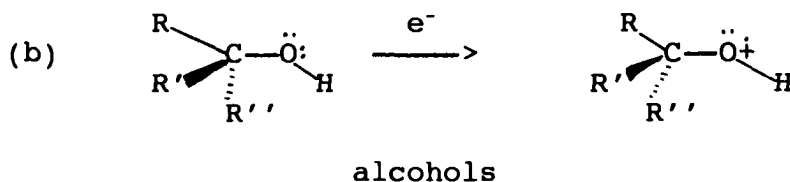
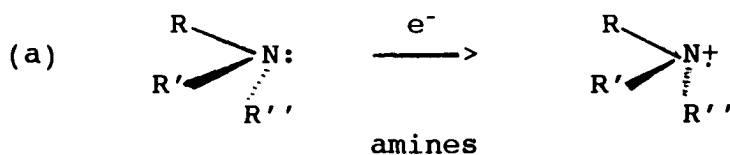
## MOLECULAR IONIZATION

Before we proceed any further, let us discuss the radical cation, referred to as the molecular ion. Why is this species called a radical cation? Simply stated, the ejection of an electron from a molecule (reaction 1) forms a positively charged ion, a cation. This cation contains an unpaired electron, thus it also is a radical.

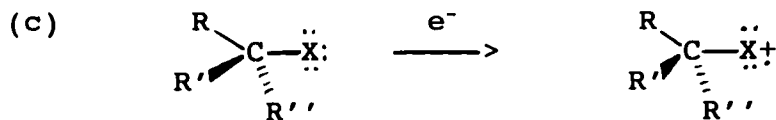


The beam of high-energy electrons ejects the electron that is most easily removed from the sample. For molecules with specific functional groups and structural features, certain trends help us to determine the part of the compound that will ionize. Below are examples illustrating the formation of the  $M^+$  ion of various functional groups.

- (1) Electrons are most easily removed from a nonbonded pair of electrons:

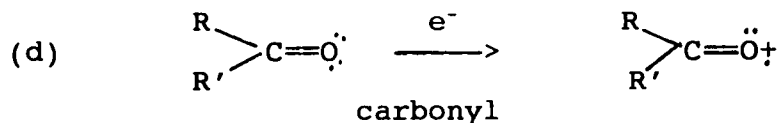


(ethers follow suit, losing an electron from oxygen)



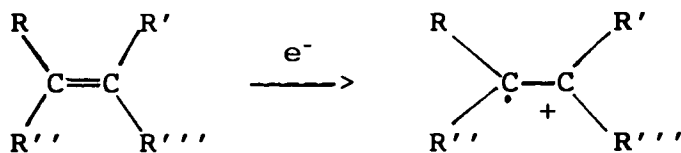
alkyl halides

(X = F, Cl, Br, I)



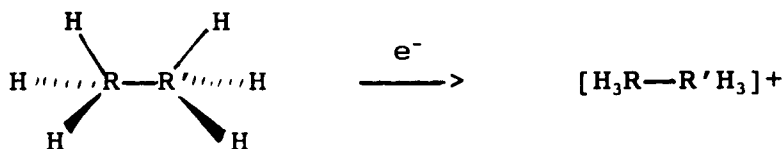
carbonyl

(2) Electrons removed from a pi bond:



alkenes

(3) Electrons emitted from a sigma bond:



alkyl groups

(The alkyl ion above is indicated in such a fashion because it is difficult to determine which sigma bond actually lost the electron.)

## FRAGMENTATION

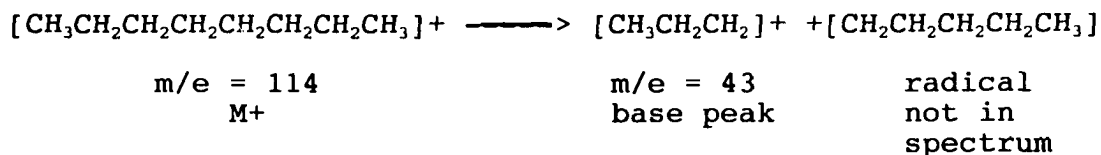
The newly charged species lacks the thermodynamic stability it once experienced as a neutral molecule. In order to regain some of its stability, the molecular ion splits into fragments as shown in reaction 2. Sometimes several fragmentations take place. Those cation fragments that

reach the ion collector are recorded on a mass spectrum (remember, the spectrometer is not able to detect particles that do not carry a positive charge).



#### Carbocation Formation of Alkyl Groups

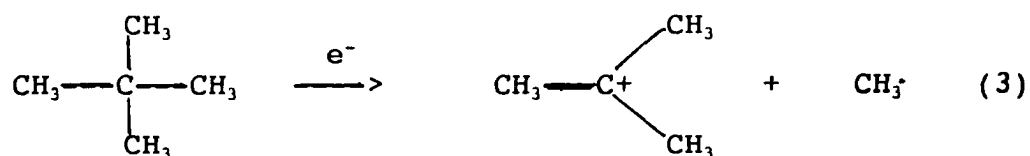
Molecular fragmentations are not random as one might think. In order to regain a semblance of stability, a molecule will form the most stable carbocations and radicals. Recall that the stability of both the carbocation and radical is  $3^\circ > 2^\circ > 1^\circ > \text{CH}_3$ . For example, let us consider the molecule octane, whose mass spectrum is pictured in Figure 4.2. Besides the  $M^+$  peak at 114, many other peaks are found in the spectrum. One significant piece of data is found at  $m/e$  of 43. Notice that the peak extends to the top of the spectrum. This peak is referred to as the base peak and has a relative intensity of one hundred percent. An intensity of one hundred percent is arbitrarily given to the fragment of the greatest abundance. After studying the structure of the compound,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ , it can be determined that the  $m/e$  43 fragment probably belongs to the carbocation,  $[\text{CH}_3\text{CH}_2\text{CH}_2]^+$ .



Other peaks found in this spectrum refer to less significant, but important, fragmentations:  $m/e = 85$ ,  $\text{CH}_3(\text{CH}_2)_5]^+$ ;

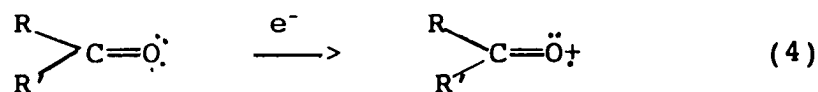
$m/e = 71$ ,  $[\text{CH}_3(\text{CH}_2)_4]^+$ ;  $m/e = 57$ ,  $[\text{CH}_3(\text{CH}_2)_3]^+$ ; and  $m/e = 29$ ,  $[\text{CH}_3\text{CH}_2]^+$ .

Sometimes the molecular ion fragmentation takes place so quickly that the  $M^+$  peak does not even appear in the spectrum. For example refer to Figure 4.3, the mass spectrum of neopentane. Notice that the  $M^+$  ion at 72  $m/e$  is absent, and the base peak has an  $m/e$  of 57. By studying the structure of the molecule, it can readily be seen that cleavage of a methyl group leaves a very stable tertiary carbocation, which has a mass of 57. (See reaction 3.)

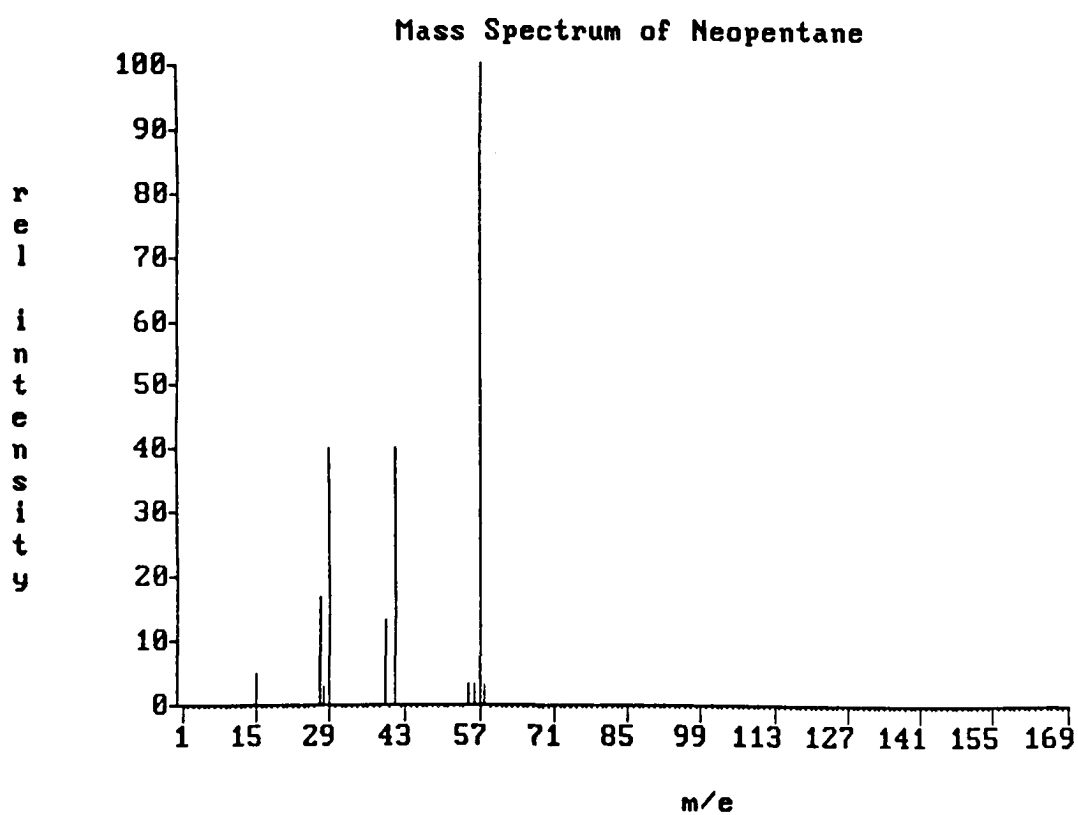


#### Acylium Ion Formation

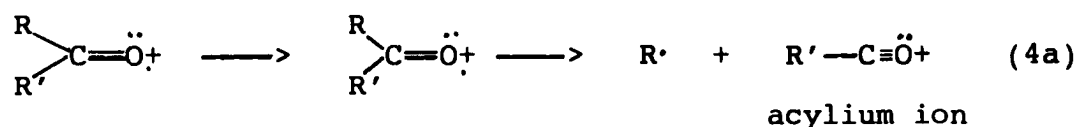
In addition to carbocation formation, any other factor that adds stability to a charged particle must be considered. For example, let us investigate possible fragmentation of a carbonyl compound (these include aldehydes, ketones, acids, esters and amides). Initially, an electron is ejected from the nonbonded pair of electrons located on the carbonyl oxygen (reaction 4).



As fragmentation continues, the following species (reactions 4a through 4f) are produced:



**Figure 4.3** Mass spectrum of Neopentane (adapted from NBS/Wiley Registry of Mass Spectral Data).



or:

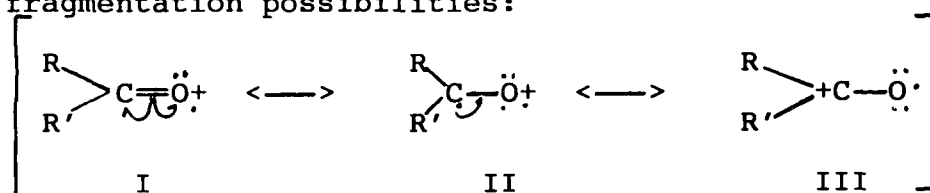


Notice that the ionization of the nonbonded pair of electrons on oxygen occurred as expected. Now oxygen, being very electronegative, is not very "happy" about carrying a positive charge. In order to compensate for this, the molecule fragments in such a fashion that oxygen regains its octet (note that the molecular ion left oxygen not only as a cation, but a radical as well) by forming a triple bond with the carbon atom. To make this bond, the carbon atom experienced homolytic cleavage (an electron moved with each fragment) resulting in the creation of a radical, R or R' and an exceptionally stable new intermediate, the acylium ion. Special attention should be paid to this example. Notice that homolytic cleavage is denoted by a single sided arrow, (reactions 4a and 4b) while heterolytic bond cleavage which involves the migration of two electrons is shown by an arrow that has two sides. (Reactions 4c - 4f illustrate homolytic bond cleavages.)

#### Resonance Stabilization

In determining the complete pattern of fragmentation experienced by a carbonyl compound, another factor must also

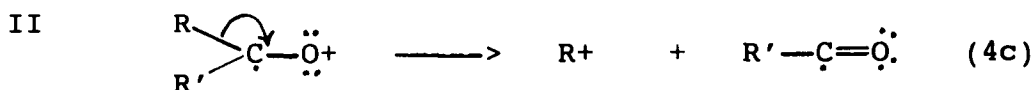
be considered. This factor is known as resonance stabilization, and involves the migration of electrons involved in a pi bond. The electrons involved in this bond are free to delocalize, and do so to enhance stability of a radical cation. The delocalization of electrons produces new fragmentation possibilities:



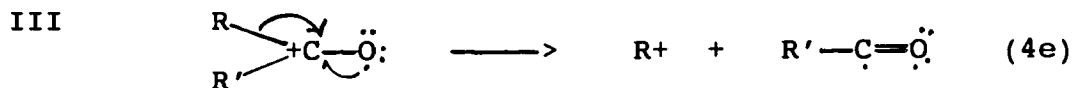
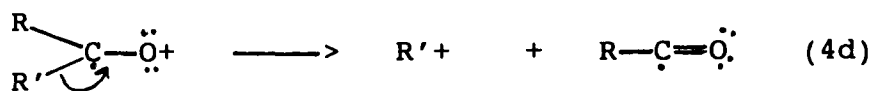
(The double headed arrows indicate resonance structures for reaction 4 are being considered.)

#### Resonance Structures

We have already looked at the splitting of resonance structure I (reactions 4a and 4b) on the previous page, therefore II and III need only be considered.



or:



or:





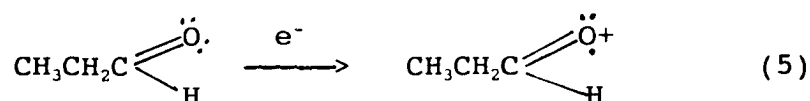
Fragmentations of structures II and III result from heterolytic bond cleavages. Notice that identical products are formed in each process.

=====

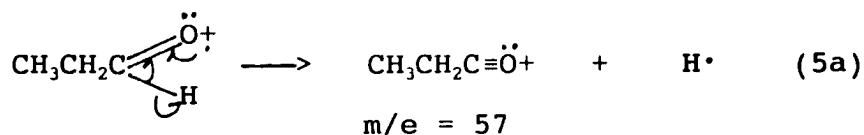
### Example 1

Consider the molecule propanal. Write out equations to show the formation of the molecular ion and all important fragmentations.

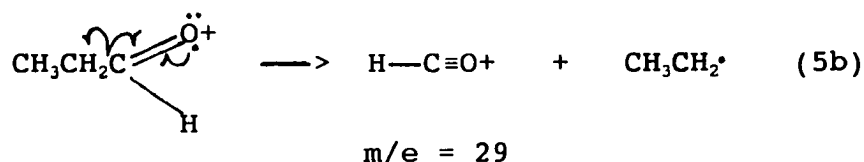
Propanal is not symmetric and therefore offers the possibility (not assurance) of more than one fragmentation.



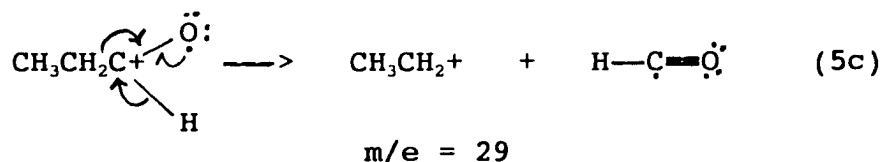
The molecular ion may experience homolytic cleavage either of the carbon-hydrogen bond of the carbonyl or of the carbon-carbon bond of the alkyl group. Either cleavage produces different cations both of which will be found in the spectrum.

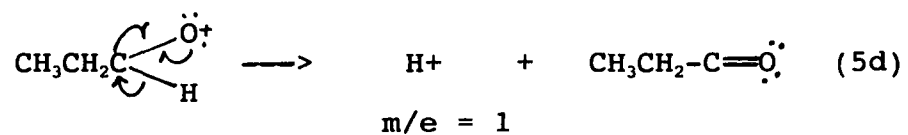


or:



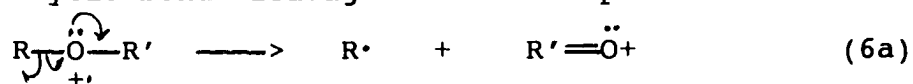
If on the other hand, the resonance-stabilized structure cleaves heterolytically, different ions will result:



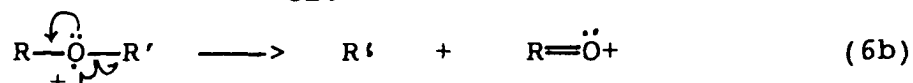


**Exercise 2:** Predict the  $m/e$  for fragments formed from 2-heptanone, butanal, and pentanoic acid. Write the appropriate equations associated with these fragmentations.

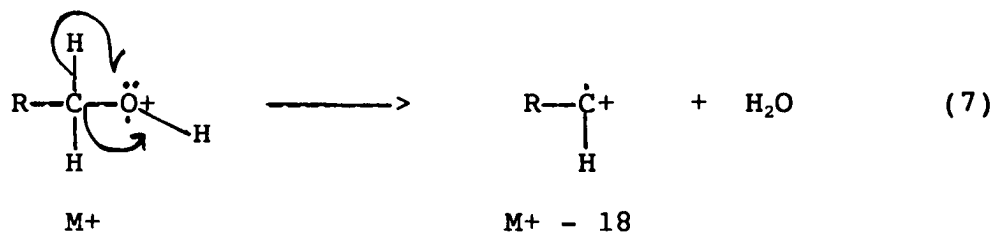
As previously mentioned, each functional group and carbon structure has characteristic splitting patterns that reflect the molecular ion's desire to attain stability. The principles outlined in the carbonyl fragmentation example may be employed as a guideline in determining the patterns of other compounds. For instance, alkenes that lose an electron from a pi bond undergo resonance stabilization to produce allylic carbocations. Those compounds that contain functional groups with nonbonded electrons (such as alcohols, ethers, amines, and alkyl halides) all experience similar homolytic bond cleavages. For example:



or:

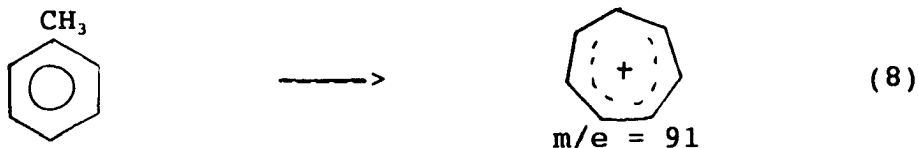


Alcohols cleave a hydrogen with the OH group eliminating a molecule of water (reaction 7). Many times an alcohol can be identified if a peak of significant size is present at  $M^+ - 18$  m/e.



Arenes (alkyl-substituted benzenes) form a stable tropylium ion by eliminating a hydrogen or methyl group. This ion is usually a predominate peak in the mass spectrum

of such a compound. Other substituted benzenes lose a substituent to form a phenyl cation.



Exercise 3: Predict the fragmentation pattern of 2-aminobutane.

#### ISOTOPIC PEAKS

Before we actually analyze an unknown spectrum, (we are almost there!) the presence of isotopes must be addressed. Recall that the atomic mass of an element as found on the periodic table, is a weighted average of the atomic masses of all the isotopes. For example, in all samples containing carbon, one percent of the carbon is carbon-13, ninety-nine percent is carbon-12. Approximately fifty percent of bromine exists as bromine-79, the other half, bromine-81. At this point in time, you are probably very tired, and wonder what difference this information makes in your life. In mass spectroscopy, the presence of isotopes can be very important in identification of a compound. Remember that the ion detector senses a particular ion, therefore it

"knows" if an ion contains carbon-12 or carbon-13 (or any other isotope for that matter). Any ion that contains carbon-13 will have a mass of one unit greater than the same ion of carbon-12. Since the abundance of carbon-13 is only one percent of the carbon-12, this peak will have a very small intensity (one percent of the carbon-12 peak). If an isotopic peak is found one unit after the  $M^+$  peak, it is referred to as the  $M+1$  peak. If it is located two units above the  $M^+$  ion, it is called the  $M+2$  peak. Compounds that contain bromine may have an  $M+2$  ion. Table IV lists some of the common isotopes associated with organic molecules. When reading this list, pay special attention to the percent abundance of the isotope. This information will help determine the intensity of the peak.

**Exercise 4:** From the information obtained from the mass spectrum given here, determine what halogen or halogens are present in the molecule. (Spectrum adapted from NBS/Wiley Registry of Mass Spectral Data.)

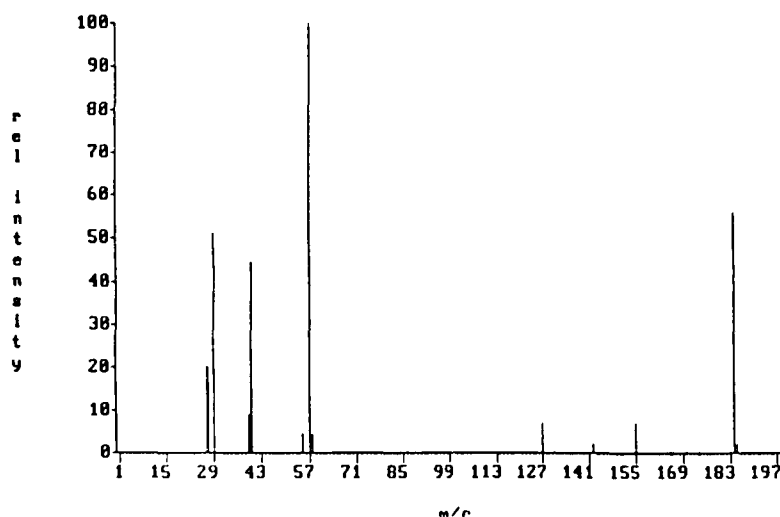
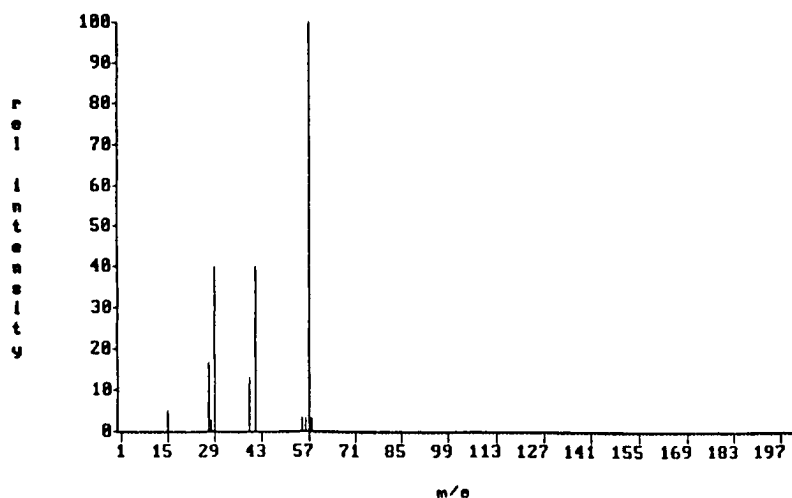
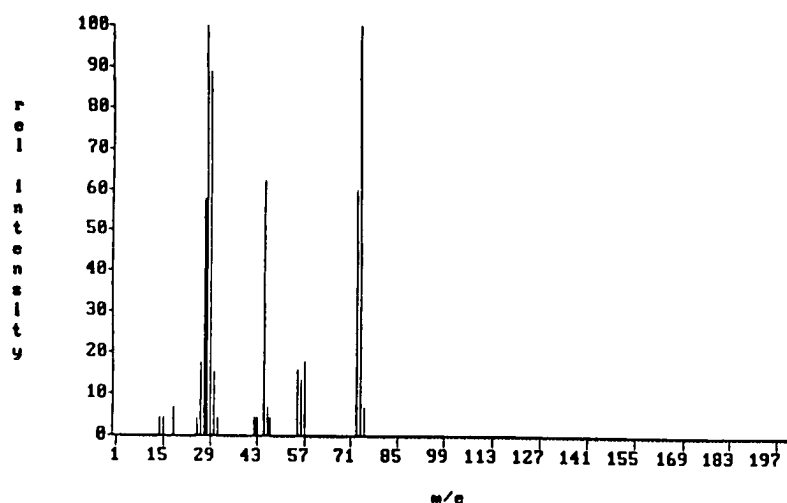


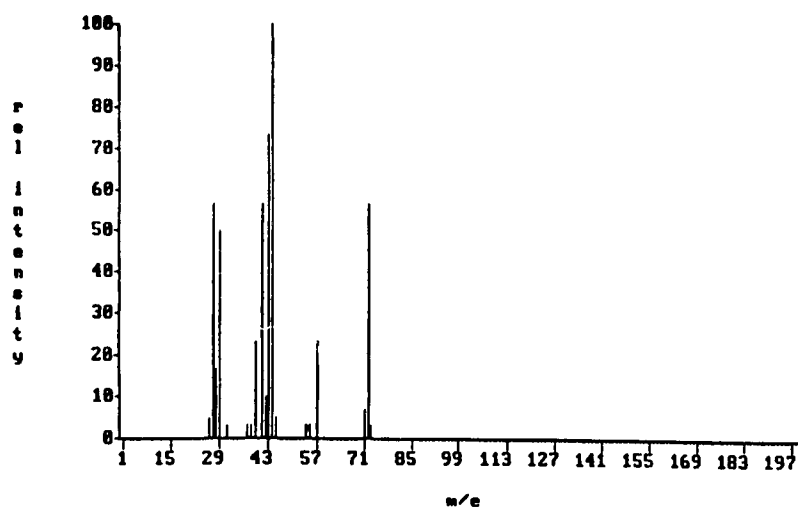
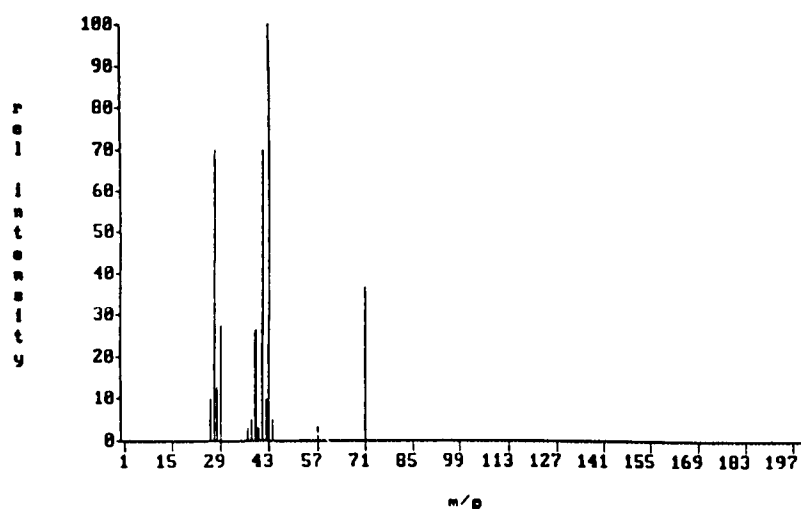
Table IV. Isotopic Masses of  
Various Elements

Element	Isotope	Mass	Abundance %
Carbon	C-12	12.000	98.89
	C-13	13.003	1.11
Nitrogen	N-14	14.003	99.63
	N-15	15.000	0.37
Oxygen	O-16	15.995	99.759
	O-17	16.999	0.037
	O-18	17.999	0.204
Fluorine	F-19	18.999	100.0
Chlorine	Cl-35	34.969	75.53
	Cl-37	36.966	24.47
Bromine	Br-79	78.918	50.54
	Br-81	80.916	49.46
Iodine	I-127	126.900	100.0

**Exercise 5:** Below are the mass spectra of an alcohol and an acid. Both compounds contain the same number of carbons. Determine the identity of each compound.  
(Spectrum adapted from NBS/Wiley Registry of Mass Spectral Data.)



Exercise 6: Here are the spectra of two isomeric aldehydes. Predict the structures of each.  
(Spectra adapted from NBS/Wiley Registry of Mass Spectral Data.)





**Exercise 7:** Let us tie it all together! Obtain the IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and mass spectra of the following compounds. Identify the structure of each.  
a) 273    b) 95    c) 68    d) 106

**Exercise 8:** Infrared spectra numbers 101, 102 and 274 have the same carbon structure. Identify their functional groups.

## **APPENDIX**

FILENAMES OF  $^{13}\text{C}$  NMR AND MASS SPEC SIMULATED SPECTRA

Propanoic acid	ms2	cmr2
Isopropyl alcohol	ms6	cmr6
acetophenone	ms27	cmr27
Bromobenzene	ms99	cmr99
1-Bromobutane	ms273	cmr273
Cyclohexane	ms101	cmr101
Cyclohexene	ms274	cmr274
1-Iodobutane	ms284	cmr284
Isopropyl benzene	ms29	cmr29
Isopropyl bromide	ms59	cmr59
Benzyl alcohol	ms95	cmr95
Cyclohexanol	ms102	cmr102
Phenol	ms318	cmr318
Triethyl amine	ms348	cmr348
Ethyl formate	ms68	cmr68
Methyl benzoate	ms119	cmr119
Methyl salicylate	ms82	cmr82
Benzaldehyde	ms93	cmr93
Cyclopentanone	ms105	cmr105
Heptanal	ms260	cmr260
2-Heptanone	ms106	cmr106
4-Heptanone	ms107	cmr107
3-Methyl-2-butanone	ms112	cmr112
Propanaldehyde	ms266	cmr266
t-Butyl alcohol	ms325	cmr325

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