CHEMISTRY 219 - HEFFERN

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This text was compiled on 11/03/2025

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Detailed Licensing

Detailed Licensing

Licensing

*A detailed breakdown of this resource's licensing can be found in **Back Matter/Detailed Licensing**.*

CHAPTER OVERVIEW

1: Introduction to Organic Spectroscopy

1.1: What is Spectroscopy and Why Does It Matter?
1.2: The Analytical Workflow
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1.1: What is Spectroscopy and Why Does It Matter?

What is spectroscopy?

Spectroscopy is the study of how matter interacts with energy. Within the context of organic chemistry, it is the language by which molecules communicate their structure, dynamics, and reactivities. Every bond vibration, electron transition, and nuclear spin leaves a measurable signature that can be translated into chemical insight. Every bond vibration, electron transition, and nuclear spin leaves a measurable signature that can be translated into chemical insight.

Organic spectroscopy encompasses a range of experimental methods that operate across the electromagnetic spectrum and beyond. EVery technique probes a different physical phenomenon, allowing us to probe different aspects of molecular behavior.

Spectroscopic Method/Analytical Method	Molecular Information	Typical Energy Range
Infrared/Raman	Bond vibrations, functional groups, hydrogen bonding	4000 - 400 cm^{-1}
Ultraviolet/Visible (UV-Vis)	Electronic transitions, conjugation, chromophores	200 - 800 nm
Nuclear Magnetic Resonance (NMR)	Connectivity, stereochemistry, dynamics, quantitative composition	Radiofrequency
X-ray/Solid-state/Thermal	Crystal packing, polymoprhism, melting and glass transitions	X-ray/thermal energy
Mass Spectrometry (MS)	Molecular mass, elemental composition, fragmentation patterns	Not EM-based (ionization/acceleration)
Computational Spectroscopy	Predicted vibrational and magnetic parameters, advanced methods allow for excited state calculations	Calculated

Why does spectroscopy matter to an organic chemist or chemical biologist?

Spectroscopy permeates every stage of modern organic chemistry:

1. ***Molecular Identification***: identifying and verifying the structure and purity of a synthesized compound

2. ***Reaction Monitoring:*** following chemical transformations over time

3. ***Mechanistic elucidation:*** detecting intermediates and transition states

4. ***Quantitative analysis:*** determining yields, concentrations, or impurity levels

5. ***Material and pharmaceutical development:*** assessing polymorphs, stability, and solid-state form.

In the academic research setting, spectroscopy bridges reaction design and mechanistic understanding. In industry, it is applied across a range of functions including process analytical technology, quality control, and regulatory compliance.

Practicing spectroscopy:

Spectroscopy requires hypothesis and logic. Successful practitioners approach data with some guiding principles:

- **Integration of techniques:** No single technique is complete.

- **Reasoning over recall:** While tables and databases are helpful, chemical intuition and mechanistic thinking are key to coherent interpretation.
- **Skepticism and verification:** Always question whether your data fits your hypothesis as unexpected signals or "blips" in the spectrum can often teach us the most about our systems and techniques.
- **Quantitative awareness:** Peak areas, intensities, and linewidths carry information about kinetics, equilibrium, and concentration
- **Logical Communication:** Spectroscopy is your evidence behind your scientific claims. Make sure your reasoning follows clear logic with acknowledgements of any gaps that requires presumptions or assumptions.

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1.2: The Analytical Workflow

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CHAPTER OVERVIEW

2: Mass Spectrometry

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2.1: Chapter Objectives and Preview of Mass Spectrometry

Learning Objectives

After completing this chapter, you should be able to

- fulfill all of the detailed objectives listed under each individual section.
- solve fragmentation problems which may require the interpretation of mass spectrometry.
- define, and use in context, the key terms introduced in this chapter.

Every time a reaction is run, the products must be identified. Every time a new molecule is found in nature, its structure must be determined. After reading this chapter and the following chapters, you will have an idea of what techniques are used to elucidate structures as well as how and when to use them. The powerful techniques used for structure determination are mass spectrometry (MS), ultraviolet spectroscopy (UV), infrared spectroscopy (IR), and nuclear magnetic spectroscopy (NMR). Want to know the size and formula of the molecule - use mass spectrometry. Does the molecule have a conjugated pi-system? Ultraviolet spectroscopy will help identify those. Need to determine the functional groups present, then turn to infrared spectroscopy. Looking to piece together the framework of the molecule, then look no further then nuclear magnetic spectroscopy.

In this chapter, the focus will be on mass spectrometry. In short, mass spectrometry is a way to determine the molecular weight of a molecule. In the process, it can give insight into the structure of the molecule by the fragment sizes formed. This chapter will begin to introduce the techniques used to determine the structure of organic molecules, starting with mass spectrometry.

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2.2: Instrumentation

Learning Objectives

- Understand how mass spectrometer works
- Learn about the different parts of a mass spectrometer

Principles of Mass Spectrometry

Mass spectrometry (MS) is a powerful characterization technique used for the identification of a wide variety of chemical compounds. At its minimum, MS is merely a tool for determining the molecular weight of the chemical species in a sample. However, with the high resolution obtainable from modern machines, it is possible to determine structural information from the fragments. There are libraries of mass spectra have been compiled which allow rapid identification of most known compounds, including proteins. MS relies on the ability of a compound to be ionized, so the limitations of this technique are when the compound of interest is not readily ionized or if it decomposes upon ionization.

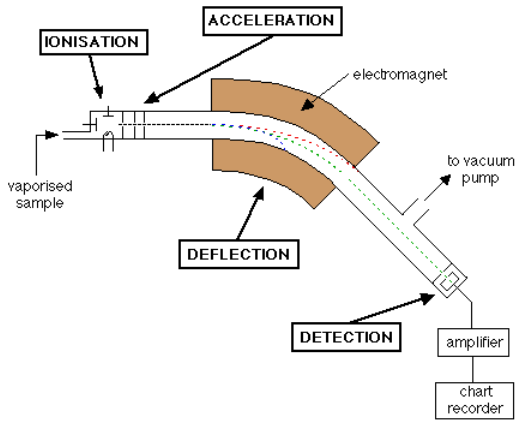
There are many mass spectrometers on the market, but they all have the same basic parts. There is an ionization source, where the molecules are broken into fragments. The mass analyzer is where the ions are separated into their mass/charge ratios before moving to the detector to be observed and counted. Collisions force the fragments to move forward. Consider if something is moving and you subject it to a sideways force, instead of moving in a straight line, it will move in a curve - deflected out of its original path by the sideways force. Suppose you had a cannonball traveling past you and you wanted to deflect it as it went by you. All you've got is a jet of water from a hose-pipe that you can squirt at it. Frankly, its not going to make a lot of difference! Because the cannonball is so heavy, it will hardly be deflected at all from its original course. But suppose instead, you tried to deflect a table tennis ball traveling at the same speed as the cannonball using the same jet of water. Because this ball is so light, you will get a huge deflection. The amount of deflection you will get for a given sideways force depends on the mass of the ball. If you knew the speed of the ball and the size of the force, you could calculate the mass of the ball if you knew what sort of curved path it was deflected through. The less the deflection, the heavier the ball. You can apply exactly the same principle to atomic sized particles.

Atoms can be deflected by magnetic fields - provided the atom is first turned into an ion. Electrically charged particles are affected by a magnetic field although electrically neutral ones aren't.

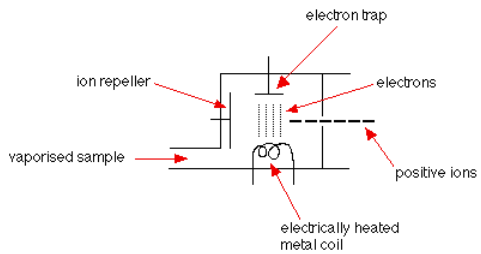
The sequence is :

- **Stage 1: Ionization**: The atom is ionised by knocking one or more electrons off to give a positive ion. This is true even for things which you would normally expect to form negative ions (chlorine, for example) or never form ions at all (argon, for example). Mass spectrometers always work with positive ions.
- **Stage 2: Acceleration:** The ions are accelerated so that they all have the same kinetic energy.
- **Stage 3: Deflection:** The ions are then deflected by a magnetic field according to their masses. The lighter they are, the more they are deflected. The amount of deflection also depends on the number of positive charges on the ion - in other words, on how many electrons were knocked off in the first stage. The more the ion is charged, the more it gets deflected.
- **Stage 4: Detection**: The beam of ions passing through the machine is detected electrically.

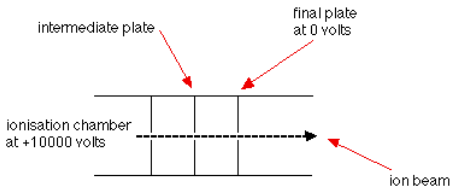
A full diagram of a mass spectrometer is below.



Let's break down the stages in more detail. In order for the ions to have free run of the machine, a vacuum is created in the ionization chamber to avoid air molecules getting in the way. The vaporized sample passes into the ionization chamber. The electrically heated metal coil gives off electrons which are attracted to the electron trap which is a positively charged plate.



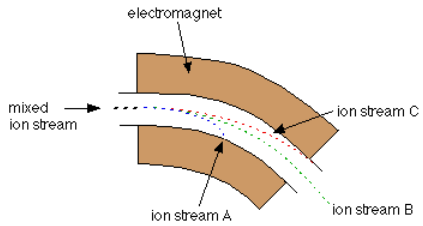
The particles in the sample (atoms or molecules) are therefore bombarded with a stream of electrons, and some of the collisions are energetic enough to knock one or more electrons out of the sample particles to make positive ions. Most of the positive ions formed will carry a charge of +1 because it is much more difficult to remove further electrons from an already positive ion. These positive ions are persuaded out into the rest of the machine by the ion repeller which is another metal plate carrying a slight positive charge. The positive ions are repelled away from the very positive ionization chamber and pass through three slits, the final one of which is at 0 volts. The middle slit carries some intermediate voltage. All the ions are accelerated into a finely focused beam.



Different ions are deflected by the magnetic field by different amounts. The amount of deflection depends on:

- the mass of the ion. Lighter ions are deflected more than heavier ones.
- the charge on the ion. Ions with 2 (or more) positive charges are deflected more than ones with only 1 positive charge.

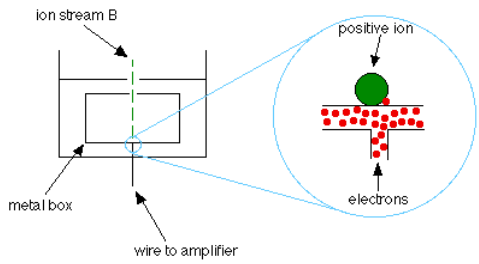
These two factors are combined into the mass/charge ratio. Mass/charge ratio is given the symbol m/z (or sometimes m/e). For example, if an ion had a mass of 28 and a charge of 1+, its mass/charge ratio would be 28. An ion with a mass of 56 and a charge of 2+ would also have a mass/charge ratio of 28. In the diagram below, ion stream A is the most deflected - it will contain ions with the smallest mass/charge ratio. Ion stream C is the least deflected - it contains ions with the greatest mass/charge ratio.



It makes it simpler to talk about this if we assume that the charge on all the ions is 1+. Most of the ions passing through the mass spectrometer will have a charge of 1+, so that the mass/charge ratio will be the same as the mass of the ion. Assuming 1+ ions, stream A has the lightest ions, stream B the next lightest and stream C the heaviest. Lighter ions are going to be more deflected than heavy ones.

Only ion stream B makes it right through the machine to the ion detector. The other ions collide with the walls where they will pick up electrons and be neutralized. Eventually, they get removed from the mass spectrometer by the vacuum pump.

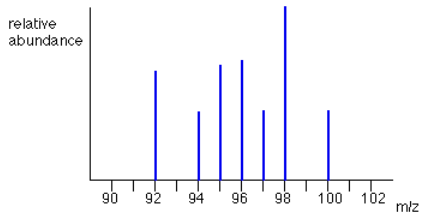
For those ions that make it to the detector, the ion hits the metal box and its charge is neutralized by an electron jumping from the metal on to the ion (diagram below). That leaves a space amongst the electrons in the metal, and the electrons in the wire shuffle along to fill it. A flow of electrons in the wire is detected as an electric current which can be amplified and recorded. The more ions arriving, the greater the current.



How might the other ions be detected - those in streams A and C which have been lost in the machine?

Remember that stream A was most deflected - it has the smallest value of m/z (the lightest ions if the charge is 1+). To bring them on to the detector, you would need to deflect them less - by using a smaller magnetic field (a smaller sideways force). To bring those with a larger m/z value (the heavier ions if the charge is +1) on to the detector you would have to deflect them more by using a larger magnetic field. If you vary the magnetic field, you can bring each ion stream in turn on to the detector to produce a current which is proportional to the number of ions arriving. The mass of each ion being detected is related to the size of the magnetic field used to bring it on to the detector. The machine can be calibrated to record current (which is a measure of the number of ions) against m/z directly. The mass is measured on the ^{12}C scale.

The output from the chart recorder is usually simplified into a "stick diagram". This shows the relative current produced by ions of varying mass/charge ratio. The stick diagram for molybdenum looks like this:



You may find diagrams in which the vertical axis is labeled as either "relative abundance" or "relative intensity". Whichever is used, it means the same thing. The vertical scale is related to the current received by the chart recorder - and so to the number of ions arriving at the detector: the greater the current, the more abundant the ion.

As you will see from the diagram, the commonest ion has a mass/charge ratio of 98. Other ions have mass/charge ratios of 92, 94, 95, 96, 97 and 100. That means that molybdenum consists of 7 different isotopes. Assuming that the ions all have a charge of 1+,

that means that the masses of the 7 isotopes on the carbon-12 scale are 92, 94, 95, 96, 97, 98 and 100.

Coupling Mass Spectrometry to Other Instruments

Mass spectrometry is a powerful tool for identification of compounds, and is frequently combined with separation techniques such as liquid or gas chromatography for rapid identification of the compounds within a mixture. Typically, liquid chromatography systems are paired with ESI-quadrupole mass spectrometers to take advantage of the solvated sample. GC-MS systems usually employ electron impact ionization and quadrupole or ion trap mass analyzers to take advantage of the gas-phase molecules and fragmentation libraries associated with EI for rapid identification.

Mass spectrometers are also often coupled in tandem to form MS-MS systems. Typically the first spectrometer utilizes a hard ionization technique to fragment the sample. The fragments are passed on to a second mass analyzer where they may be further fragmented and analyzed. This technique is particularly important for studying large, complex molecules such as proteins.

? Exercise 2.2.1

Does a mass spectrum show the results from just one molecule?

Answer

A mass spectrum does not show the results from one molecule, but from millions of molecules. Because it is displaying results for a population of molecules, more than one mass is shown

? Exercise 2.2.1

Where would you expect to find the molecular weight of the molecule?

Answer

A mass spectrum is a bar graph showing the weights of entire molecules as well as smaller pieces of molecules. The entire molecule must have the largest mass, the one farthest to the right, because if a molecule falls into pieces the pieces would be smaller than the whole.

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2.3: Ionization Techniques

Learning Objectives

- Learn about different ionization techniques
- Explain common ionization methods

A small amount of sample is injected into the mass spectrometer, which is vaporized upon entering. It is then bombarded with a stream of high-energy electrons. When the molecule of interest is struck by this high-energy electron beam, a valence electron is knocked out and the molecule becomes a positive ion. It has become ionized. There are a variety of ways for the instrument to ionize the molecule, which will be discussed here.

Electron Impact (EI)

In electron impact ionization, a vaporized sample is passed through a beam of electrons. The high energy (typically 70 eV) beam strips electrons from the sample molecules leaving a positively charged radical species. The molecular ion is typically unstable and undergoes decomposition or rearrangement to produce fragment ions. Because of this, electron impact is classified as a “hard” ionization technique. One of the main limitations of EI is that the sample must be volatile and thermally stable.

Chemical Ionization (CI)

In chemical ionization, the sample is introduced to a chamber filled with excess reagent gas (such as methane). The reagent gas is ionized by electrons, forming a plasma with species such as CH_5^+, which react with the sample to form the pseudomolecular ion $[M+H]^+$. Because CI does not involve radical reactions, fragmentation of the sample is generally much lower than that of EI. CI can also be operated in negative mode (to generate anions) by using different reagent gases. For example, a mixture of CH_4 and NO_2 will generate hydroxide ions, which can abstract protons to yield the $[M-H]^-$ species. A related technique, atmospheric pressure chemical ionization (APCI) delivers the sample as a neutral spray, which is then ionized by corona discharge, producing ions in a similar manner as described above. APCI is particularly suited for low molecular weight, nonpolar species that cannot be easily analyzed by other common techniques such as ESI.

Field Ionization/Desorption

Field ionization and desorption are two closely related techniques which use quantum tunneling of electrons to generate ions. Typically, a highly positive potential is applied to an electrode with a sharp point, resulting in a high potential gradient at the tip (see figure below). As the sample reaches this field, electron tunneling occurs to generate the cation, which is repelled into the mass analyzer. Field ionization utilizes gaseous samples whereas in field desorption the sample is adsorbed directly onto the electrode. Both of these techniques are *soft*, resulting in low energy ions which do not easily fragment.

Schematic of field ionization.

Electrospray Ionization (ESI)

Electrospray ionization mass spectrometry is a desorption ionization method. Desorption ionization methods can be performed on solid or liquid samples, and allows for the sample to be nonvolatile or thermally unstable. Electrospray ionization is a soft ionization technique that is typically used to determine the molecular weights of proteins, peptides, and other biological macromolecules. Soft ionization is a useful technique when considering biological molecules of large molecular mass, such as the aformetioned, because this process does not fragment the macromolecules into smaller charged particles, rather it turns the macromolecule being ionized into small droplets. These droplets will then be further desolvated into even smaller droplets, which creates molecules with attached protons. These protonated and desolvated molecular ions will then be passed through the mass analyzer to the detector, and the mass of the sample can be determined. As the droplets shrink due to evaporation, the charge density increases until a *coulombic explosion* occurs, producing daughter droplets that repeat the process until individualized sample ions are generated (see figure below). One of the limitations of is the requirement that the sample be soluble. ESI is best applied to charged, polar, or basic compounds.

Schematic of electrospray ionization.

Matrix Assisted Laser Desorption Ionization (MALDI)

Laser desorption ionization generates ions by ablation from a surface using a pulsed laser. This technique is greatly improved by the addition of a matrix co-crystallized with the sample. As the sample is irradiated, a plume of desorbed molecules is generated. It is believed that ionization occurs in this plume due to a variety of chemical and physical interactions between the sample and the matrix (see figure below). One of the major advantages of MALDI is that it produces singly charged ions almost exclusively and can be used to volatilize extremely high molecular weight species such as polymers and proteins. A related technique, desorption ionization on silicon (DIOS) also uses laser desorption, but the sample is immobilized on a porous silicon surface with no matrix. This allows the study of low molecular weight compounds which may be obscured by matrix peaks in conventional MALDI.

Schematic of matrix assisted laser desorption ionization.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

A plasma torch generated by electromagnetic induction is used to ionize samples. Because the effective temperature of the plasma is about 10,000 °C, samples are broken down to ions of their constituent elements. Thus, all chemical information is lost, and the technique is best suited for elemental analysis. ICP-MS is typically used for analysis of trace elements.

Fast Atom Bombardment (FAB) and Secondary Ion Mass Spectrometry (SIMS)

Both of these techniques involve sputtering a sample to generate individualized ions; FAB utilizes a stream of inert gas atoms (argon or xenon) whereas SIMS uses ions such as Cs^+. Ionization occurs by charge transfer between the ions and the sample or by protonation from the matrix material (Figure 2.3.4). Both solid and liquid samples may be analyzed. A unique aspect of these techniques for analysis of solids is the ability to do depth profiling because of the destructive nature of the ionization technique.

Schematic of fast atom bombardment ionization.

Choosing an Ionization Technique

Depending on the information desired from mass spectrometry analysis, different ionization techniques may be desired. For example, a hard ionization method such as electron impact may be used for a complex molecule in order to determine the component parts by fragmentation. On the other hand, a high molecular weight sample of polymer or protein may require an ionization method such as MALDI in order to be volatilized. Often, samples may be easily analyzed using multiple ionization methods, and the choice is simplified to choosing the most convenient method. For example, electrospray ionization may be easily coupled to liquid chromatography systems, as no additional sample preparation is required. Table 2.3.1 provides a quick guide to ionization techniques typically applied to various types of samples.

Table **2.3.1** Strengths of various ionization techniques

Information Desired	Ionization Technique
Elemental analysis	Inductively coupled plasma
Depth profiling	Fast atom bombardment/secondary ion mass spectroscopy
Chemical speciation/component analysis (fragmentation desired)	Electron impact
Molecular species identification of compounds soluble in common solvents	Electrospray ionization
Molecular species identification of hydrocarbon compounds	Field ionization
Molecular species identification of high molecular weight compounds	Matrix assisted laser desorption ionization
Molecular species identification of halogen containing compounds	Chemical ionization (negative mode)

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2.4: 2.4 Mass Analyzers

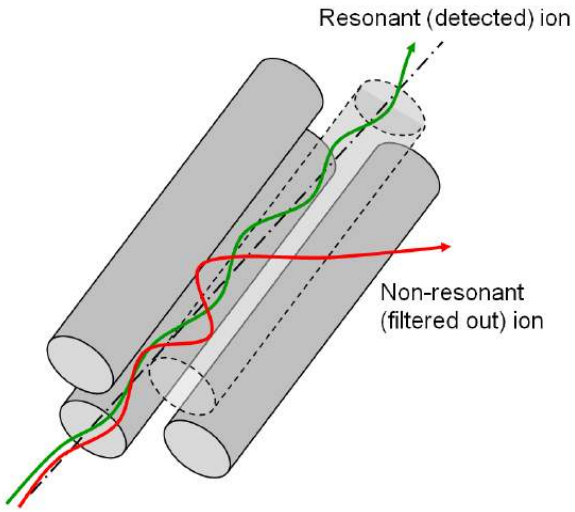
Learning Objectives

- Describe the function of common mass analyzers

Mass spectrometry is an analytic method that employs ionization and mass analysis of compounds to determine the mass, formula and structure of the compound being analyzed. A mass analyzer is the component of the mass spectrometer that takes ionized masses and separates them based on charge to mass ratios and outputs them to the detector where they are detected and later converted to a digital output. There are six general types of mass analyzers that can be used for the separation of ions in a mass spectrometry.

Quadrupole Mass Analyzer

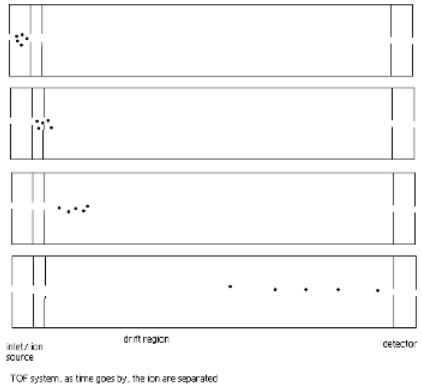
Ions are passed through four parallel rods which apply a varying voltage and radiofrequency (RF) potential (figure below). As the field changes, ions respond by undergoing complex trajectories. Depending on the applied voltage and RF frequencies, only ions of a certain *m*/*z* ratio will have stable trajectories and pass through the analyzer. If their course goes off too far they will hit the metal rods or the sides of the container and be absorbed. A great deal of selectivity to molecules charge to mass ratio can be obtained because the rods bias can be tuned to specific charge to mass ratios hitting the detector. Quadrupole analyzers are relatively inexpensive, but have limited resolution and low mass range.



A quadrupole

TOF (Time of Flight) Mass Analyzer

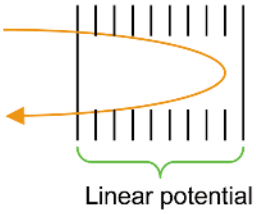
The amount of time required for an ion to travel a known distance is measured. A pulse of ions is accelerated through and electric analyzer such that they have identical kinetic energies. As a result, their velocity is directly dependent on their mass. Extremely high vacuum conditions are required to extend the mean free path of ions and avoid collisions. TOF mass analyzers are fastest, have unlimited mass ranges, and allow simultaneous detection of all species, but are best coupled with pulsed ionization sources. TOF Analyzers separate ions by time without the use of an electric or magnetic field. In a crude sense, TOF is similar to chromatography, except there is no stationary/ mobile phase, instead the separation is based on the kinetic energy and velocity of the ions.

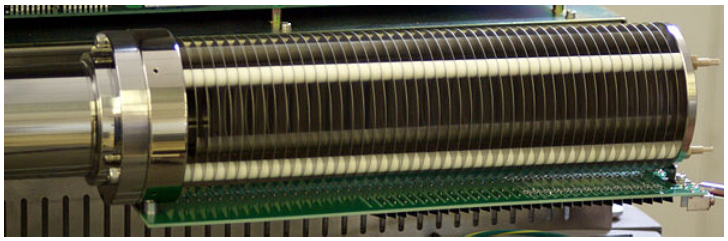


As time evolves, the ions (formed at the source) are separated.

Ions of the same charges have equal kinetic energies; kinetic energy of the ion in the flight tube is equal to the kinetic energy of the ion as it leaves the ion source.

Unfortunately, at higher masses, resolution is difficult because flight time is longer. Also at high masses, not all of the ions of the same m/z values reach their ideal TOF velocities. To fix this problem, often a reflectron is added to the analyzer. The reflectron consists of a series of ring electrodes of very high voltage placed at the end of the flight tube. When an ion travels into the reflectron, it is reflected in the opposite direction due to the high voltage. The reflectron increases resolution by narrowing the broadband range of flight times for a single m/z value. Faster ions travel further into the reflectrons, and slower ions travel less into the reflector. This way both slow and fast ions, of the same m/z value, reach the detector at the same time rather then at different times, narrowing the bandwidth for the output signal.



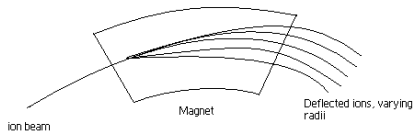


(top) A reflection. from Wikipedia. (bottom) A photo of a reflectron. An ion mirror attached to a flight tube of the reflectron. Voltages applied to a stack of metal plates create the electric field reflecting the ions back to the flight tube. In this particular design, gaps between the mirror electrodes are too large. This can lead to a distortion of the field inside the mirror caused by a proximity of metal surface of the enveloping vacuum tube. from Wikipedia.

Magnetic Sector Mass Analyzer

Similar to time of flight (TOF) analyzer mentioned earlier, in magnetic sector analyzers ions are accelerated through a flight tube, where the ions are separated by charge to mass ratios. The difference between magnetic sector and TOF is that a magnetic field is used to separate the ions. As moving charges enter a magnetic field, the charge is deflected to a circular motion of a unique radius

in a direction perpendicular to the applied magnetic field. Ions in the magnetic field experience two equal forces; force due to the magnetic field and centripetal force.



A magnetic sector separator.

Basically the ions of a certain m/z value will have a unique path radius which can be determined if both magnetic field magnitude, and voltage difference for region of acceleration are held constant. When similar ions pass through the magnetic field, they all will be deflected to the same degree and will all follow the same trajectory path. Those ions which are not selected by voltage and magnetic field values, will collide with either side of the flight tube wall or will not pass through the slit to the detector. Magnetic sector analyzers are used for mass focusing, they focus angular dispersions.

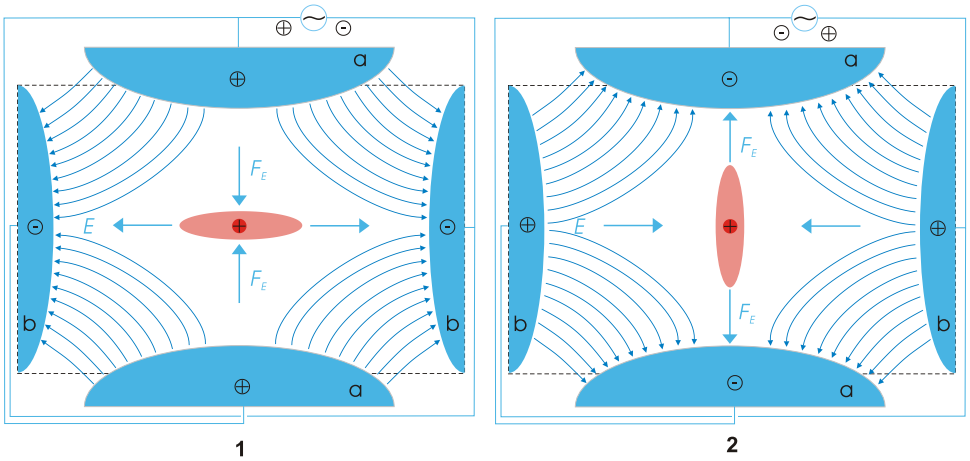
Electrostatic Sector Mass Analyzer

Again, this is similar to time of flight analyzer in that it separates the ions while in flight, but it separates using an electric field. Electrostatic sector analyzer consists of two curved plates of equal and opposite potential. As the ion travels through the electric field, it is deflected and the force on the ion due to the electric field is equal to the centripetal force on the ion. Here the ions of the same kinetic energy are focused, and ions of different kinetic energies are dispersed.

Electrostatic sector analyzers are energy focusers, where an ion beam is focused for energy. Electrostatic and magnetic sector analyzers when employed individually are single focusing instruments. However when both techniques are used together, it is called a double focusing instrument, because in this instrument both the energies and the angular dispersions are focused.

Quadrupole Ion Trap Mass Analyzers

This analyzer employs similar principles as the quadrupole analyzer mentioned above, it uses an electric field for the separation of the ions by mass to charge ratios. The analyzer is made with a ring electrode of a specific voltage and grounded end cap electrodes. The ions enter the area between the electrodes through one of the end caps. After entry, the electric field in the cavity due to the electrodes causes the ions of certain m/z values to orbit in the space. As the radio frequency voltage increases, heavier mass ion orbits become more stabilized and the light mass ions become less stabilized, causing them to collide with the wall, and eliminating the possibility of traveling to and being detected by the detector.



Scheme of a Quadrupole ion trap of classical setup with a particle of positive charge (dark red), surrounded by a cloud of similarly charged particles (light red). The electric field E (blue) is generated by a quadrupole of endcaps (a, positive) and a ring electrode (b). Picture 1 and 2 show two states during an AC cycle. (CC BY 2.5; Arian Kriesch Akriesch via Wikipedia).

Ion traps are uniquely suited for repeated cycles of mass spectrometry because of their ability to retain ions of desired *m*/*z* ratios. Selected fragments can be further fragmented by collision induced dissociation with helium gas. Ion traps are compact, relatively inexpensive, and can be adapted to many hybrid instruments.

Ion Cyclotron Resonance (ICR)

ICR is an ion trap that uses a magnetic field in order to trap ions into an orbit inside of it. In this analyzer there is no separation that occurs rather all the ions of a particular range are trapped inside, and an applied external electric field helps to generate a signal. As mentioned earlier, when a moving charge enters a magnetic field, it experiences a centripetal force making the ion orbit. Again the force on the ion due to the magnetic field is equal to the centripetal force on the ion.

Frequency of the orbit depends on the charge and mass of the ions, not the velocity. If the magnetic field is held constant, the charge to mass ratio of each ion can be determined by measuring the angular velocity. The relationship is that, at high angular velocity, there is low m/z value, and at low angular velocity, there is a high m/z value. Charges of opposite signs have the same angular velocity, the only difference is that they orbit in the opposite direction.

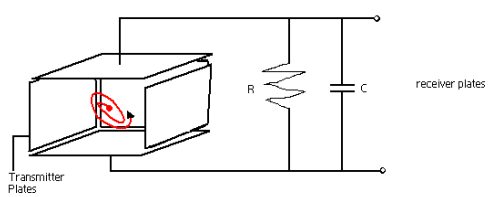


Figure 2.3.4.62.3.4.6: An ICR trap.

? Exercise 2.4.1

How are ions separated?

Answer

By accelerating them through magnetic and electric fields.

References

1. K. Downard, *Mass Spectrometry: A Foundation Course*, The Royal Society of Chemistry: UK 2004, Chapter 3
2. Skoog, Holler, Grouch, *Principles of Instrumental Analysis*, Thomson Brooks/Cole 2007, chapter 20
3. C. Herbert, R. Johnstone, *Mass Spectrometry Basics*, CRC Press LLC, 2003 chapter 25, 26, 39
4. E. De Hoffman, V. Stroobant, *Mass Spectrometry: Principles and Applications*, 2nd ed.;Wiley: England, 2001, chapter 2

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2.5: Applications of Mass Spectrometry

Learning Objectives

- Learn how mass spectrometry is applied in real-world applications
- Understand what mass spectrometry's use is in science

Mass spectrometry is applicable across diverse fields with specific applications including, but not limited to drug testing and discovery, food contamination detection, pesticide residue analysis, isotope ratio determination, protein identification, and carbon dating. One of the new ways that clinical mass spectrometry is being used is to quantitatively detect small amounts of proteins, biomarkers, or drug molecules, with very low concentrations. Some drugs have been given to patients in microdoses and with the ability to use small samples with low concentrations, it allows researchers to determine pharmacokinetic profiles of drugs that have been given. The reason for this is that it protects the patient from possible adverse effects of the drug while allowing scientists to determine what happens to the drug in the body. This will be especially helpful with pediatric patients. Below is a summary of a study detecting quinolones in animal food using mass spectrometry.

Application of LC/ESI-QTOF-MS in the Detection of Quinolones in Edible Animal Food

Quinolones are a family of common antibacterial veterinary medicine which can inhibit DNA-gyrase in bacterial cells. However, the residues of quinolone in edible animal products may be directly toxic or cause resistant pathogens in humans. Therefore, sensitive methods are required to monitor such residues possibly present in different animal-producing food, such as eggs, chicken, milk and fish. The molecular structures of eight quinolones, ciprofloxacin (CIP), anofloxacin methanesulphonate (DAN), enrofloxacin (ENR), difloxacin (DIF), sarafloxacin (SARA), oxolinic, acid (OXO), flumequine (FLU), ofloxacin (OFL), are shown in Figure **2.5.1**.

Figure **2.5.1** The molecular structure of eight quinolones. Adapted from M. M. Zheng, G. D. Ruan, and Y. Q. Feng, *J. Chromatogr. A*, 2009, **1216**, 7510.

LC-MS is a common detection approach in the field of food safety. But because of the complex matrix of the samples, it is always difficult to detect those target molecules of low concentration by using single quadrupole MS. The following gives an example of the application of LC/ESI-QTOF-MS.

Using a quaternary pump system, a Q-TOF-MS system, a C18 column (250 mm × 2.0 mm I.D., 5 µm) with a flow rate of 0.2 mL/min, and a mixture of solvents as the mobile phase comprising of 0.3% formic acid solution and acetonitrile. The gradient phofile for mobile phase is shown in Table **2.5.1**. Since at acidic pH condition, the quinolones carried a positive charge, all mass spectra were acquired in the positive ion mode and summarizing 30,000 single spectra in the mass range of 100-500 Da.

Table **2.5.1** The gradient phofile for mobile phase

Time (min)	Volume % of Formic Acid Solution	Volume % of Acetonitrile
0	80	20
12	65	35
15	20	80
20	15	85
30	15	85
30.01	80	20

The optimal ionization source working parameters were as follows: capillary voltage 4.5 kV; ion energy of quadrupole 5 eV/z; dry temperature 200 °C; nebulizer 1.2 bar; dry gas 6.0 L/min. During the experiments, HCO_2Na (62 Da) was used to externally calibrate the instrument. Because of the high mass accuracy of the TOF mass spectrometer, it can extremely reduce the matrix

effects. Three different chromatographs are shown in Figure 2.5.2. The top one is the total ion chromatograph at the window range of 400 Da. It's impossible to distinguish the target molecules in this chromatograph. The middle one is at one Da resolution, which is the resolution of single quadrupole mass spectrometer. In this chromatograph, some of the molecules can be identified. But noise intensity is still very high and there are several peaks of impurities with similar mass-to-charge ratios in the chromatograph. The bottom one is at 0.01 Da resolution. It clearly shows the peaks of eight quinolones with very high signal to noise ratio. In other words, due to the fast acquisition rates and high mass accuracy, LC/TOF-MS can significantly reduce the matrix effects.

Figure 2.5.2 Different chromatographs of 4 ng/g eight quinolones spiked in fish samples at different mass resolutions. Peaks: 1 = OFL; 2 = CIP; 3 =DAN; 4 = ENR; 5 = SARA; 6 = DIF; 7 =OXO; 8 = FLU. Adapted from M. M. Zheng, G. D. Ruan, and Y. Q. Feng, *J. Chromatogr. A*, 2009, **1216**, 7510.

The quadrupole MS can be used to further confirm the target molecules. Figure 2.5.3 shows the chromatograms obtained in the confirmation of CIP (17.1 ng/g) in a positive milk sample and ENR (7.5 ng/g) in a positive fish sample. The chromatographs of parent ions are shown on the left side. On the right side, they are the characteristic daughter ion mass spectra of CIP and ENR.

Figure 2.5.3 Chromatograms obtained in the confirmation of CIP (17.1 ng/g) in positive milk sample and ENR (7.5 ng/g) in positive fish sample. Adapted from M. M. Zheng, G. D. Ruan, and Y. Q. Feng, *J. Chromatogr. A*, 2009, **1216**, 7510.

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- **4.10: ESI-QTOF-MS Coupled to HPLC and its Application for Food Safety** by Pavan M. V. Raja & Andrew R. Barron is licensed CC BY 4.0. Original source: http://cnx.org/contents/ba27839d-5042-4a40-afcf-c0e6e39fb45425.2.

2.6: Interpretation of Mass Spectra

Learning Objectives

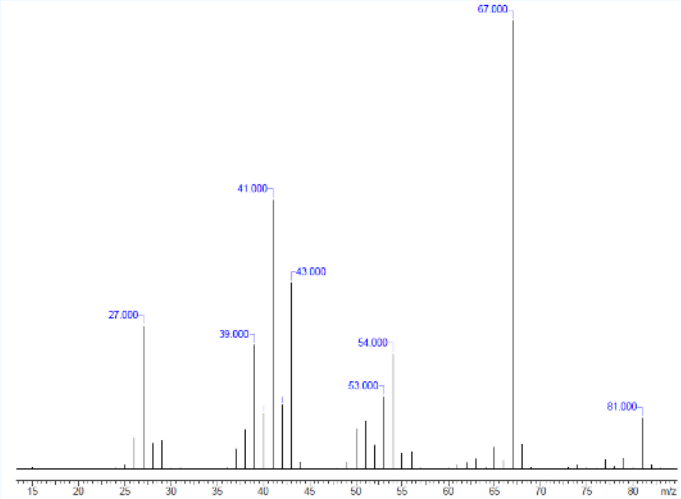
- understand how to determine molecular weight.
- interpret mass spectra.

The first piece of information mass spectra can get is the molecular weight of a molecule. In a mass spectrum of a compound, the x axis is the m/z values and the y axis represents the intensity or relative abundance of a given m/z. In addition, there are a number of other lines at a variety of values of m/z; these correspond to the masses of smaller pieces of those that fall apart during the experiment as well as the unfragmented cation. For these smaller pieces, the more stable an ion is, the more likely it is to form. The more of a particular sort of ion that's formed, the higher its peak height will be. The tallest peak is called the base peak and is assigned 100% intensity. The peak that represents the unfragmented cation radical is called the parent peak or molecular ion (M^+). The parent peak is how you determine the molecular weight of a molecule. Often, the molecular ion peak is not the same as the base peak. Usually, whole numbers are used for the molecular weights in mass spectrometry. The atomic masses in the periodic table are average masses including different isotopes and because mass spectrometry examines individual molecules, whole numbers are used. Complications can arise with determining the molecular ion peak because it is not always abundant, especially when molecules fragment easily. This is where the soft ionization techniques come into play.

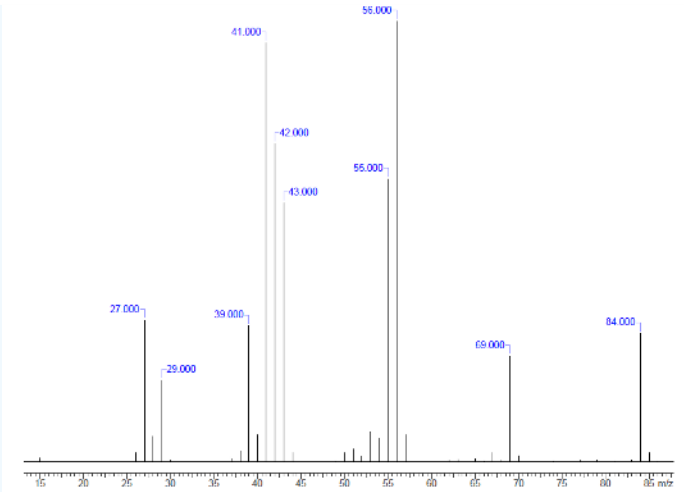
Exercise 2.6.1

Which mass spectrum corresponds to hexane, 1-hexene, and 1-hexyne.

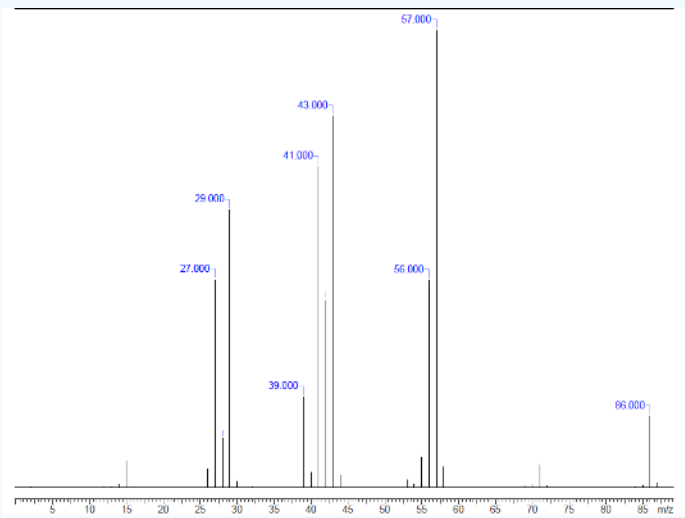
(A)



(B)



(C)



Answer

Each molecule has a different molecular weight. Hexane MW = 86; 1-hexene MW = 84, and 1-hexyne MW = 82

To determine which molecule belongs to which look for the molecular ion peak, which will indicate what the molecular weight is of each molecule.

(A) 1-hexyne

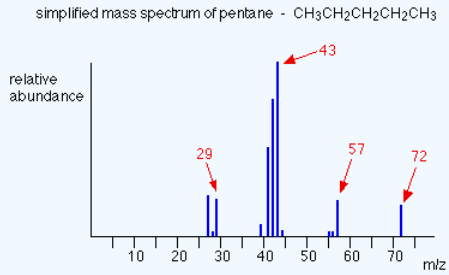
(B) 1-hexene

(C) hexane

Another piece to note is that if you look closely at the mass spectrum of C in exercise 1 above, you will notice a little peak at m/z = 87. This is referred to as the M+1 peak (one greater than the molecular ion), and it arises because of ^{13}C. This compound is referred to as an isotopomer; that means the same compound with a different isotope. The chance that a molecule in a sample contains a ^{13}C atom is related to the number of carbons present. If there is just one carbon atom in the molecule, it has a 1% chance of being a ^{13}C. That means the M+1 peak would be only 1/100th as tall as M+, the peak for the molecular ion.

Example 2.6.1

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



What causes the line at m/z = 57?

Solution

How many carbon atoms are there in this ion? There can't be 5 because 5 x 12 = 60. What about 4? 4 x 12 = 48. That leaves 9 to make up a total of 57. How about $C_4H_9^+$ then?

$C_4H_9^+$ would be $[CH_3CH_2CH_2CH_2]^+$, and this would be produced by the following fragmentation:

$$[CH_3CH_2CH_2CH_2CH_3]^{\ddagger} \longrightarrow [CH_3CH_2CH_2CH_2]^+ + \bullet CH_3$$

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

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

$$[CH_3CH_2CH_2CH_2CH_3]^{\ddagger} \longrightarrow [CH_3CH_2CH_2]^+ + \bullet CH_2CH_3$$

The line at m/z = 29 is typical of an ethyl ion, $[CH_3CH_2]^+$:

$$[CH_3CH_2CH_2CH_2CH_3]^{\ddagger} \longrightarrow [CH_3CH_2]^+ + \bullet CH_2CH_2CH_3$$

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

What happens when the molecular weight is the same for the compounds? The fragmentation pattern should be different for the molecules. While knowing the molecular weight is invaluable, mass spectrometry can lend a hand in structure determination. The mass spectrum of a particular compound acts as a "fingerprint," since each compound will fragment in its own unique way (just like a person's fingerprint). In the next section, the fragmentation of functional groups will be discussed.

Exercise 2.6.2

The male sex hormone testosterone contains C, H, and O. It has a mass of 288.2089 amu as determined by mass spectrometry. What is the likely molecular formula for testoterone?

Answer

$C_{19}H_{28}O_2$

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2.7: 2.7 Mass Spectrometry of Some Common Functional Groups

Learning Objectives

- Learn common fragmentation patterns for functional groups
- Interpret the fragmentations of mass spectra

Some fragment ions are very common in mass spectrometry. These ions are seen frequently for either of two reasons:

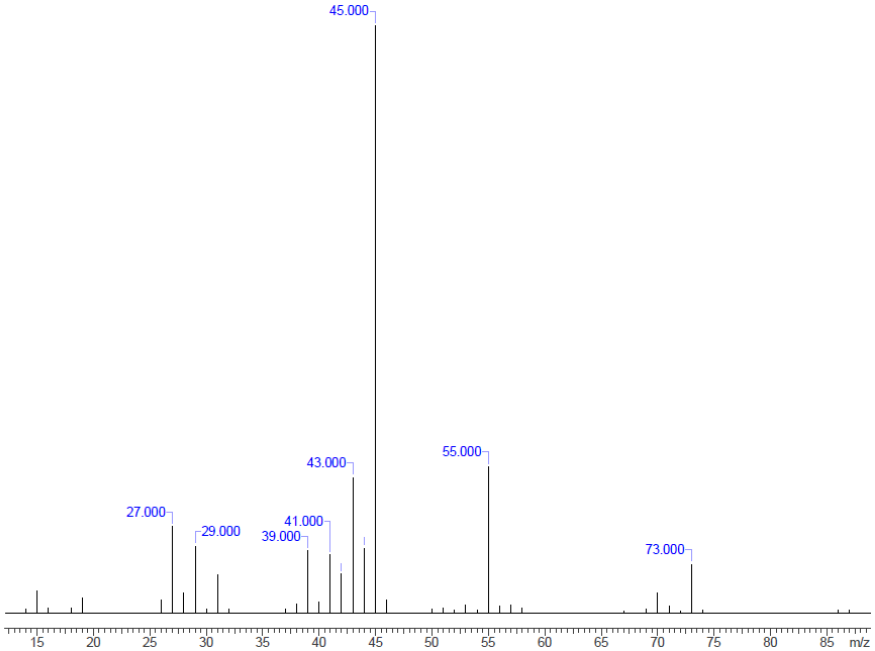
- there is not a pathway available to break the ion down.
- the ion is relatively stable, so it forms easily.

There are a number of ions commonly seen in mass spectrometry that tell you a little bit about the structure. Just like with anions, there are a couple of common factors influence cation stability:

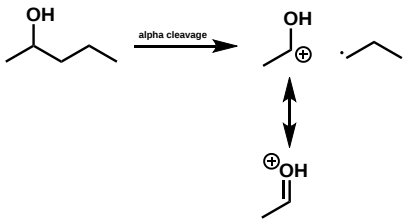
- Electronegativity plays a role. More electronegative atoms are less likely to be cations.
- Polarizability also plays a role. More polarizable atoms are more likely to be cations.
- Delocalization stabilizes a cation by spreading out the charge onto two or more different atoms. Resonance is a common way to delocalize charge.

Alcohols

When alcohols are subjected to ionization, two fragmentation pathways can occur - alpha cleavage and dehydration. Alpha cleavage occurs by a C-C bond nearest the hydroxyl group being broken. This yields a neutral radical plus a resonance stabilized, oxygen-containing cation. As an example let's look at the mass spectrum of 2-pentanol below.



The parent peak is m/z = 88. The base peak is m/z = 45, which correlates to a fragmentation that occurs with an alpha cleavage. This fragment is the piece due to the resonance stabilized oxygen-containing cation, which is shown in the pathway below.

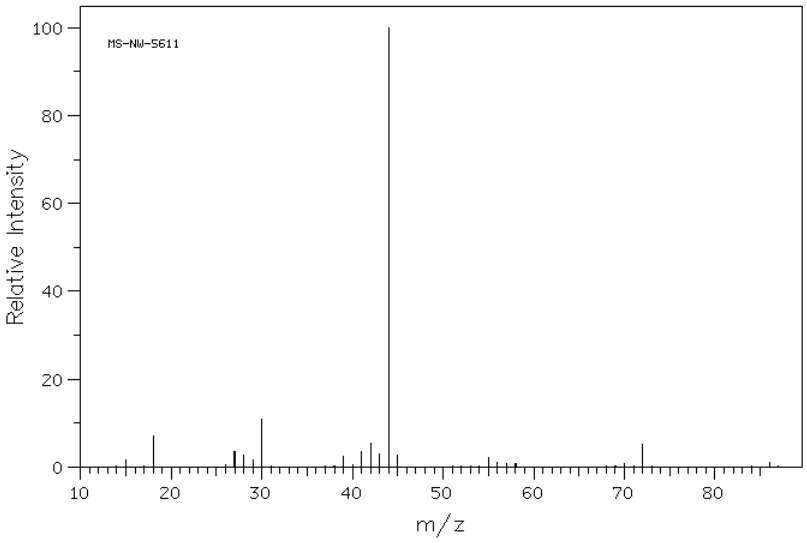


In dehydration, water is eliminated. This leaves an alkene radical cation that is 18 units less than the molecular ion peak. Using our example of 2-pentanol, this would lead to a peak at m/z = 70 and there is.

Amines

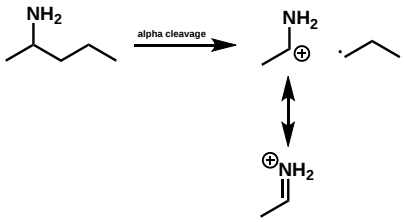
A general principle when nitrogen is part of a molecule is that if there is an odd number of nitrogens, then the molecular weight will be an odd number. This is also known as the nitrogen rule and stems from the fact that nitrogen is a trivalent atom. It also goes that if the molecule contains an even molecular weight, then there will be zero or two nitrogen atoms.

As with alcohols, primary amines undergo a characteristic alpha cleavage. As an example, the mass spectrum of 2-aminopentane is below.



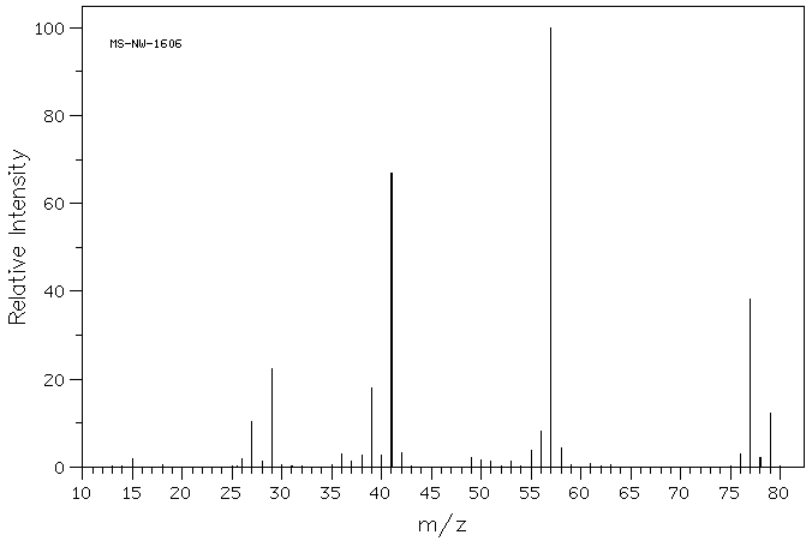
Source: SDBSWeb : https://sdbs.db.aist.go.jp/sdbs/cgi-..._frame_top.cgi (National Institute of Advanced Industrial Science and Technology of Japan) [Accessed August 16, 2022]

The parent peak is very small, but is at m/z = 87. The base peak (m/z = 44) is due to an alpha cleavage and forming a fragment of a resonance stabilized nitrogen-containing cation (see pathway below).



Halides

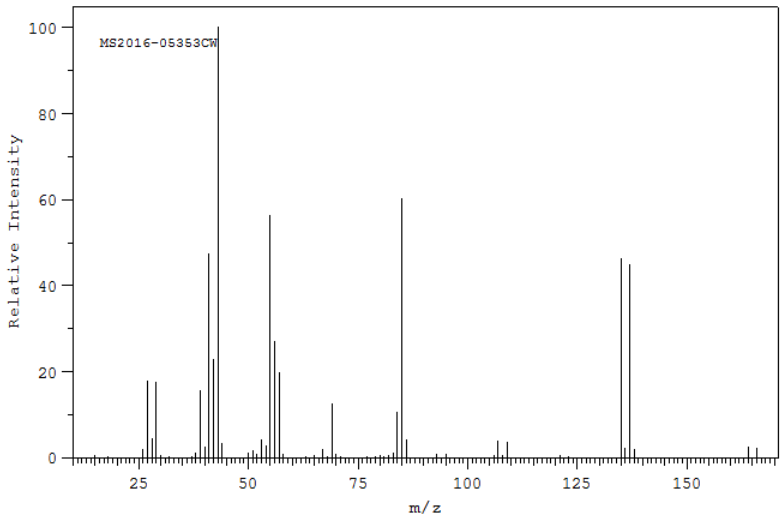
Halides have isotopes that give distinct appearances in a mass spectrum. Chlorine has two isotopes ^{35}C and ^{37}C with a 3:1 ratio (roughly). This ratio shows up in the mass spectrum for a chlorine-containing compound. Below is the mass spectrum of 2-chloro-2-methylpropane.



Source: SDBSWeb : https://sdbs.db.aist.go.jp/sdbs/cgi-..._frame_top.cgi (National Institute of Advanced Industrial Science and Technology of Japan) [Accessed August 16, 2022]

Looking at the molecular ion peak (m/z = 77 peak), there is another peak at m/z= 79. The peak at 79 is called the M + 2 peak. The ratio of the relative abundance/intensity of the M:M + 2 is about 3:1, which reflecting the isotopic abundance of ^{35}C:^{37}C.

With bromine, the isotopic distribution of ^{79}Br and ^{81}Br is more like 50:50. Again, the ratio of the relative abundance/intensity of the M:M + 2 is about 50:50. In the example below, the mass spectrum of 1-bromohexane is shown.



Source: SDBSWeb : https://sdbs.db.aist.go.jp/sdbs/cgi-..._frame_top.cgi (National Institute of Advanced Industrial Science and Technology of Japan) [Accessed August 16, 2022]

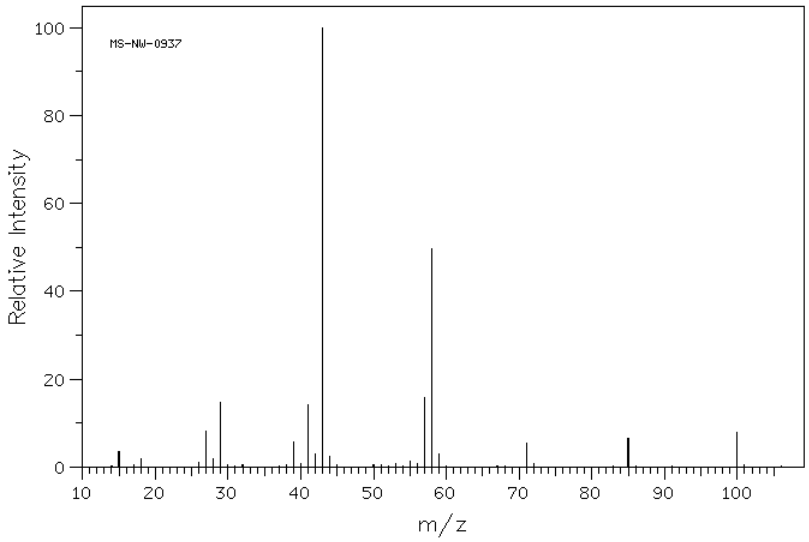
The roughly 50:50 distribution can be seen in the parent peak and M + 2 (m/z = 164 and 165). It is again showing up at the peaks m/z = 135 and 137. The two peaks in each are nearly the same height. In the fragments that contain the bromine, this ratio will be reflected.

Carbonyl Compounds

The McLafferty rearrangement is a common cleavage that occurs in carbonyl compounds that have a hydrogen three atoms away from carbonyl group. This rearragnement yields a carbonyl-containing radical cation via β-cleavage to produce an enol cation and

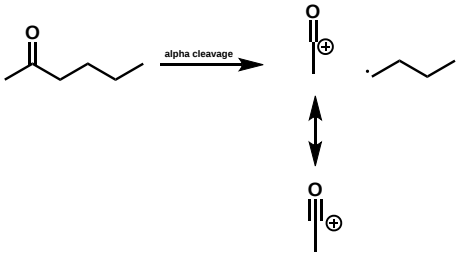
an alkene. This fragmentation is shown below.

In the mass spectrum of 2-hexanone (below), the m/z peak = 59 represents the enol cation that would form from the McLafferty rearrangement.



Source: SDBSWeb : https://sdbs.db.aist.go.jp/sdbs/cgi-..._frame_top.cgi (National Institute of Advanced Industrial Science and Technology of Japan) [Accessed August 16, 2022]

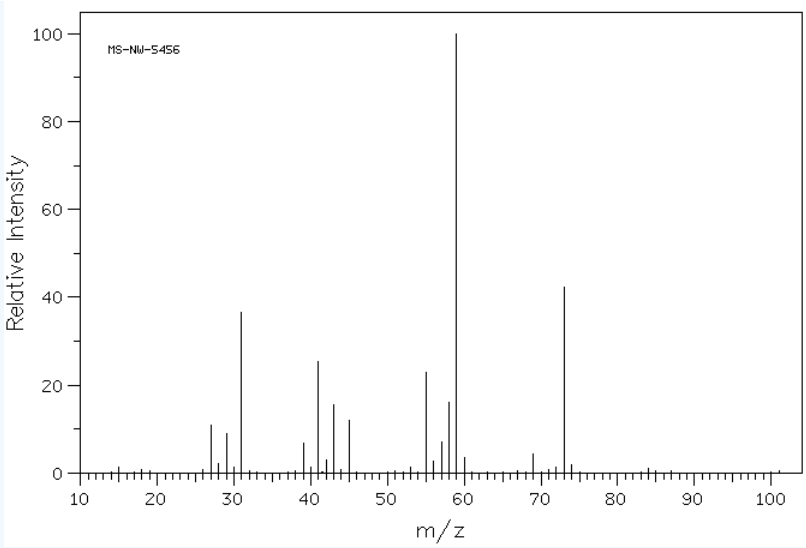
The carbonyl compounds can also undergo alpha cleavage as was seen with the alcohol and primary amines. The alpha cleavage occurs between the carbonyl carbon and the neighboring carbon yielding an acylium ion and a neutral radical (see below).



The acylium ion has an m/z =43. This fragment shows up at m/z = 43. This cleavage can also be seen as the loss of the acylium ion from the parent ion (100-43 = 57). There is a m/z peak at 57 to represent this loss.

Example 2.7.1

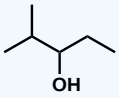
The mass spectrum of 2-methyl-3-penatonol is shown below.



Source: SDBSWeb : https://sdbs.db.aist.go.jp/sdbs/cgi-...p;sdbsno=13488 (National Institute of Advanced Industrial Science and Technology of Japan) [Accessed August 16, 2022]

What fragments can you identify?

Solution

First, you want to look up the draw or look up the structure. 2-methyl-3-pentanol: 

Next, calculate the mass of the molecular ion and identify the functional groups in the molecule. M+1 = 102 and there is an alcohol present.

Then write down the fragmentation patterns you may expect and calculate the masses for those peaks and compare it to the mass spectrum. With an alcohol, there are two pathways for fragmentation - alpha cleavage and dehydration. From the alpha cleavage, one would expect two peaks m/z = 73 and 59. From dehydration, one would expect an m/z of 84. The dehydration fragment peak is not observed, but both the fragments from the alpha cleavage are observed.

? Exercise 2.7.1

What are the masses of the charged fragments produced in the following cleavage pathways?

a. alpha cleavage of triethylamine

b. McLafferty rearrangment of 4-methyl-2-pentanone

Answer

a. m/z = 86

b. m/z = 58

? Exercise 2.7.2

Nicotine is a diamino compound with two rings and a molecular ion peak of 162.1157. Remembering the nitrogen rule, give the molecular formula for nicotine and calculate the number of double bonds.

Answer

$C_{10}H_{14}N_2$

2.7: 2.7 Mass Spectrometry of Some Common Functional Groups is shared under a not declared license and was authored, remixed, and/or curated by Lauren Reutenauer.

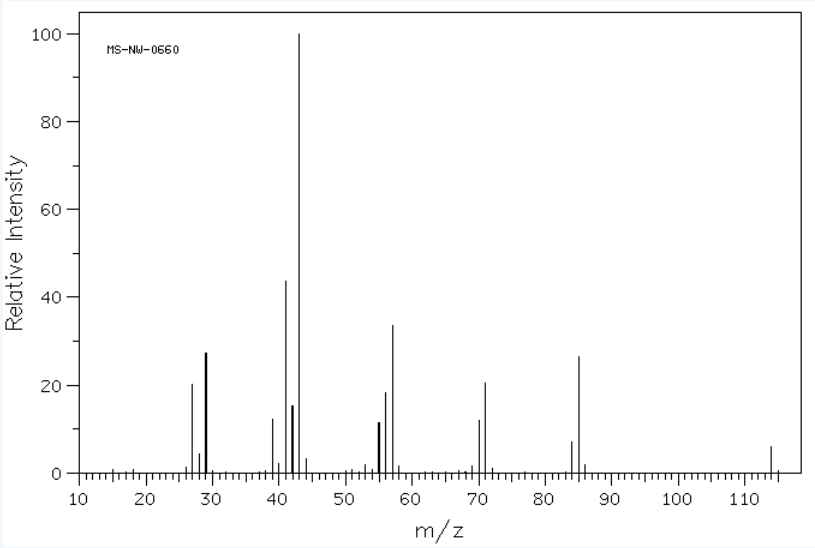
2.8: Mass Spectrometry Problems

Learning Objectives

- Interpret mass spectra

Exercise 2.8.1

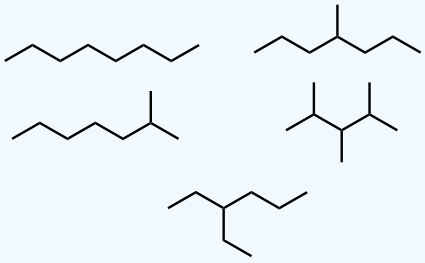
The following figure shows the mass spectrum of a saturated hydrocarbon (containing only carbon and hydrogen with only single bonds between carbons, not double bonds).

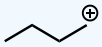


1. Draw five different structures that would have the molecular weight of this compound.
2. Choose three smaller m/z values from the spectrum and draw one structure for each of them. Note that these fragments will not have complete Lewis structures.

Answer

1. Molecular Weight = 114, which cooresponds to a C_8H_{18} hydrocarbon. There is the possibility of 18 isomers, but here are a few isomers:



2. m/z = 57; $[CH_3CH_2CH_2CH_2]^+$ 

m/z = 43; $[CH_3CH_2CH_2]^+$

m/z = 29; $[CH_3CH_2]^+$

Exercise 2.8.2

Caffeine has a mass of 194.19 amu, determined by mass spectrometry, and contains C, N, H, O. What is a molecular formula for this molecule?

Answer

$C_8H_{10}N_4O_2$

C = 12 × 8 = 96

N = 14 × 4 = 56

H = 1 × 10 = 10

O = 2 × 16 = 32

96+56+10+32 = 194 g/mol

Exercise 2.8.3

The following are the spectra for 2-methyl-2-hexene and 2-heptene, which spectra belongs to the correct molecule. Explain.

A:

B:

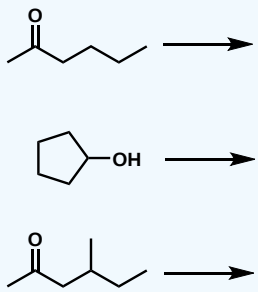
Source: SDBSWeb : http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, 2 December 2016)

Answer

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

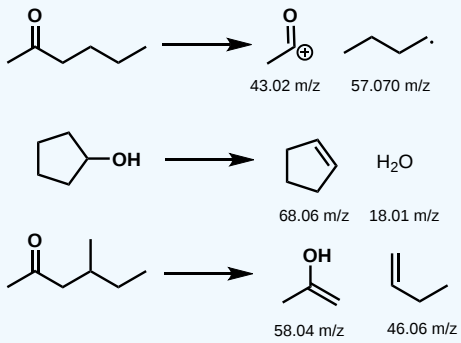
Exercise 2.8.4

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



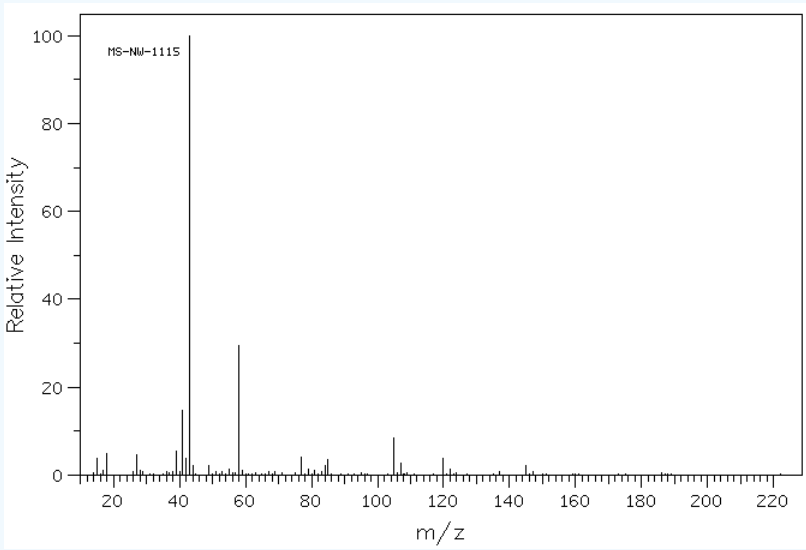
Answer

The first undergoes an alpha cleavage. The second undergoes a dehydration. The final one goes througha McLafferty rearrangement.



Exercise 2.8.5

5-Chloro-2-pentanone has the mass spectrum shown. Which peak represents the M^+? Which is the base peak? Why is there a peak at 122? Explain what the fragment for the base peak would be.



Source: SDBSWeb : https://sdbs.db.aist.go.jp/sdbs/cgi-bin/cre_frame_disp.cgi?sdbsno=10178 (National Institute of Advanced Industrial Science and Technology, 16 August 2022)

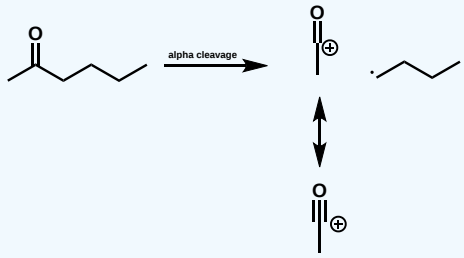
Answer

M+ = 120

base peak = 43

The m/z peak at 122 is the M + 2 peak. It occurs because chlorine has two isotopes ^{35}C and ^{37}C in a 3:1 ratio.

The m/z = 43 occurs due to the alpha cleavage. The acylium ion has an m/z of 43. This fragment is particularly stable due to resonance.



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2.9: 2.S Summary of Mass Spectrometry

Concepts & Vocabulary

2.1: Chapter Objectives and Preview of Mass Spectrometry

- Mass spectrometry is a way to determine the molecular weight of a structure to begin structure elucidation.

2.2 Instrumentation

- Mass spectrometry breaks apart molecules to detect fragments based on a mass to charge ratio.
- The particles in the sample (atoms or molecules) are bombarded with a stream of electrons, and some of the collisions are energetic enough to knock one or more electrons out of the sample particles to make positive ions.
- Most of the positive ions formed will carry a charge of +1 because it is much more difficult to remove further electrons from an already positive ion.
- Different ions are deflected by the magnetic field by different amounts, which depends on the mass of the ion and the charge of the ion.
- The output from the chart recorder is usually simplified into a "stick diagram". This shows the relative current produced by ions of varying mass/charge ratio.

2.3 Ionization Techniques

- There is a variety of ionization techniques. The ones discussed in this section are electron impact, chemical ionization, field ionization/desorption, electrospray ionization, matrix assisted laser desorption ionization, inductively coupled plasma mass spectrometry, and fast atom bombardment.
- Depending on the information desired from mass spectrometry analysis, different ionization techniques may be desired.

2.4 Mass Analyzers

- A mass analyzer is the component of the mass spectrometer that takes ionized masses and separates them based on charge to mass ratios and outputs them to the detector where they are detected and later converted to a digital output.
- There are six general types of mass analyzers that can be used for the separation of ions in a mass spectrometry (quadrapole, time of flight, magnetic sector, electrostatic sector, quadropole ion trap, and ion cyclotron resonance).

2.5 Applications of Mass Spectrometry

- Mass spectrometry is applicable across diverse fields with specific applications including, but not limited to drug testing and discovery, food contamination detection, pesticide residue analysis, isotope ratio determination, protein identification, and carbon dating.
- One of the new ways that clinical mass spectrometry is being used is to quantitatively detect small amounts of proteins, biomarkers, or drug molecules, with very low concentrations.

2.6 Interpretation of Mass Spectra

- Mass spectrum looks like a bar graph with the x axis as the m/z values and the y axis represents the intensity or relative abundance of a given m/z.
- The lines correspond to the fragments of the different ions with different m/z values.
- The more of a particular sort of ion that's formed, the higher its peak height will be. The tallest peak is called the base peak and is assigned 100% intensity.
- The peak that represents the unfragmented cation radical is called the parent peak or molecular ion (M^+).
- There is often an M+1 peak (one greater than the molecular ion), and it arises because of ^{13}C. This compound is referred to as an isotopomer.

2.7 Mass Spectrometry of Common Functional Groups

- Some fragment ions are very common in mass spectrometry often due to having no pathway available to break the ion down or the ion is relatively stable, so it forms easily.

- When alcohols are subjected to ionization, two fragmentation pathways can occur - alpha cleavage and dehydration.
- A general principle when nitrogen is part of a molecule is that if there is an odd number of nitrogens, then the molecular weight will be an odd number. This is also known as the nitrogen rule.
- Primary amines undergo a characteristic alpha cleavage.
- Other isotopomers are common when chlorine and bromine are part of the molecule. For chlorine and bromine there will be an additional M + 2 peak representing one of the isotopomers.
- Chlorine has two isotopes ^{35}C and ^{37}C with a 3:1 ratio (roughly), which appears in the mass spectrum in the fragments containing chlorine.
- The ratio of the relative abundance/intensity of the M:M + 2 is about 3:1, which reflecting the isotopic abundance of ^{35}C:^{37}C.
- With bromine, the isotopic distribution of ^{79}Br and ^{81}Br is more like 50:50. The ratio of the relative abundance/intensity of the M:M + 2 is about 50:50.
- Carbonyl compounds can undergoe an alpha cleavage and the McLafferty rearragnement.

Skills to Master

- Skill 2.1 Know what mass to charge means and measures.
- Skill 2.2 Distinguish between different types of ionization techniques.
- Skill 2.3 Determine the best mass analyzer to use for sample.
- Skill 2.4 Determine the ratio of different types of protons present in an organic compound.
- Skill 2.5 Interpret fragmentation patterns
- Skill 2.6 Interpret mass spectra

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CHAPTER OVERVIEW

3: Conjugated Compounds and Ultraviolet Spectroscopy

3.1: Chapter Objectives and Preview of Ultraviolet Spectroscopy
3.2: Conjugated Dienes
3.3: Electronic Transitions
3.4: Ultraviolet Absorption
3.5: UV-Visible Spectrometer
3.6: Interpreting Ultraviolet Spectra
3.7: Conjugation and the Absorption of Light in the Real World
3.S: Summary

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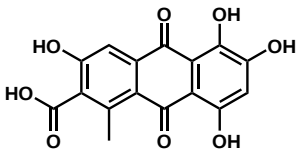
3.1: Chapter Objectives and Preview of Ultraviolet Spectroscopy

Learning Objectives

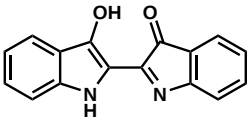
After completing this chapter, you should be able to

- fulfill all of the detailed objectives listed under each individual section.
- analyze problems which may require the interpretation of ultraviolet spectroscopy.
- define, and use in context, the key terms introduced in this chapter.

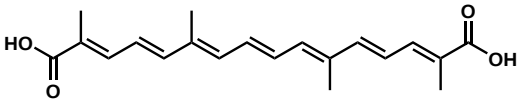
Many of the pigments that are responsible for the beautiful colors in nature are conjugated compounds. Many of the early organic dyes used for pigmenting cloth and art are conjugated compounds. These included the crimson pigment - kermesic acid, the blue dye - indigo, and the yellow saffron pigment - crocetin. A common feature of all these colored compounds, displayed below, is a system of extensive pi bonds. In this chapter, we will look at how ultraviolet (UV) spectroscopy is a technique that is only applicable to conjugated compounds giving information on the nature of the conjugated pi electron system.



Kermesic Acid



Indigo



Crocetin

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3.2: Conjugated Dienes

Objective

- Determine whether or not a molecule contains a conjugated system, given its Kekulé, condensed or shorthand formula.

Key Terms

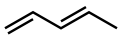
Make certain that you can define, and use in context, the key terms below.

- conjugated diene
- conjugated double bonds
- diene
- enone
- polyene

A diene is a hydrocarbon chain that has two double bonds that may or may not be adjacent to each other. The arrangements of these double bonds can have varying affects on the compounds reactivity and stability. This section focuses on the delocalization of pi systems by comparing two neighboring double bonds, specifically conjugated molecules. A molecule is defined as conjugated when there is a system of connected p orbitals where electron density can be shared across the system. The arrangement of bonds alternates between single and multiple bonds in conjugated molecules.

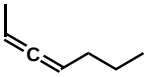
Conjugated vs. Nonconjugated vs. Cumulated Dienes

Conjugated dienes are two double bonds separated by a single bond. An example of this is penta-1,3-diene.

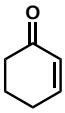


Nonconjugated dienes are two double bonds are separated by more than one single bond. The double bonds are considered isolated from each other. An example of this is 2,5-heptadiene.

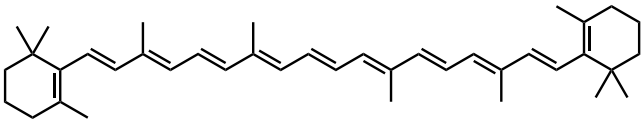
Cumulated dienes are two double bond connected to a similar atom. These are also known as allenes. An example of this is 2,3-heptadiene.



Another conjugated diene is a enone, which is compound containing both a double bond and carbonyl where the double bond is conjugated to the carbonyl. An example of this is cyclohex-2-enone.

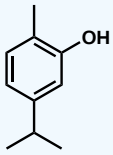


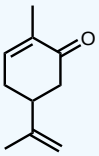
There are many compounds that have more than two double bonds present in the molecule. The term given to describe these molecules is polyene. An example of a polyene is beta-carotene (below). Beta-carotene is a red-orange pigment found in plants and fruits like carrots, which is converted to vitamin A in the human body.

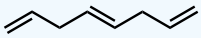


Exercise \(\PageIndex{1}\)

Are the following structures conjugated?

(A) 

(B) 

(C) 

Answer

(A) Yes - conjugated

(B) Yes - conjugated

(C) No - not conjugated

Contributors and Attributions

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- Shravan Rao

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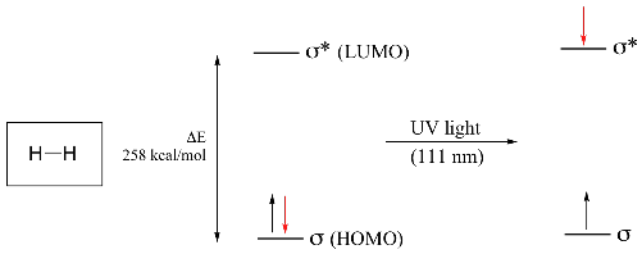
3.3: Electronic Transitions

Objectives

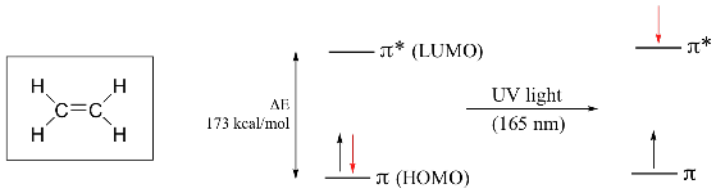
- discuss the bonding in 1,3-butadiene in terms of the molecular orbital theory, and draw a molecular orbital for this and similar compounds.
- understand how electronic transitions occur.
- get an understanding of when electronic transitions can be observed with UV spectroscopy

Let's take as our first example the simple case of molecular hydrogen, H_2. The molecular orbital picture for the hydrogen molecule consists of one bonding σ MO, and a higher energy antibonding σ* MO. When the molecule is in the ground state, both electrons are paired in the lower-energy bonding orbital – this is the Highest Occupied Molecular Orbital (HOMO). The antibonding σ* orbital, in turn, is the Lowest Unoccupied Molecular Orbital (LUMO).



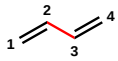
If the molecule is exposed to light of a wavelength with energy equal to ΔE, the HOMO-LUMO energy gap, this wavelength will be absorbed and the energy used to bump one of the electrons from the HOMO to the LUMO – in other words, from the σ to the σ* orbital. This is referred to as a σ - σ* transition. ΔE for this electronic transition is 258 kcal/mol, corresponding to light with a wavelength of 111 nm.

When a double-bonded molecule such as ethene (common name ethylene) absorbs light, it undergoes a π - π* transition. Because π-π* energy gaps are narrower than σ - σ* gaps, ethene absorbs light at 165 nm - a longer wavelength (lower energy) than molecular hydrogen.



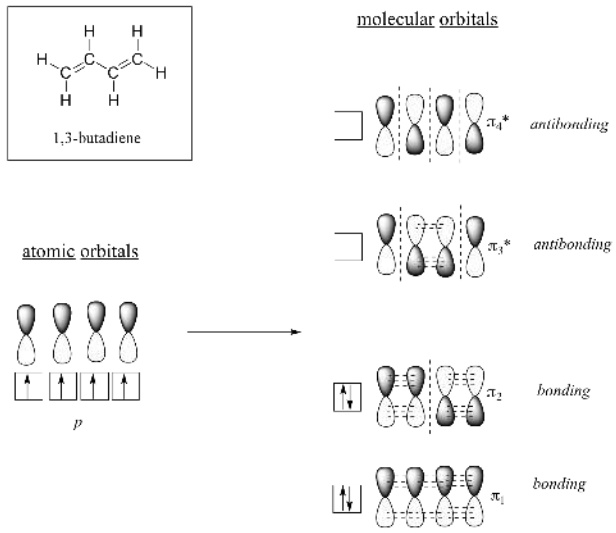
The electronic transitions of both molecular hydrogen and ethene are too energetic to be accurately recorded by standard UV spectrophotometers, which generally have a range of 220 – 700 nm. Where UV-vis spectroscopy becomes useful to most organic and biological chemists is in the study of molecules with conjugated pi systems. In these groups, the energy gap for π -π* transitions is smaller than for isolated double bonds, and thus the wavelength absorbed is longer. Molecules or parts of molecules that absorb light strongly in the UV-vis region are called chromophores.

Next, we'll consider the 1,3-butadiene molecule (below). From valence orbital theory alone we might expect that the C_2-C_3 bond in this molecule, because it is a sigma bond, would be able to rotate freely.



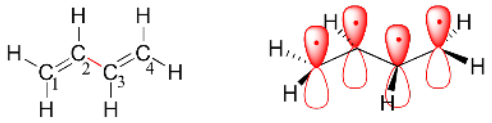
Experimentally, however, it is observed that there is a significant barrier to rotation about the C_2-C_3 bond (colored in red above), and that the entire molecule is planar. In addition, the C_2-C_3 bond is 148 pm long, shorter than a typical carbon-carbon single bond (about 154 pm), though longer than a typical double bond (about 134 pm). Molecular orbital theory accounts for these observations with the concept of delocalized π bonds. In this picture, the four *p* atomic orbitals combine mathematically to form four pi

molecular orbitals of increasing energy. Two of these - the bonding pi orbitals - are lower in energy than the *p* atomic orbitals from which they are formed, while two - the antibonding pi orbitals - are higher in energy.



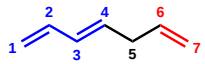
The lowest energy molecular orbital, pi_1, has only constructive interaction and zero nodes. Higher in energy, but still lower than the isolated *p* orbitals, the pi_2 orbital has one node but two constructive interactions - thus it is still a bonding orbital overall. Looking at the two antibonding orbitals, pi_3* has two nodes and one constructive interaction, while pi_4* has three nodes and zero constructive interactions.

By the aufbau principle, the four electrons from the isolated $2p_z$ atomic orbitals are placed in the bonding pi_1 and pi_2 MO's. Because pi_1 includes constructive interaction between C_2 and C_3, there is a degree, in the 1,3-butadiene molecule, of pi-bonding interaction between these two carbons, which accounts for its shorter length and the barrier to rotation. The valence bond picture of 1,3-butadiene shows the two pi bonds as being isolated from one another, with each pair of pi electrons 'stuck' in its own pi bond. However, molecular orbital theory predicts (accurately) that the four pi electrons are to some extent delocalized, or 'spread out', over the whole pi system.

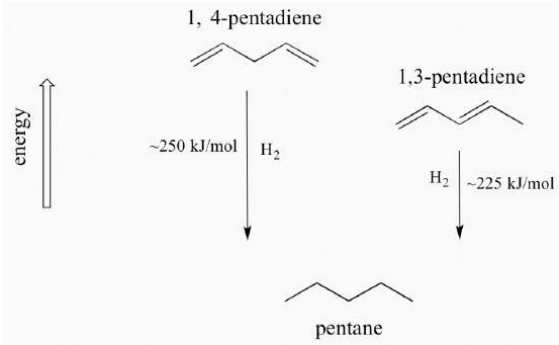


1,3-butadiene

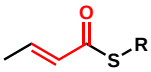
1,3-butadiene is the simplest example of a system of conjugated pi bonds. Remember to be considered conjugated, two or more pi bonds must be separated by only one single bond – in other words, there cannot be an intervening sp^3-hybridized carbon, because this would break up the overlapping system of parallel *p* orbitals. In the compound below, for example, the C_1-C_2 and C_3-C_4 double bonds are conjugated (highlighted in blue), while the C_6-C_7 double bond (highlighted in red) is isolated from the other two pi bonds by sp^3-hybridized C_5.



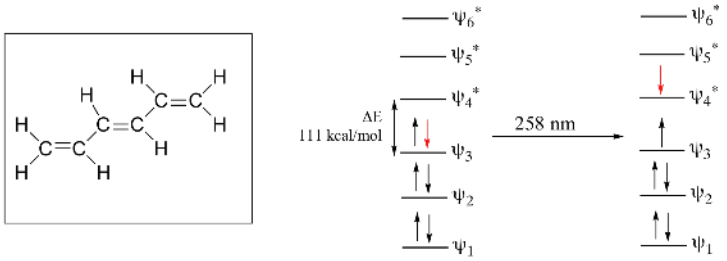
A very important concept to keep in mind is that there is an inherent thermodynamic stability associated with conjugation. This stability can be measured experimentally by comparing the heat of hydrogenation of two different dienes. When the two conjugated double bonds of 1,3-pentadiene are 'hydrogenated' to produce pentane, about 225 kJ is released per mole of pentane formed. Compare that to the approximately 250 kJ/mol released when the two isolated double bonds in 1,4-pentadiene are hydrogenated, also forming pentane.



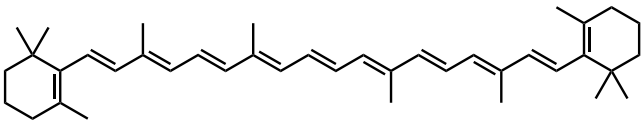
The conjugated diene is lower in energy: in other words, it is more stable. In general, conjugated pi bonds are more stable than isolated pi bonds. Conjugated pi systems can involve heteroatoms like oxygen and nitrogen as well as carbon. In the metabolism of fat molecules, some of the key reactions involve alkenes that are conjugated to carbonyl groups.



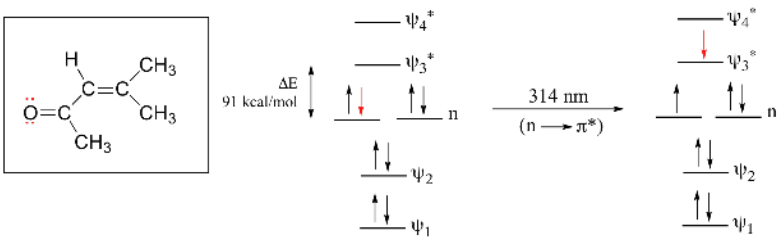
As conjugated pi systems become larger, the energy gap for a π - π* transition becomes increasingly narrow, and the wavelength of light absorbed correspondingly becomes longer. The absorbance due to the π - π* transition in 1,3,5-hexatriene, for example, occurs at 258 nm, corresponding to a **Δ**E of 111 kcal/mol.



In molecules with extended pi systems, the HOMO-LUMO energy gap becomes so small that absorption occurs in the visible rather then the UV region of the electromagnetic spectrum. Beta-carotene, with its system of 11 conjugated double bonds, absorbs light with wavelengths in the blue region of the visible spectrum while allowing other visible wavelengths – mainly those in the red-yellow region - to be transmitted. This is why carrots are orange.



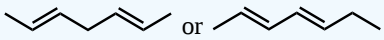
The conjugated pi system in 4-methyl-3-penten-2-one gives rise to a strong UV absorbance at 236 nm due to a π - π* transition. However, this molecule also absorbs at 314 nm. This second absorbance is due to the transition of a non-bonding (lone pair) electron on the oxygen up to a π* antibonding MO:



This is referred to as an n - π* transition. The nonbonding (n) MO's are higher in energy than the highest bonding p orbitals, so the energy gap for an n - π* transition is smaller that that of a π - π* transition – and thus the n - π* peak is at a longer wavelength. In general, n - π* transitions are weaker (less light absorbed) than those due to π - π* transitions.

Exercise 3.3.1

Without calculations, which molecule (2,5-heptadiene or 2,4-heptadiene) would you predict to have a lower heat of hydrogenation?

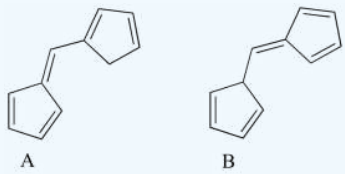


Answer

I would predict 2,4-heptadiene to have a lower heat of hydrogenation than 2,5-heptadiene. This is due to the conjugation between the double bonds in 2,4-heptadiene, which is stabilizing.

Exercise 3.3.2

Which of the following molecules would you expect to have a smaller gap in the electronic transition? Explain your answer.



Answer

B. The entire molecule is conjugated, so it has a more extended pi system than A. More extended pi systems typically have smaller absorption gaps.

Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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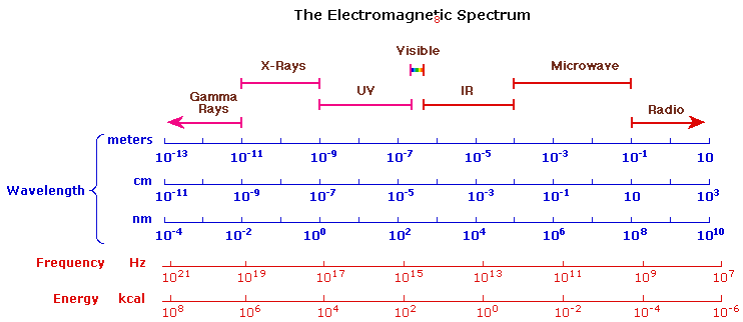
3.4: Ultraviolet Absorption

Objectives

- identify the ultraviolet region of the electromagnetic spectrum which is of most use to organic chemists.

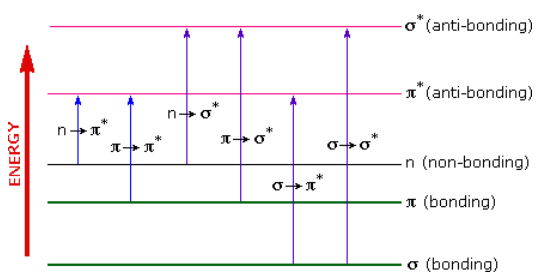
The electromagnetic spectrum was discussed in Chapter 1, but as a reminder most of the radiation that surrounds us is not visible. However, this radiation can be detected by instruments. The following chart displays many of the important regions of the electromagnetic spectrum, and demonstrates the inverse relationship between wavelength and frequency.



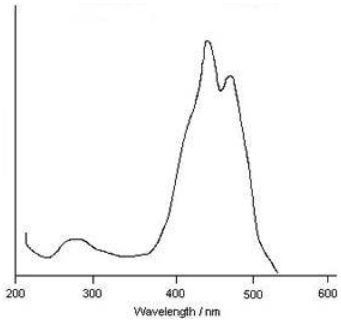
UV-Visible Absorption Spectra

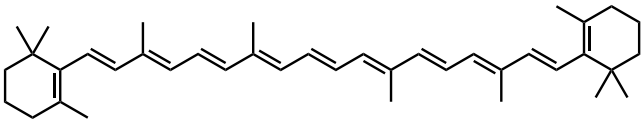
To understand why some compounds are colored and others are not, and to determine the relationship of conjugation to color, we must make accurate measurements of light absorption at different wavelengths in and near the visible part of the spectrum. Commercial optical spectrometers enable such experiments to be conducted with ease, and usually survey both the near ultraviolet and visible portions of the spectrum. The visible region of the spectrum comprises photon energies of 36 to 72 kcal/mol, and the near ultraviolet region, out to 200 nm, extends this energy range to 143 kcal/mol. Ultraviolet radiation having wavelengths less than 200 nm is difficult to handle, and is seldom used as a routine tool for structural analysis.

The energies noted above are sufficient to promote or excite a molecular electron to a higher energy orbital. Consequently, absorption spectroscopy carried out in this region is sometimes called "electronic spectroscopy". In Section 3.3, the electronic transitions were discussed, but a summary of the various kinds of electronic excitation that may occur in organic molecules is shown in the diagram below. Of the six transitions outlined, only the non-bonding to anti-bonding and bonding to anti-bonding are achieved by the energies available in the 200 to 800 nm spectrum. As a rule, energetically favored electron promotion will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and the resulting species is called an excited state.



When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance (A) versus wavelength, as in the spectrum shown below of beta-carotene as well as the structure. Beta-carotene absorbs most strongly from 400 to 500 nm. This is the blue/green part of the spectrum and beta-carotene appears orange because it reflects back red/yellow. Absorbance usually ranges from 0 (no absorption) to 2 (99% absorption), and is precisely defined in context with spectrometer operation.





Spectrum from: https://scilearn.sydney.edu.au/organ...The%20Spectrum

Exercise 3.4.1

What is the energy range for 400 nm to 500 nm in the ultraviolet spectrum where beta-carotene absorbs?

Answer

$E = hc/\lambda$

$E = (6.62 \times 10^{-34}\ \text{Js})(3.00 \times 10^{8}\ \text{m/s})/(4.00 \times 10^{-7}\ \text{m})$

$E = 6.62 \times 10^{-19}\ \text{J}$

The range of 3.972×10^{-19} to 4.965×10^{-19} joules.

Exercise 3.4.2

Would 1,3-cyclohexadiene or 1,4-cyclohexadiene absorb a longer wavelength?

1,3-cyclohexadiene 1,4-cyclohexadiene

Answer

1,3-cyclohexadiene would absorb a longer wavelength. Typically, the more conjugation in the molecule, the longer the wavelength absorbed.

Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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3.5: UV-Visible Spectrometer

Ultraviolet-visible (UV-vis) spectroscopy is used to obtain the absorbance spectra of a compound in solution or as a solid. What is actually being observed spectroscopically is the absorbance of light energy or electromagnetic radiation, which excites electrons from the ground state to the first singlet excited state of the compound or material. The UV-vis region of energy for the electromagnetic spectrum covers 1.5 - 6.2 eV which relates to a wavelength range of 800 - 200 nm. The Beer-Lambert Law, Equation 3.5.1 , is the principle behind absorbance spectroscopy. For a single wavelength, A is absorbance (unitless, usually seen as arb. units or arbitrary units), ε is the molar absorptivity of the compound or molecule in solution ($M^{-1}cm^{-1}$), *b* is the path length of the cuvette or sample holder (usually 1 cm), and *c* is the concentration of the solution (M).

$$A = \varepsilon bc \tag{3.5.1}$$

All of these instruments have a light source (usually a deuterium or tungsten lamp), a sample holder and a detector, but some have a filter for selecting one wavelength at a time. The single beam instrument (Figure 3.5.1) has a filter or a monochromator between the source and the sample to analyze one wavelength at a time. The double beam instrument (Figure 3.5.2) has a single source and a monochromator and then there is a splitter and a series of mirrors to get the beam to a reference sample and the sample to be analyzed, this allows for more accurate readings. In contrast, the simultaneous instrument (Figure 3.5.3) does not have a monochromator between the sample and the source; instead, it has a diode array detector that allows the instrument to simultaneously detect the absorbance at all wavelengths. The simultaneous instrument is usually much faster and more efficient, but all of these types of spectrometers work well.

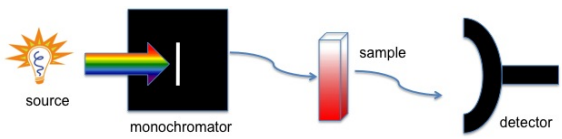

Figure 3.5.1 Illustration of a single beam UV-vis instrument.

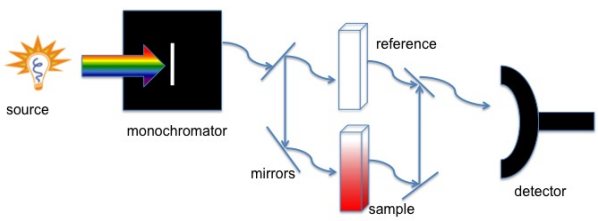

Figure 3.5.2 Illustration of a double beam UV-vis instrument.

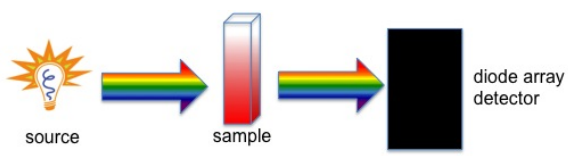

Figure 3.5.3 Illustration of a simultaneous UV-vis instrument.

What Information can be Obtained from UV-vis Spectra?

UV-vis spectroscopic data can give qualitative and quantitative information of a given compound or molecule. Irrespective of whether quantitative or qualitative information is required it is important to use a reference cell to zero the instrument for the solvent the compound is in. For quantitative information on the compound, calibrating the instrument using known concentrations of the compound in question in a solution with the same solvent as the unknown sample would be required. If the information needed is just proof that a compound is in the sample being analyzed, a calibration curve will not be necessary; however, if a degradation study or reaction is being performed, and concentration of the compound in solution is required, a calibration curve is needed.

To make a calibration curve, at least three concentrations of the compound will be needed, but five concentrations would be ideal for a more accurate curve. The concentrations should start at just above the estimated concentration of the unknown sample and should go down to about an order of magnitude lower than the highest concentration. The calibration solutions should be spaced relatively equally apart, and they should be made as accurately as possible using digital pipettes and volumetric flasks instead of

graduated cylinders and beakers. An example of absorbance spectra of calibration solutions of Rose Bengal (4,5,6,7-tetrachloro-2',4',5',7'-tetraiodofluorescein, Figure **3.5.4**, can be seen in Figure **3.5.5**. To make a calibration curve, the value for the absorbances of each of the spectral curves at the highest absorbing wavelength, is plotted in a graph similar to that in Figure **3.5.6** of absorbance versus concentration. The correlation coefficient of an acceptable calibration is 0.9 or better. If the correlation coefficient is lower than that, try making the solutions again as the problem may be human error. However, if after making the solutions a few times the calibration is still poor, something may be wrong with the instrument; for example, the lamps may be going bad.

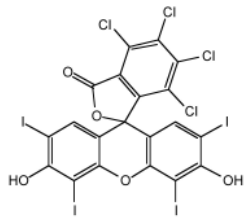

Figure **3.5.4** The molecular structure of Rose Bengal (4,5,6,7-tetrachloro-2',4',5',7'-tetraiodofluorescein).

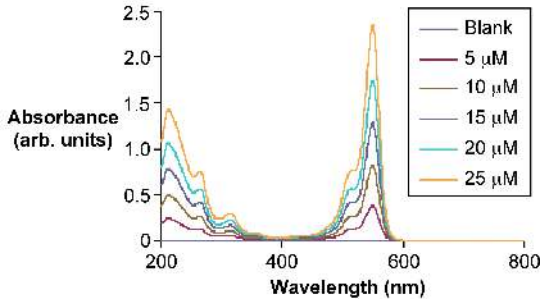

Figure **3.5.5** UV-vis spectra of different concentrations of Rose Bengal.

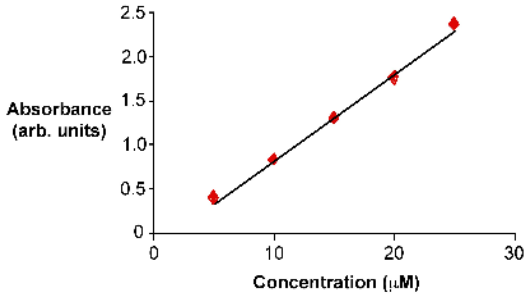

Figure **3.5.6** Calibration curve of Rose Bengal. Equation of line: y = 0.0977x – 0.1492 (R^2 = 0.996)

Limitations of UV-vis Spectroscopy

Sample

UV-vis spectroscopy works well on liquids and solutions, but if the sample is more of a suspension of solid particles in liquid, the sample will scatter the light more than absorb the light and the data will be very skewed. Most UV-vis instruments can analyze solid samples or suspensions with a diffraction apparatus (Figure **3.5.7**), but this is not common. UV-vis instruments generally analyze liquids and solutions most efficiently.

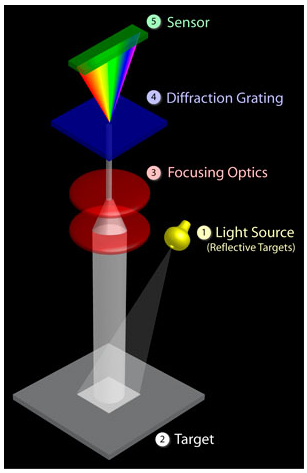

Figure 3.5.7 Schematic representation of the apparatus for collecting UV-vis spectra from solid materials.

Choice of Solvent or Container

Every solvent has a UV-vis absorbance cutoff wavelength. The solvent cutoff is the wavelength below which the solvent itself absorbs all of the light. So when choosing a solvent be aware of its absorbance cutoff and where the compound under investigation is thought to absorb. If they are close, chose a different solvent. Table 3.5.1 provides an example of solvent cutoffs.

Table 3.5.1: UV absorbance cutoffs of various common solvents

Solvent	UV Absorbance Cutoff (nm)
Acetone	329
Benzene	278
Dimethylformamide	267
Ethanol	205
Toluene	285
Water	180

The material the cuvette (the sample holder) is made from will also have a UV-vis absorbance cutoff. Glass will absorb all of the light higher in energy starting at about 300 nm, so if the sample absorbs in the UV, a quartz cuvette will be more practical as the absorbance cutoff is around 160 nm for quartz (Table 3.5.2).

Table 3.5.2: Three different types of cuvettes commonly used, with different usable wavelengths.

Material	Wavelength Range (nm)
Glass	380-780
Plastic	380-780
Fused Quartz	< 380

Concentration of Solution

To obtain reliable data, the peak of absorbance of a given compound needs to be at least three times higher in intensity than the background noise of the instrument. Obviously using higher concentrations of the compound in solution can combat this. Also, if the sample is very small and diluting it would not give an acceptable signal, there are cuvettes that hold smaller sample sizes than the 2.5 mL of a standard cuvettes. Some cuvettes are made to hold only 100 μL, which would allow for a small sample to be analyzed without having to dilute it to a larger volume, lowering the signal to noise ratio.

Exercise 3.5.1

What are the two most common light sources used in a UV-Vis spectrophotometer?

Answer

deuterium or tungsten lamp

Exercise 3.5.2

How does concentration affect UV-Vis?

Answer

The concentration of sample present is directly proportional to the intensity of light absorption, thus influencing the spectrum.

Exercise 3.5.3

When should you use a calibration curve in UV-Vis?

Answer

To determine the concentration of the sample from absorbance.

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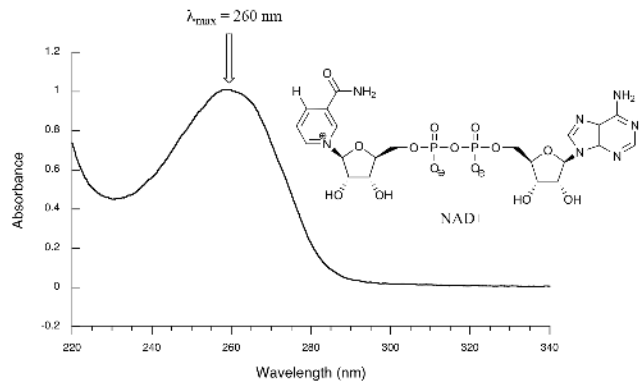
3.6: Interpreting Ultraviolet Spectra

Objective

- be able to interpret UV-Vis spectra.
- understand the effect of conjugation.

The wavelength necessary to make the transition from π -π* in a conjugated molecule depends on the energy gap between the HOMO and LUMO. This energy gap depends on the conjugated system of the molecule being studied. If you recall from Section 3.3, the energy gap for π -π* transitions is smaller for conjugated systems than for isolated double bonds, and thus the wavelength absorbed is longer. Therefore, by measuring the UV spectrum of a molecule, structural information can be derived about the nature of the conjugated pi electron system present.

We have been talking in general terms about how molecules absorb UV and visible light – now let's look at some actual examples of data from a UV-vis absorbance spectrophotometer. The basic setup is: radiation with a range of wavelengths is directed through a sample of interest, and a detector records which wavelengths were absorbed and to what extent the absorption occurred. Below is the absorbance spectrum of an important biological molecule called nicotinamide adenine dinucleotide, abbreviated NAD^+. This compound absorbs light in the UV range due to the presence of conjugated pi-bonding systems.

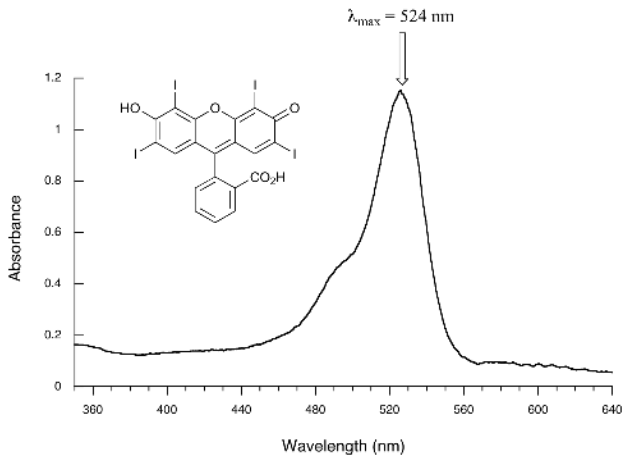


You'll notice that this UV spectrum has only one peak, although many molecules have more than one. Notice also that the convention in UV-vis spectroscopy is to show the baseline at the bottom of the graph with the peaks pointing up. Wavelength values on the x-axis are generally measured in nanometers (nm). Peaks in UV spectra tend to be quite broad, often spanning well over 20 nm at half-maximal height. Typically, there are two things that we look for and record from a UV-Vis spectrum. The first is lambda max (λ_{max}), which is the wavelength at maximal light absorbance. As you can see, NAD^+ has $\lambda_{max,}$ = 260 nm. We also want to record how much light is absorbed at $\lambda_{max.}$ Here we use a unitless number called absorbance, abbreviated 'A'. To calculate absorbance at a given wavelength, the computer in the spectrophotometer simply takes the intensity of light at that wavelength before it passes through the sample (I_0), divides this value by the intensity of the same wavelength after it passes through the sample (I), then takes the $\log_{10}$ of that number:

$$A = \log I_0/I$$

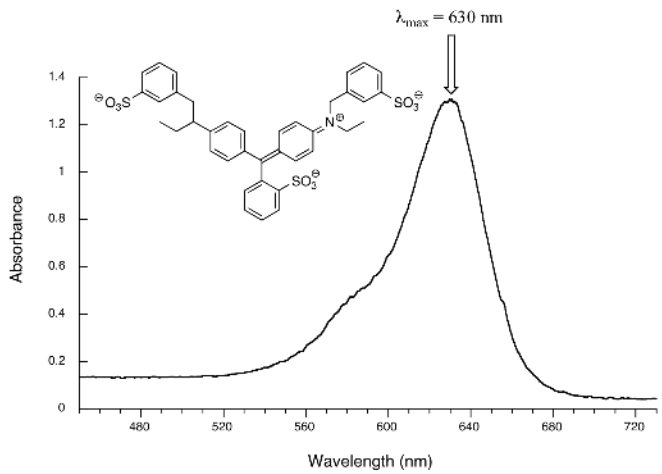
You can see that the absorbance value at 260 nm (A_{260}) is about 1.0 in this spectrum.

Here is the absorbance spectrum of the common food coloring Red #3:



Here, we see that the extended system of conjugated pi bonds causes the molecule to absorb light in the visible range. Because the λ_{max} of 524 nm falls within the green region of the spectrum, the compound appears red to our eyes.

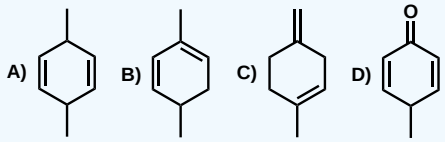
Now, take a look at the spectrum of another food coloring, Blue #1:



Here, maximum absorbance is at 630 nm, in the orange range of the visible spectrum, and the compound appears blue.

? Exercise 3.6.1

Which of the following would show UV absorptions in the 200-300 nm range?

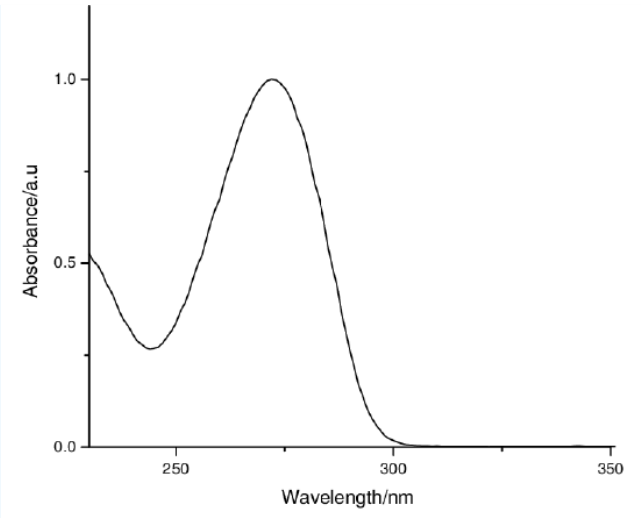


Answer

You are looking for conjugated systems, which leads to B and D.

? Exercise 3.6.2

What is the lambda max for caffeine?



UV-vis spectra of caffeine in water

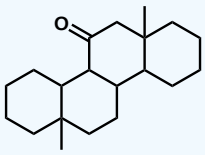
Belay, Abebe & Beketie, Kassahun & Redi, Mesfin & Asfaw, Araya. (2008). Measurement of Caffeine in Coffee Beans with UV/Vis Spectrometer. Food Chemistry. 108. 310-315. 10.1016/j.foodchem.2007.10.024.

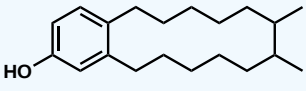
Answer

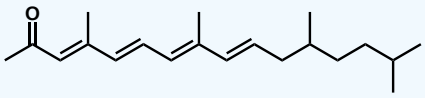
λ_{max} of 275 nm.

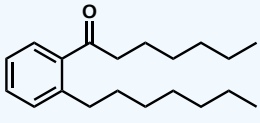
? Exercise 3.6.3

A colleague has isolated a compound that has the formula $C_{20}H_{32}O$ and a λ_{max} of 275 nm. Your colleague subjected the product to hydrogenation (Pd/C and H_2), which resulted in no change in the λ_{max}. They then tried to reduce the molecule with sodium borohydride, which led to no change in λ_{max}. They have proposed four different structures, but cannot figure out what structure they have isolated. Which do you think is most likely?

A) 

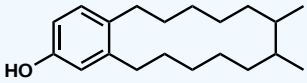
B) 

C) 

D) 

Answer

With a λ_{max}, there needs to be a conjugated pi system. A is lacking a conjugated pi system, so it can't be molecule A. Ketones can be reduced to alcohols when treated with sodium borohydride, which means the λ_{max} would change for both C and D. Therefore it can't be C or D. In additon, C would react under the hydrogenation conditions, so again its λ_{max} would

change. It can definitely not be C. Which leaves us B. It has a conjugated pi system and would not react in either set of conditions, so its λ_{max} would stay the same. The isolated compound is B - 

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

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3.7: Conjugation and the Absorption of Light in the Real World

Objectives

- explain why some organic compounds have different colours based on compound structure and our perception of light.
- state the relationship between frequency of light absorbed and the extent of conjugation in an extended pi electron system.

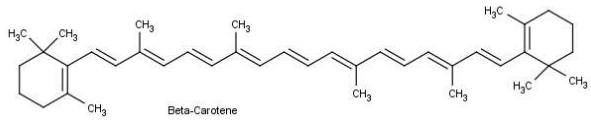
Eyes receive light energy then transfer and passing the energy into neural impulses to brain. This page will show the role of light plays in vision.

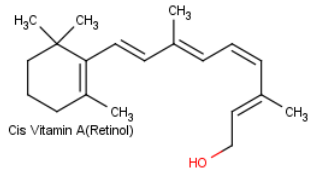
Introduction

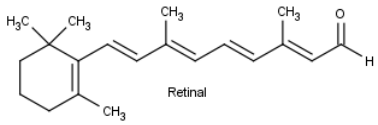
Light is one of the most important resources for civilization, it provides energy as it pass along by the sun. Light influence our everyday live. Living organisms sense light from the environment by photoreceptors. Light, as waves carry energy, contains energy by different wavelength. In vision, light is the stimulus input. Light energy goes into eyes stimulate photoreceptor in eyes. However, as an energy wave, energy is passed on through light at different wavelength. For example, "white" light from a lamp consists of all the wavelengths in the visible region. When this white light hits beta-carotene, the wavelengths from 400 to 500 nm are absorbed and all the other wavelengths are transmitted to our eyes. The carrot looks orange because the wavelengths of 400 to 500 nm that were absorbed occur in the blue range, when blue is removed our eyes see an orange color for beta-carotene.

Energy converting chemicals

Light energy can convert chemicals to other forms. Vitamin A, also known as retinol, anti-dry eye vitamins, is a required nutrition for human health. The predecessor of vitamin A is present in the variety of plant carotene. Vitamin A is critical for vision because it is needed by the retina of eye. Retinol can be converted to retinal, and retinal is a chemical necessary for rhodopsin. As light enters the eye, the 11-*cis*-retinal is isomerized to the all-"trans" form.

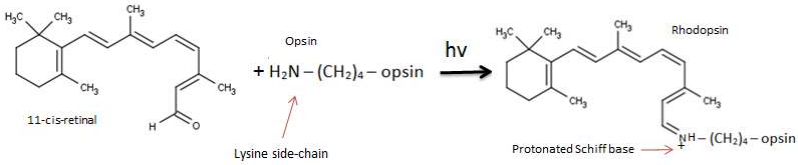






Mechanism of Vision

We now know in rhodopsin, there is protein and retinal. The large protein is called opsin. Opsin does not absorb visible light, but when it bonded with 11-cis-retinal by its lysine side-chain to from rhodopsin, the new molecule has a very broad absorption band in the visible region of the spectrum.[2][3]

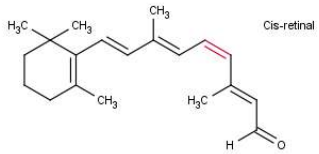


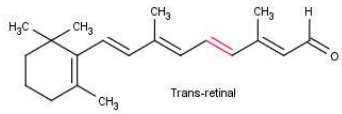
The reaction above shows Lysine side-chain from the opsin react with 11-cis-retinal when stimulated. By removing the oxygen atom form the retinal and two hydrogen atom form the free amino group of the lysine, the linkage show on the picture above is formed, and it is called Schiff base.

Signal transduction pathway

In human eyes, rod and cones react to light stimulation, and a series of chemical reactions happen in cells. These cells receive light, and pass on signals to other receiver cells. This chain of process is class signal transduction pathway. Signal transduction pathway is a mechanism that describes the ways cells react and respond to stimulation.

The molecule cis-retinal can absorb light at a specific wavelength. When visible light hits the cis-retinal, the cis-retinal undergoes an isomerization, or change in molecular arrangement, to all-trans-retinal. The new form of trans-retinal does not fit as well into the protein, and so a series of geometry changes in the protein begins. The resulting complex is referred to a bathrhodopsin (there are other intermediates in this process, but we'll ignore them for now).





As the protein changes its geometry, it initiates a cascade of biochemical reactions that results in changes in charge so that a large potential difference builds up across the plasma membrane. This potential difference is passed along to an adjoining nerve cell as an electrical impulse. The nerve cell carries this impulse to the brain, where the visual information is interpreted.

? Exercise 3.7.1

Indigo is an organic dye with a distinctive blue color. What wavelength does indigo absorb? What color is absorbed for our eyes to perceive blue?

Answer

Indigo absorbs orange light, which is a wavelength of 375-475 nm.

References

1. Biochemistry, L. Stryer (W.H. Freeman and Co, San Francisco, 1975).
2. *The Cambridge Guide to the Material World*, Rodney Cotterill (Cambridge University Press, Cambridge, 1985)

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3.S: Summary

Concepts & Vocabulary

3.1 Chapter Objectives and Preview of Ultraviolet Spectroscopy

- Ultraviolet (UV) spectroscopy is a technique that is only applicable to conjugated compounds giving information on the nature of the conjugated pi electron system.

3.2 Conjugated Dienes

- A diene is a hydrocarbon chain that has two double bonds that may or may not be adjacent to each other.
- The arrangements of these double bonds can have varying affects on the compounds reactivity and stability.
- A molecule is defined as conjugated when there is a system of connected p orbitals where electron density can be shared across the system.
- Enones are a type of conjugated diene.
- Polyenes are compounds that have more than two double bonds present in the molecule.

3.3 Electronic Transitions

- When both electrons are paired in the lower-energy bonding orbital – this is the Highest Occupied Molecular Orbital (HOMO). The antibonding σ* orbital, in turn, is the Lowest Unoccupied Molecular Orbital (LUMO).
- If the molecule is exposed to light of a wavelength with energy equal to ΔE, the HOMO-LUMO energy gap, this wavelength will be absorbed and the energy used to bump one of the electrons from the HOMO to the LUMO.
- π- π* energy gaps are narrower than σ - σ* gaps.
- Where UV-vis spectroscopy becomes useful to most organic and biological chemists is in the study of molecules with conjugated pi systems.
- In these groups, the energy gap for π -π* transitions is smaller than for isolated double bonds, and thus the wavelength absorbed is longer.

3.4 Ultraviolet Absorption

- To understand why some compounds are colored and others are not, and to determine the relationship of conjugation to color, we must make accurate measurements of light absorption at different wavelengths in and near the visible part of the spectrum.
- The visible region of the spectrum comprises photon energies of 36 to 72 kcal/mol, and the near ultraviolet region, out to 200 nm, extends this energy range to 143 kcal/mol.
- When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital.

3.5 UV- Visible Spectrometer

- UV-Vis spectrometers have a light source (usually a deuterium or tungsten lamp), a sample holder and a detector.
- UV-vis spectroscopic data can give qualitative and quantitative information of a given compound or molecule.
- For a sample, it is important to use a reference cell to zero the instrument for the solvent the compound is in.
- For quantitative information on the compound, calibrating the instrument using known concentrations of the compound in question in a solution with the same solvent as the unknown sample would be necessary for accurate results.
- UV-vis spectroscopy works well on liquids and solutions, but if the sample is more of a suspension of solid particles in liquid, the sample will scatter the light more than absorb the light and the data will be very skewed.
- Every solvent has a UV-vis absorbance cutoff wavelength, which is the wavelength below which the solvent itself absorbs all of the light.

3.6 Interpreting Ultraviolet Spectra

- The basic setup is: radiation with a range of wavelengths is directed through a sample of interest, and a detector records which wavelengths were absorbed and to what extent the absorption occurred.
- Some UV spectra have only one broad peak, although many molecules have more than one broad peak.

- The convention in UV-vis spectroscopy is to show the baseline at the bottom of the graph with the peaks pointing up. Wavelength values on the x-axis are generally measured in nanometers (nm).
- There are two things that we look for and record from a UV-Vis spectrum. The first is lambda max (λ_{max}), which is the wavelength at maximal light absorbance and the secon is to record how much light is absorbed at λ_{max}.

3.7 Conjugation and the Absorption of Light in the Real World

- Light influence our everyday lives.
- Eyes receive light energy then transfer and passing the energy into neural impulses to brain.
- As an energy wave, energy is passed on through light at different wavelength.
- Light energy can convert chemicals to other forms.
- In human eyes, rod and cones react to light stimulation, and a series of chemical reactions happen in cells.

Skills to Master

- Skill 3.1 Distinguish between different types of dienes.
- Skill 3.2 Compare molecules to determine if there is a larger or smaller energy gap.
- Skill 3.3 Understand which molecules will absorb longer wavelengths.
- Skill 3.4 Calculate the energy to excite a molecule from HOMO to LUMO.
- Skill 3.5 Understand how the spectrometer works.
- Skill 3.6 Understand the limitations of a spectrometer.
- Skill 3.7 Determine λ_{max}.
- Skill 3.8 Gather information from a UV-vis spectrum.
- Skill 3.9 Understand why humans see different colors.

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CHAPTER OVERVIEW

4: Infrared Spectroscopy

4.1: Chapter Objectives and Preview of Infrared Spectroscopy
4.2: Theory
4.3: Instrumentation
4.4: 4.4 The IR Spectrum
4.5: 4.5 IR Data Table
4.6: Interpretation
4.7: 4.7 Identifying Characteristic Functional Groups
4.8: 4.8 Infrared Spectroscopy Problems
4.9: Application
4.10: 4.S Summary

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4.1: Chapter Objectives and Preview of Infrared Spectroscopy

Learning Objectives

After completing this chapter, you should be able to

- fulfill all of the detailed objectives listed under each individual section.
- solve problems which may require the interpretation of IR spectra in addition to other spectral data.
- define, and use in context, the key terms introduced in this chapter.

When a molecule absorbs infrared (IR) radiation, the molecule vibrates, which causes the irradiated molecules to heat up. Molecules in the atmosphere, such as carbon dioxide, methane, and water, absorb IR radiation, which in turn creates more heat at the earth's surface. This in turn responsible for the greenhouse effect. In structure determination, IR spectroscopy is an important tool. It provides valuable information on what functional groups are present or absent in the molecule. An IR spectrum can be thought of as a fingerprint for the molecule.

This chapter will focus on IR spectroscopy. To start, some basic theory behind this technique will be discussed, followed by what type of information you can glean from spectra.

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4.2: Theory

Objectives

After completing this section, you should be able to

- identify (by wavelength, wavenumber, or both) the region of the electromagnetic spectrum which is used in infrared (IR) spectroscopy.
- discuss, in general terms, the effect that the absorption of infrared radiation can have on a molecule.

Infrared (IR) spectroscopy is one of the most common and widely used spectroscopic techniques employed mainly by inorganic and organic chemists due to its usefulness in determining structures of compounds and identifying them. Chemical compounds have different chemical properties due to the presence of different functional groups.

Introduction

Absorbing groups in the infrared region absorb within a certain wavelength region. The absorption peaks within this region are usually sharper when compared with absorption peaks from the ultraviolet and visible regions. In this way, IR spectroscopy can be very sensitive to determination of functional groups within a sample since different functional group absorbs different particular frequency of IR radiation. Also, each molecule has a characteristic spectrum often referred to as the fingerprint. A molecule can be identified by comparing its absorption peak to a data bank of spectra, which will be discussed in detail in other sections. IR spectroscopy is very useful in the identification and structure analysis of a variety of substances, including both organic and inorganic compounds. It can also be used for both qualitative and quantitative analysis of complex mixtures of similar compounds.

The use of infrared spectroscopy began in the 1950's by Wilbur Kaye. He had designed a machine that tested the near-infrared spectrum and provided the theory to describe the results. Karl Norris started using IR Spectroscopy in the analytical world in the 1960's and as a result IR Spectroscopy became an accepted technique. There have been many advances in the field of IR Spectroscopy, the most notable was the application of Fourier Transformations to this technique thus creating an IR method that had higher resolution and a decrease in noise. The year this method became accepted in the field was in the late 1960's.

Absorption Spectroscopy

There are three main processes by which a molecule can absorb radiation and each of these routes involves an increase of energy that is proportional to the light absorbed. The first route occurs when absorption of radiation leads to a higher rotational energy level in a rotational transition. The second route is a vibrational transition which occurs on absorption of quantized energy. This leads to an increased vibrational energy level. The third route involves electrons of molecules being raised to a higher electron energy, which is the electronic transition. It’s important to state that the energy is quantized and absorption of radiation causes a molecule to move to a higher internal energy level. This is achieved by the alternating electric field of the radiation interacting with the molecule and causing a change in the movement of the molecule. There are multiple possibilities for the different possible energy levels for the various types of transitions.

The energy levels can be rated in the following order: electronic > vibrational > rotational. Each of these transitions differs by an order of magnitude. Rotational transitions occur at lower energies (longer wavelengths) and this energy is insufficient and cannot cause vibrational and electronic transitions but vibrational (near infra-red) and electronic transitions (ultraviolet region of the electromagnetic spectrum) require higher energies.

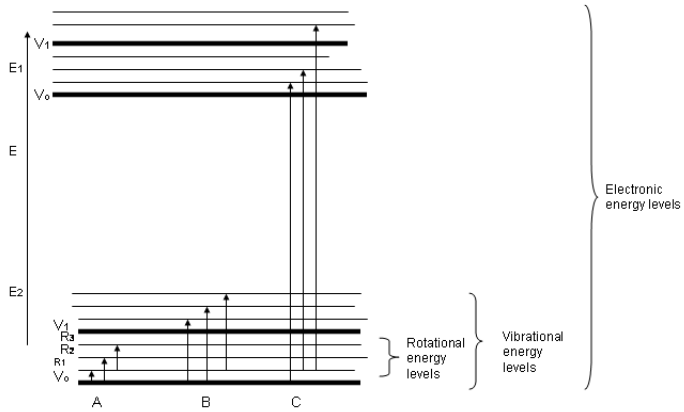


Figure 1: Energy levels for a molecule. Possible transitions that occur: (A): Pure rotational Transitions, (B) rotational-Vibrational Transitions, (C) Rotational-Vibrational-Electronic Transitions

The energy of IR radiation is weaker than that of visible and ultraviolet radiation, and so the type of radiation produced is different. Absorption of IR radiation is typical of molecular species that have a small energy difference between the rotational and vibrational states. A criterion for IR absorption is a net change in dipole moment in a molecule as it vibrates or rotates. Using the molecule HBr as an example, the charge distribution between hydrogen and bromine is not evenly distributed since bromine is more electronegative than hydrogen and has a higher electron density. HBr thus has a large dipole moment and is thus polar. The dipole moment is determined by the magnitude of the charge difference and the distance between the two centers of charge. As the molecule vibrates, there is a fluctuation in its dipole moment; this causes a field that interacts with the electric field associated with radiation. If there is a match in frequency of the radiation and the natural vibration of the molecule, absorption occurs and this alters the amplitude of the molecular vibration. This also occurs when the rotation of asymmetric molecules around their centers results in a dipole moment change, which permits interaction with the radiation field.

Diatomic Molecular Vibration

The absorption of IR radiation by a molecule can be likened to two atoms attached to each other by a massless spring. Considering simple diatomic molecules, only one vibration is possible. The Hook's law potential on the other hand is based on an ideal spring

$$F = -kx \tag{4.2.1}$$

$$= -\frac{dV(x)}{dx} \tag{4.2.2}$$

this results in one dimensional space

$$V(r) = \frac{1}{2}k(r - r_{eq})^2 \tag{4.2.3}$$

One thing that the Morse and Harmonic oscillator have in common is the small displacements ($x = r - r_{eq}$) from the equilibrium. Solving the Schrödinger equation for the harmonic oscillator potential results in the energy levels results in

$$E_v = \left(v + \frac{1}{2}\right) hv_e \tag{4.2.4}$$

with $v = 0, 1, 2, 3, \ldots, infinity$

$$v_e = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{4.2.5}$$

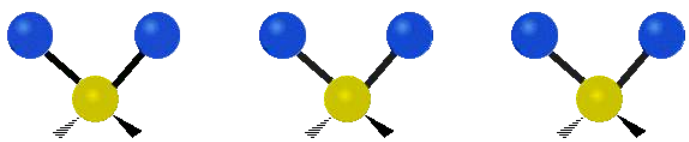
When calculating the energy of a diatomic molecule, factors such as anharmonicity (has a similar curve with the harmonic oscillator at low potential energies but deviates at higher energies) are considered. The energy spacing in the harmonic oscillator is equal but not so with the anharmonic oscillator. The anharmonic oscillator is a deviation from the harmonic oscillator. Other considered terms include; centrifugal stretching, vibrational and rotational interactions have to be taken into account. The energy can be expressed mathematically as

$$E_v = \underbrace{\left(v+\frac{1}{2}\right)hv_e}_{\text{Harmonic Oscillator}} - \underbrace{\left(v+\frac{1}{2}\right)^2 X_e hv_e}_{\text{anharmonicity}} + \underbrace{B_e J(J+1)}_{\text{Rigid Rotor}} - \underbrace{D_e J^2(J+1)^2}_{\text{centrifugal stretching}} - \underbrace{\alpha_e\left(v+\frac{1}{2}\right)J(J+1)}_{\text{rovibrational coupling}} \tag{4.2.6}$$

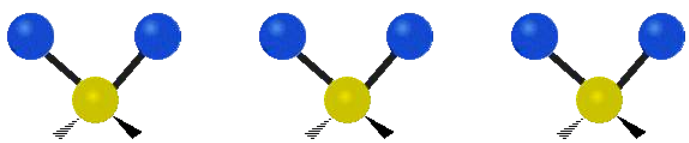
The first and third terms represent the *harmonicity* and rigid rotor behavior of a diatomic molecule such as HCl. The second term represents anharmonicity and the fourth term represents centrifugal stretching. The fifth term represents the interaction between the vibration and rotational interaction of the molecule.

Polyatomic Molecular Vibration

The bond of a molecule experiences various types of vibrations and rotations. This causes the atom not to be stationary and to fluctuate continuously. Vibrational motions are defined by stretching and bending modes. These movements are easily defined for diatomic or triatomic molecules. This is not the case for large molecules due to several vibrational motions and interactions that will be experienced. When there is a continuous change in the interatomic distance along the axis of the bond between two atoms, this process is known as a stretching vibration. A change in the angle occurring between two bonds is known as a bending vibration. Four bending vibrations exist namely, wagging, twisting, rocking and scissoring. A CH_2 group is used as an example to illustrate stretching and bending vibrations below.



Symmetric Stretch Asymmetric Stretch Twisting



Wagging Scissoring Rocking

Types of Vibrational Modes. To ensure that no center of mass motion occurs, the center atom (yellow ball) will also move. Figure from Wikipedia

As stated earlier, molecular vibrations consist of stretching and bending modes. A molecule consisting of (N) number of atoms has a total of 3N degrees of freedom, corresponding to the Cartesian coordinates of each atom in the molecule. In a non-linear molecule, 3 of these degrees of freedom are rotational, 3 are translational and the remainder is fundamental vibrations. In a linear molecule, there are 3 translational degrees of freedom and 2 are rotational. This is because in a linear molecule, all of the atoms lie on a single straight line and hence rotation about the bond axis is not possible. Mathematically the normal modes for a linear and non linear can be expressed as

Linear Molecules: (3N - 5) degrees of freedom

Non-Linear molecules: (3N - 6) degrees of freedom

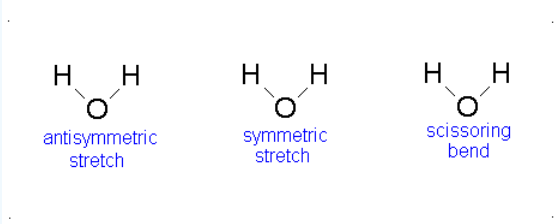
Example 1: Vibrations of Water

Diagram of Stretching and Bending Modes for H_2O.

Solution

H_2O molecule is a non-linear molecule due to the uneven distribution of the electron density. O_2 is more electronegative than H_2 and carries a negative charge, while H has a partial positive charge. The total degrees of freedom for H_2O will be 3(3)-6 =

9-6 = 3 degrees of freedom which correspond to the following stretching and bending vibrations. The vibrational modes are illustrated below:



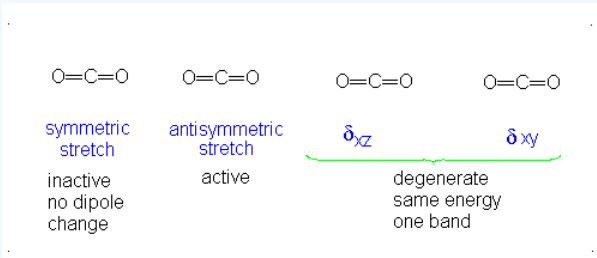
The vibrational modes of H_2O

Example Vibrations of CO_2

Diagram of Stretching and Bending Modes for CO_2.

Solution

CO_2 is a linear molecule and thus has the formula (3N-5). It has 4 modes of vibration (3(3)-5). CO_2 has 2 stretching modes, symmetric and asymmetric. The CO_2 symmetric stretch is not IR active because there is no change in dipole moment because the net dipole moments are in opposite directions and as a result, they cancel each other. In the asymmetric stretch, O atom moves away from the C atom and generates a net change in dipole moments and hence absorbs IR radiation at 2350 cm^{-1}. The other IR absorption occurs at 666 cm^{-1}. CO_2 symmetry with $D_{\infty h}$ CO_2 has a total of four of stretching and bending modes but only two are seen. Two of its bands are degenerate and one of the vibration modes is symmetric hence it does not cause a dipole moment change because the polar directions cancel each other. The vibrational modes are illustrated below:



The vibrational modes of CO_2

Selection Rules of IR

In order for vibrational transitions to occur, they are normally governed by some rules referred to as selection rules.

1. An interaction must occur between the oscillating field of the electromagnetic radiation and the vibrational molecule for a transition to occur. This can be expressed mathematically as

$$\left(\frac{d\mu}{dr}\right)_{r_{eq}} \neq 0$$

$$\triangle v = +1 \text{ and } \triangle J = +1$$

2. This holds for a harmonic oscillator because the vibrational levels are equally spaced and that accounts for the single peak observed in any given molecular vibration. For gases J changes +1 for the R branch and -1 for the P branch.$\triangle J = 0$ is a forbidden transition and hence a q branch for a diatomic will not be present. For any anharmonic oscillator, the selection rule is not followed and it follows that the change in energy becomes smaller. This results in weaker transitions called overtones, then $\triangle v = +2$ (first overtone) can occur, as well as the 2nd overtone $\triangle v = +3$. The frequencies of the 1st and 2nd overtones provides information about the potential surface and about two to three times that of the fundamental frequency.
3. For a diatomic, since μ is known, measurement of u_e provides a value for k, the force constant.

$$k = \left(\frac{d^2V(r)}{dr^2}\right)_{r_{eq}}$$

where k is the force constant and indicates the strength of a bond.

Influence Factors of IR

- **Isotope Effects:** It's been observed that the effect on k when an atom is replaced by an isotope is negligible but it does have an effect on ν due to changes in the new mass. This is because the reduced mass has an effect on the rotational and vibrational behavior.
- **Solvent Effects:** The polarity of solvent will have an influence on the IR spectra of organic compounds due to the interactions between solvent and compounds, which is called solvent effects. If we place a compound, which contains n, pi and pi* orbitals, into a polar solvent, the solvent will stabilizes these three orbitals in different extent. The stabilization effects of polar solvent on n orbital is the largest one, the next larger one is pi* orbital, and the effects on pi orbital is the smallest one. The spectra of n→pi* transition will shift to blue side, which means it will move to shorter wavelengths and higher energies since the polar solvent causes the energy difference between n orbital and pi* orbital to become bigger. The spectra of pi→pi* transition will shift to red side, which means it will move to longer wavelengths and lower energies since the polar solvent causes the energy difference between n orbital and pi* orbital to become smaller.

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

Exercise 4.2.1

Which of the three main processes a molecule can absorb radiation leads to IR absorptions? What

Answer

Absorption of IR radiation is typical of molecular species that have a small energy difference between the rotational and vibrational states.

Exercise 4.2.2

What is key for a molecule to be IR active?

Answer

A criterion for IR absorption is a net change in dipole moment in a molecule as it vibrates or rotates.

Exercise 4.2.3

Define a stretching vibration.

Answer

In a stretching vibration, the distance between two atoms increases and decreases in a rhythmic manner, but the atoms remain aligned along the bond axis.

Exercise 4.2.4

Define a bending vibration.

Answer

In a bending vibration, the positions of the atoms change relative to the bond axis.

Exercise 4.2.5

What are the vibrational modes of the methylene group, CH_2?

Answer

The stretching and bending vibrations of methylene chloride are:

- symmetric stretching
- asymmetric stretching
- wagging
- twisting
- rocking
- scissoring

Exercise 4.2.6

The intensity of C=O stretching is stronger than that of C=C stretching. The C=O also appears at a higher wavenumber than a C=C. Explain it.

Answer

The carbonyl bond is very polar, and absorbs very strongly. The carbon-carbon double bond in most alkenes, in contrast, is much less polar, and thus a stretching vibration does not result in a large change in the overall dipole moment of the molecule. Alkene groups absorb rather weakly compared to carbonyls.

A C=O bond is stronger than a C=C bond. Stronger bonds lead to a higher frequency absorbed due to Hooke's Law.

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4.3: Instrumentation

Learning Objectives

After completing this section, you should be able to:

- have basic understanding of how the IR spectrometer works
- understand the basic components of the IR spectrometer

There are two types of instruments used to measure IR absorption: Fourier transform (FT) spectrometers and dispersive spectrometers. FTIR spectrometers are the most commonly used instruments for obtaining IR spectra. FTIR spectrometers have several prominent advantages:

1. The signal-to-noise ratio of spectrum is significantly higher than the previous generation infrared spectrometers.
2. The accuracy of wavenumber is high. The error is within the range of ± 0.01 cm^{-1}.
3. The scan time of all frequencies is short (approximately 1 s).
4. The resolution is extremely high (0.1 ~ 0.005 cm^{-1}).
5. The scan range is wide (1000 ~ 10 cm^{-1}).
6. The interference from stray light is reduced.

Due to these advantages, FTIR Spectrometers have replaced dispersive IR spectrometers.

The Infrared Spectrometer

Development of IR Spectrometers

Up till FTIR spectrometers, there have been three generations of IR spectrometers.

1. The first generation IR spectrometer was invented in late 1950s. It utilizes prism optical splitting system. The prisms are made of NaCl. The requirement of the sample's water content and particle size is extremely strict. Further more, the scan range is narrow. Additionally, the repeatability is fairly poor. As a result, the first generation IR spectrometer is no longer in use.
2. The second generation IR spectrometer was introduced to the world in 1960s. It utilizes gratings as the monochrometer. The performance of the second generation IR spectrometer is much better compared with IR spectrometers with prism monochrometer, But there are still several prominent weaknesses such as low sensitivity, low scan speed and poor wavelength accuracy which rendered it out of date after the invention of the third generation IR spectrometer.
3. The invention of the third generation IR spectrometer, Fourier transform infrared spectrometer, marked the abdication of monochrometer and the prosperity of interferometer. With this replacement, IR spectrometers became exceptionally powerful. Consequently, various applications of IR spectrometer have been realized.

Dispersive IR Spectrometers

To understand the powerfulness and usefulness of FTIR spectrometer, it is essential to have some background information of dispersive IR Spectrometer. The basic components of a dispersive IR spectrometer include a radiation source, monochromator, and detector. The common IR radiation sources are inert solids that are heated electrically to promote thermal emission of radiation in the infrared region of the electromagnetic spectrum. The monochromator is a device used to disperse or separate a broad spectrum of IR radiation into individual narrow IR frequencies.

Generally, dispersive spectrometers have a double-beam design with two equivalent beams from the same source passing through the sample and reference chambers as independent beams. These reference and sample beams are alternately focused on the detector by making use of an optical chopper, such as, a sector mirror. One beam will proceed, traveling through the sample, while the other beam will pass through a reference species for analytical comparison of transmitted photon wavefront information.

After the incident radiation travels through the sample species, the emitted wavefront of radiation is dispersed by a monochromator (gratings and slits) into its component frequencies. A combination of prisms or gratings with variable-slit mechanisms, mirrors, and filters comprise the dispersive system. Narrower slits gives better resolution by distinguishing more closely spaced frequencies of

radiation and wider slits allow more light to reach the detector and provide better system sensitivity. The emitted wavefront beam (analog spectral output) hits the detector and generates an electrical signal as a response.

Detectors are devices that convert the analog spectral output into an electrical signal. These electrical signals are further processed by the computer using mathematical algorithm to arrive at the final spectrum. The detectors used in IR spectrometers can be classified as either photon/quantum detectors or thermal detectors.

It is the absorption of IR radiation by the sample, producing a change of IR radiation intensity, which gets detected as an off-null signal (e.g. different from reference signal). This change is translated into the recorder response through the actions of synchronous motors. Each frequency that passes through the sample is measured individually by the detector which consequently slows the process of scanning the entire IR region. A block diagram of a classic dispersive IR spectrometer is shown in Figure 4.3.1.

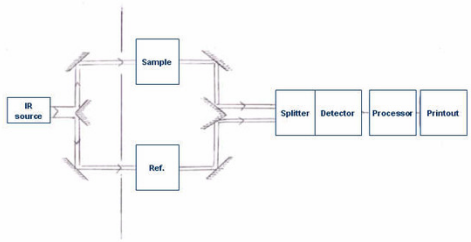

Figure 4.3.1. Simplified representation of a dispersive IR spectrometer.

FTIR Spectrometers

The Components of FTIR Spectrometers

A common FTIR spectrometer consists of a source, interferometer, sample compartment, detector, amplifier, A/D convertor, and a computer. The source generates radiation which passes the sample through the interferometer and reaches the detector. Then the signal is amplified and converted to digital signal by the amplifier and analog-to-digital converter, respectively. Eventually, the signal is transferred to a computer in which Fourier transform is carried out. Figure 4.3.2 is a block diagram of an FTIR spectrometer.

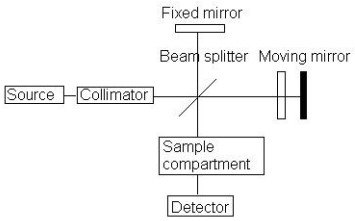

Figure 4.3.2. Block diagram of an FTIR spectrometer

The major difference between an FTIR spectrometer and a dispersive IR spectrometer is the Michelson interferometer.

Michelson Interferometer

The Michelson interferometer, which is the core of FTIR spectrometers, is used to split one beam of light into two so that the paths of the two beams are different. Then the Michelson interferometer recombines the two beams and conducts them into the detector where the difference of the intensity of these two beams are measured as a function of the difference of the paths. Figure 4.3.3 is a schematic of the Michelson Interferometer.

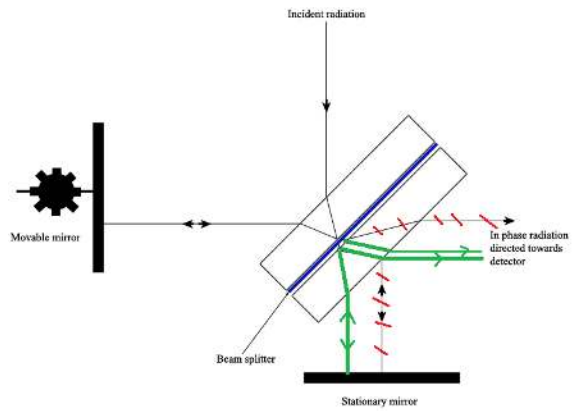

Figure 4.3.3. Schematic of the Michelson interferometer

A typical Michelson interferometer consists of two perpendicular mirrors and a beamsplitter. One of the mirror is a stationary mirror and another one is a movable mirror. The beamsplitter is designed to transmit half of the light and reflect half of the light. Subsequently, the transmitted light and the reflected light strike the stationary mirror and the movable mirror, respectively. When reflected back by the mirrors, two beams of light recombine with each other at the beamsplitter.

If the distances travelled by two beams are the same which means the distances between two mirrors and the beamsplitter are the same, the situation is defined as zero path difference (ZPD). But imagine if the movable mirror moves away from the beamsplitter, the light beam which strikes the movable mirror will travel a longer distance than the light beam which strikes the stationary mirror. The distance which the movable mirror is away from the ZPD is defined as the mirror displacement and is represented by Δ. It is obvious that the extra distance travelled by the light which strikes the movable mirror is 2Δ. The extra distance is defined as the optical path difference (OPD) and is represented by delta. Therefore,

δ=2Δ(4.3.1.1)(4.3.1.1)δ=2Δ

It is well established that when OPD is the multiples of the wavelength, constructive interference occurs because crests overlap with crests, troughs with troughs. As a result, a maximum intensity signal is observed by the detector. This situation can be described by the following equation:

δ=nλ(4.3.1.2)(4.3.1.2)δ=nλ

with n = 0,1,2,3...

In contrast, when OPD is the half wavelength or half wavelength add multiples of wavelength, destructive interference occurs because crests overlap with troughs. Consequently, a minimum intensity signal is observed by the detector. This situation can be described by the following equation:

δ=(n+12)λ(4.3.1.3)(4.3.1.3)δ=(n+12)λ

with n = 0,1,2,3...

These two situations are two extreme situations. If the OPD is neither n-fold wavelengths nor (n+1/2)-fold wavelengths, the interference should be between constructive and destructive. So the intensity of the signal should be between maximum and minimum. Since the mirror moves back and forth, the intensity of the signal increases and decreases which gives rise to a cosine wave. The plot is defined as an interferogram. When detecting the radiation of a broad band source rather than a single-wavelength source, a peak at ZPD is found in the interferogram. At the other distance scanned, the signal decays quickly since the mirror moves back and forth. Figure 4.3.1.44.3.1.4(a) shows an interferogram of a broad band source.

In an infrared spectrometer (Figure 4.3.4) the sample to be analyzed is held in front of an infrared laser beam, in order to do this, the sample must be contained in something, consequently this means that the very container the sample is in will absorb some of the infrared beam.

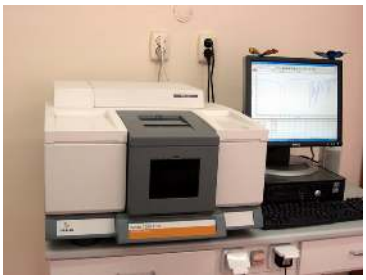

Figure 4.3.4 *An example of a modern benchtop FT-IR spectrometer (Varian Corp.)*

IR Sample Preparation

IR spectra can be obtained from solid, liquid, or gas samples. Nujol mulls and pressed pellets are typically used for collecting spectra of solids, while thin-film cells are used for solution-phase IR spectroscopy. In these methods, infrared radiation is passed through the pellet or thin-film cells. A newer method for obtaining IR spectra uses attenuated total reflectance (ATR), which is discussed below. Gas samples require a special cell for sampling, but are not often used in organic chemistry, so will not be discussed further here.

When preparing a liquid, a drop of neat sample is pressed between two disks. A thin film of solid can be prepared by placing a drop of concentrated solution of the compound in the center of a disk and then allowing the solvent to evaporate. Since all materials have some sort of vibration associated with them pellets and thin-film cells must be considered carefully. If the sample holder has an optical window made of something that absorbs near where your sample does, the sample might not be distinguishable from the optical window of the sample holder. The range that is not blocked by a strong absorbance is known as a *window* (not to be confused with the optical materials of the cell). Windows are an important factor to consider when choosing the method to perform an analysis, as seen in Table 4.3.1 there are a number of different materials each with their own characteristic absorption spectra and chemical properties. Keep these factors in mind when performing analyses and precious sample will be saved. For most organic compounds NaCl works well though it is susceptible to attack from moisture.

Table 4.3.1 Various IR-transparent materials and their solubilities and other notes. M. R. Derrick, D. Stulik, and J. M. Landry, in Scientific Tools in Conservation: Infrared Spectroscopy in Conservation Science. Getty Conservation Institute (1999).

Material	Transparent Ranges (cm^{-1})	Solubility	Notes
NaCl	40,000 - 625	H_{2O}	Easy to polish, hygroscopic
Silica glass	55,000-3,000	HF	Attacked by HF
Quartz	40,000-2,500	HF	Attacked by HF
Sapphire	20,000-1,780	-	Strong
Diamond	40,000-2,500 and 1,800-200	-	Very strong, expensive, hard, useless for pellets
CaF_2	70,000-1,110	Acids	Attacked by acids, avoid ammonium salts
BaF_2	65,000-700	-	Avoid ammonium salts
ZnSe	10,000 - 550	Acids	Brittle, attacked by acids
AgCl	25,000-400	-	Soft, sensitive to light.
KCl	40,000-500	H_2O, Et_2O, acetone	Hygroscopic, soft, easily polished, commonly used in making pellets.
KBr	40,000-400	H_2O, EtOH	Hygroscopic, soft, easily polished, commonly used in making pellets.
CsBr	10,000-250	H_2O, EtOH, acetone	Hygroscopic soft
CsI	10,000-200	H_2O, EtOH, MeOH, acetone	Hygroscopic, soft.
Teflon	5,000-1,200; 1,200-900	-	Inert, disposable
Polyethylene	4,000-3,000; 2,800-1,460; 1,380 - 730; 720- 30	-	Inert, disposable

A common method of preparing solid samples for IR analysis is mulling, which is not a true solution, but a fine dispersion of a solid compound in a viscous liquid. The principle here is by grinding the particles to below the wavelength of incident radiation that will be passing through there should be limited scattering. To suspend those tiny particles, an oil, often referred to as Nujol is used. IR-transparent salt plates are used to hold the sample in front of the beam in order to acquire data. To prepare a sample for IR analysis using a salt plate, first decide what segment of the frequency band should be studied, refer to Table 4.3.1 for the materials best suited for the sample.

Attenuated Total Reflectance- Fourier Transform Infrared Spectroscopy

First publicly proposed in 1959 by Jacques Fahrenfort from the Royal Dutch Shell laboratories in Amsterdam, ATR IR spectroscopy was described as a technique to effectively measure weakly absorbing condensed phase materials. In Fahrenfort's first article describing the technique, published in 1961, he used a hemicylindrical ATR crystal (see Experimental Conditions) to produce single-reflection ATR (Figure 4.3.5). ATR IR spectroscopy was slow to become accepted as a method of characterization due to concerns about its quantitative effectiveness and reproducibility. The main concern being the sample and ATR crystal contact necessary to achieve decent spectral contrast. In the late 1980's FTIR spectrometers began improving due to an increased dynamic range, signal to noise ratio, and faster computers. As a result ATR-FTIR also started gaining traction as an efficient spectroscopic technique. These days ATR accessories are often manufactured to work in conjunction with most FTIR spectrometers.

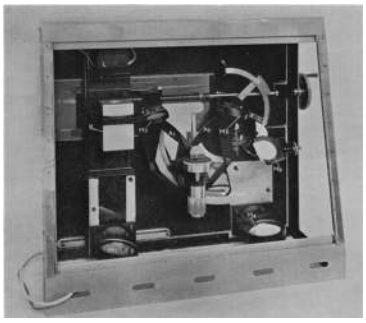

Figure 4.3.5 The first ATR Infrared Spectrometer designed by Jacques Fahrenfort featuring a hemicylindrical ATR crystal. Reproduced from J. Fahrenfort, *Spectrochim. Acta*, 1961, **17**, 698. Copyright: Elsevier (1961).

ATR-FTIR is a physical method of compositional analysis that builds upon traditional transmission FTIR spectroscopy to minimize sample preparation and optimize reproducibility. Sample accessories make obtaining IR spectra of solids and liquids easier and it is not necessary to prepare Nujol mulls or disks. With ATR, infrared radiation is passed through an infrared transmitting crystal with a high refractive index. This allows the radiation to reflect within the crystal. This should be a material that is fully transparent to the incident infrared radiation to give a real value for the refractive index, 4.3.6.

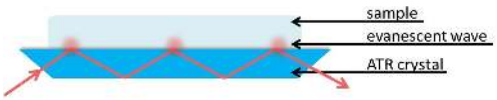

Figure 4.3.6 The ATR crystal shown in blue, within which the incident IR light shown in red is totally reflecting. Above the crystal the evanescent wave is emitted and penetrates the sample.

We can consider the sample to be absorbing in the infrared. Electromagnetic energy will pass through the crystal/sample interface and propagate into the sample via the evanescent wave. This energy loss must be compensated with the incident IR light. Thus, total reflectance is no longer occurring and the reflection inside the crystal is attenuated. If a sample does not absorb, the reflectance at the interface shows no attenuation. Therefore if the IR light at a particular frequency does not reach the detector, the sample must have absorbed it.

The penetration depth of the evanescent wave within the sample is on the order of 1µm. The expression of the penetration depth is given in 4.3.1 and is dependent upon the wavelength and angle of incident light as well as the refractive indices of the ATR crystal and sample. The effective path length is the product of the depth of penetration of the evanescent wave and the number of points that the IR light reflects at the interface between the crystal and sample. This path length is equivalent to the path length of a sample in a traditional transmission FTIR setup.

$$d_p = \frac{\lambda}{2\pi n_1}(sin\omega - (\frac{n_1}{n_2})^2)^{1/2} \tag{4.3.1}$$

Refractive Indices of ATR Crystal and Sample

Typically an ATR attachment can be used with a traditional FTIR where the beam of incident IR light enters a horizontally positioned crystal with a high refractive index in the range of 1.5 to 4, as can be seen in Table 4.3.2 will consist of organic compounds, inorganic compounds, and polymers which have refractive indices below 2 and can readily be found on a database. The most commonly used crystal is zinc selenide.

Table 4.3.2 A summary of popular ATR crystals. Data obtained from F. M. Mirabella, *Internal reflection spectroscopy: Theory and applications*, 15, Marcel Dekker, Inc., New York (1993).

Material	Refractive Index (RI)	Spectral Range (cm^{-1})
Zinc Selenide (ZnSe)	2.4	20,000 - 650
Germanium (Ge)	4	5,500 - 870
Sapphire (Al_2O_3)	1.74	50,000 - 2,000
Diamond (C)	2.4	45,000 - 2,500, 1650 - 200

Single and Multiple Reflection Crystals

Multiple reflection ATR was initially more popular than single reflection ATR because of the weak absorbances associated with single reflection ATR. More reflections increased the evanescent wave interaction with the sample, which was believed to increase the signal to noise ratio of the spectrum. When IR spectrometers developed better spectral contrast, single reflection ATR became more popular. The number of reflections and spectral contrast increases with the length of the crystal and decreases with the angle of incidence as well as thickness. Within multiple reflection crystals some of the light is transmitted and some is reflected as the light exits the crystal, resulting in some of the light going back through the crystal for a round trip. Therefore, light exiting the ATR crystal contains components that experienced different number of reflections at the crystal-sample interface.

Angle of Incidence

It was more common in earlier instruments to allow selection of the incident angle. In all cases for total internal reflection to hold, the angle of incidence must exceed the critical angle and ideally complement the angle of the crystal edge so that the light enters at a normal angle of incidence. These days 45° is the standard angle on most ATR-FTIR setups.

ATR Crystal Shape

For the most part ATR crystals will have a trapezoidal shape as shown in Figure **4.3.6**. This shape facilitates sample preparation and handling on the crystal surface by enabling the optical setup to be placed below the crystal. However, different crystal shapes (Figure **4.3.7**) may be used for particular purposes, whether it is to achieve multiple reflections or reduce the spot size. For example, a hemispherical crystal may be used in a microsampling experiment in which the beam diameter can be reduced at no expense to the light intensity. This allows appropriate measurement of a small sample without compromising the quality of the resulting spectral features.

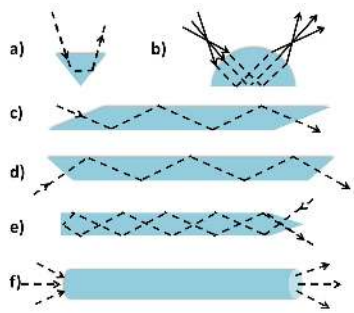

Figure **4.3.7** An assortment of ATR crystal shapes: a)triangular, b)hemispherical, c)parallelogram, d) trapezoidal, e) pentagonal, f)cylindrical. Adapted from F. M. Mirabella, *Internal reflection spectroscopy: Theory and applications*, 15, Marcel Dekker, Inc., New York (1993).

Because the path length of the evanescent wave is confined to the interface between the ATR crystal and sample, the sample should make firm contact with the ATR crystal. The sample sits atop the crystal and intimate contact can be ensured by applying pressure above the sample. However, one must be mindful of the ATR crystal hardness. Too much pressure may distort the crystal and affect the reproducibility of the resulting spectrum.

? Exercise 4.3.1

Why did FTIR spectrometers become the standard over dispersive spectrometers?

Answer

The advantages of FTIR are:

- The signal-to-noise ratio of spectrum is significantly higher than the previous generation infrared spectrometers.
- The accuracy of wavenumber is high.
- The error is within the range of ± 0.01 cm^{-1}.
- The scan time of all frequencies is short (approximately 1 s).
- The resolution is extremely high (0.1 ~ 0.005 cm^{-1}).
- The scan range is wide (1000 ~ 10 cm^{-1}).

- The interference from stray light is reduced.

Essentially, FTIR spectrometers produce more reliable data in a better and faster way.

Exercise 4.3.2

In transmission IR samples, how are solids prepared?

Answer

Nujol mulls and pressed pellets are typically used for collecting spectra of solids.

Exercise 4.3.3

What is the standard angle of incidence for an ATR-FTIR spectrometer?

Answer

These days 45° is the standard angle on most ATR-FTIR setups.

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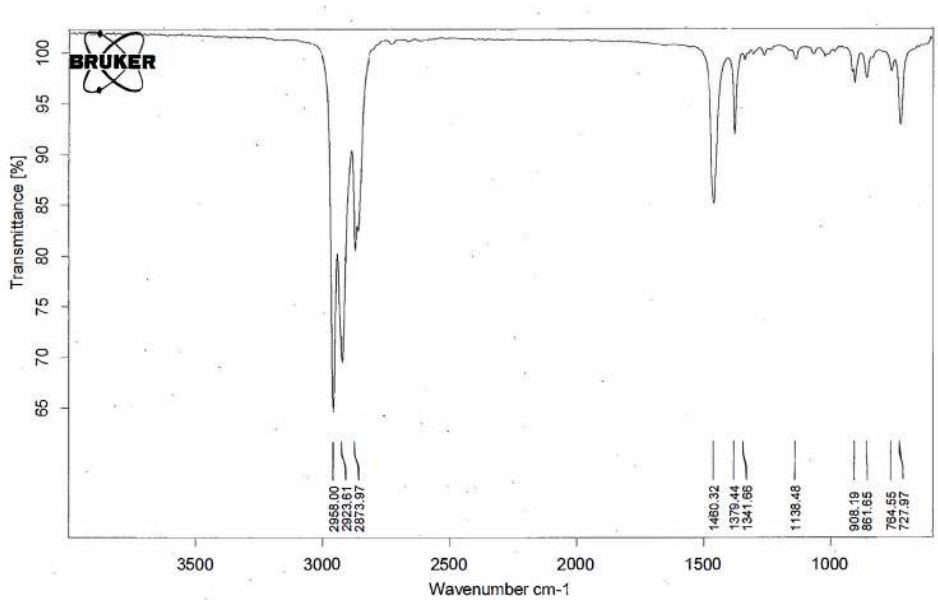
4.4: 4.4 The IR Spectrum

Learning Objectives

After completing this section, you should be able to:

- understand the idea behind why peaks fall at particular wavelengths
- begin to figure out which peaks

The IR spectrum is a graph where the x-axis is frequency and is labeled as wavenumber (cm^{-1}). The y-axis is the amount of light absorbed and labeled as Transmittance (%). This is measuring how much light has been transmitted at a particular frequency. In other words, if all of the light is detected, then the molecule has absorbed no light at that frequency. If you run your finger along the baseline, which is at the top of the spectrum, you can tell when light has been absorbed due to a dip in the line. The dips are actually called peaks. In the theory section of this chapter, it was discussed that different types of bonds will absorb at different frequencies. Below is an IR spectrum of pentane.



Now that we have oriented ourselves with what an IR spectrum looks like, let's think back to the theory of IR spectroscopy and begin to understand why peaks appear as they do.

Origin of Peak Positions, Intensities, and Widths

Peak Positions

The equation below gives the frequency of light that a molecule will absorb, and gives the frequency of vibration of the normal mode excited by that light.

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}$$

ν = frequency in cm^{-1}

k = force constant in N/cm

μ = reduced mass in Kg

There are two variables in the above equation - a chemical bond's force constant and reduced mass. Here, the reduced mass refers to $(M_1M_2)/(M_1+M_2)$ where M_1 and M_2 are the masses of the two atoms in the vibrating bond, respectively. These two molecular properties determine the wavenumber at which a molecule will absorb infrared light. No two chemical substances in the universe have the same force constants and atomic masses, which is why the infrared spectrum of each chemical substance is unique. To

understand the effect of atomic masses and force constant on the positions of infrared bands, table 1 and 2 are shown as an example, respectively.

Table 1. An Example of an Mass Effect

Bond	C-H Stretch in cm^{-1}
C-^{1}H	~3000
C-^{2}D	~2120

In this example, the force constant remains the same, while the reduced masses of C-^{1}H and C-^{2}D are different. Remember, deuterium is one of the isotopes of hydrogen - ^{2}H (or ^{2}D). Here, we simply doubled the mass of the hydrogen atom, the carbon-hydrogen stretching vibration is reduced by over 800 cm^{-1}. Mass is inversely proportional to the wavenumber.

Table 2. An Example of a Bond Strength Effect

Bond	C-H Stretch in cm^{-1}
Csp^{3}-H	~3000
Csp_{2}-H	~3100
Csp-H	~3330

In this example, the reduced mass remains the same, while the force constant changes. Here, we can see that as we increase the strength of the bond (or increase the force constant), the wavenumber increase. Therefore, force constant is proportional to the frequency.

The Origin of Peak Intensities

The different vibrations of the different functional groups in the molecule give rise to bands of differing intensity. This is because $\frac{\partial \mu}{\partial x}$ is different for each of these vibrations. For example, the most intense band in the spectrum of pentane shown above is at 2958 cm^{-1} and is due to stretching of the C-H bond. One of the weaker bands in the spectrum of pentane is at 727 cm^{-1}, and it is due to long-chain methyl rock of the carbon-carbon bonds in pentane. The change in dipole moment with respect to distance for the C-H stretching is greater than that for the C-C rock vibration, which is why the C-H stretching band is the more intense than C-C rock vibration.

Another factor that determines the peak intensity in infrared spectra is the concentration of molecules in the sample. The equation below that relates concentration to absorbance is Beer's law,

$$A = \varepsilon l c$$

A = absorbance

ε = absorptivity

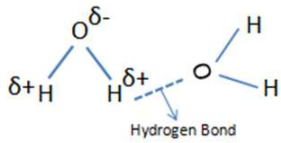
l = pathlength

c = concentration

The absorptivity is the proportionality constant between concentration and absorbance. The absorptivity is an absolute measure of infrared absorbance intensity for a specific molecule at a specific wavenumber.

The Origin of Peak Widths

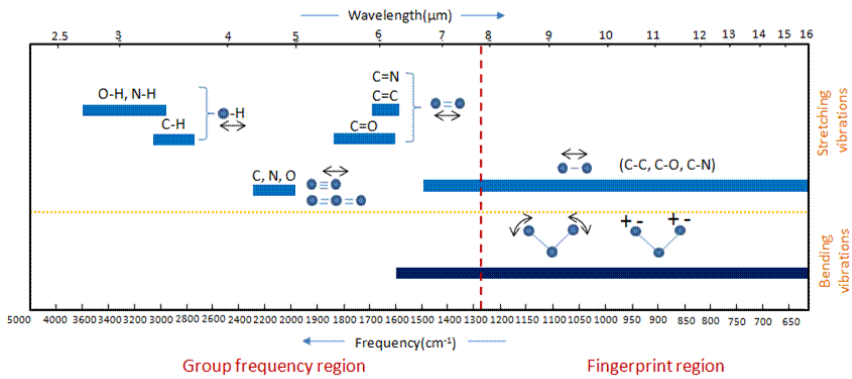
In general, the width of infrared bands for solid and liquid samples is determined by the number of chemical environments which is related to the strength of intermolecular interactions such as hydrogen bonding. The figure below shows hydrogen bond in water molecules and these water molecules are in different chemical environments. Because the number and strength of hydrogen bonds differs with chemical environment, the force constant varies and the wavenumber differs at which these molecules absorb infrared light.



In any sample where hydrogen bonding occurs, the number and strength of intermolecular interactions varies greatly within the sample, causing the bands in these samples to be particularly broad. This is common in alcohols and carboxylic acids. When intermolecular interactions are weak, the number of chemical environments is small, and narrow infrared bands are observed.

The Origin of Group Frequencies

An important observation made by early researchers is that many functional group absorb infrared radiation at about the same wavenumber, regardless of the structure of the rest of the molecule. For example, C-H stretching vibrations usually appear between 3300 and 2800 cm^{-1} and carbonyl (C=O) stretching vibrations usually appear between 1800 and 1600 cm^{-1}. This makes these bands diagnostic markers for the presence of a functional group in a sample. These types of infrared bands are called group frequencies because they tell us about the presence or absence of specific functional groups in a sample.



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

Exercise 4.4.1

Why do carbon-nitrogen triple bonds appear at a higher wavenumber than carbon-nitrogen double bonds?

Answer

If we look at the equation for frequency, there are two variables. The reduced mass and the bond strength. In this case, our reduced mass will remain the same because we are looking at bonds with the same atoms attached - carbon and nitrogen. The difference is bond strength. A triple bond is a stronger bond than a double bond. Bond strength and frequency are proportional to each other, so the stronger the bond, the larger the wavenumber.

Exercise 4.4.2

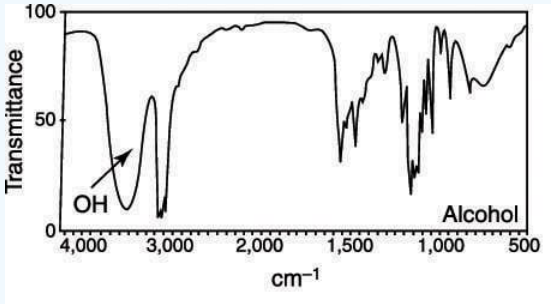
Would you expect the C=O bond to have a more intense or less intense peak?

Answer

Since there is a greater dipole change in the C=O bond stretch, this will lead to a more intense peak.

Exercise 4.4.3

Alcohols typically show up as a very wide broad (3322 cm^{-1}) as can be seen in the figure below. Why does the peak show up as broad?



Answer

The width of infrared bands for solid and liquid samples is determined by the number of chemical environments which is related to the strength of intermolecular interactions such as hydrogen bonding. Alcohols have the ability to hydrogen bond, which creates the broad band.

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4.5: 4.5 IR Data Table

Learning Objectives

- Understand where certain group frequencies are
- Be able to read and understand the data table for IR spectroscopy

As stated in the previous section, similar bonds will show up grouped near the same frequency because they tell us about the presence or absence of specific functional groups in a sample. From there, a data table of approximate frequencies for different types of bonds has been created to use to help IR spectrum analysis.

Table of Common IR Absorptions.

Approximate Frequency (cm^{-1})	Description	Bond Vibration	Notes
3500 - 3200	broad, round	O-H	much broader, lower frequency (3200-2500) if next to C=O
3400-3300	weak, triangular	N-H	stronger if next to C=O
3300	medium-strong	=C-H (sp C-H)	
3100-3000	weak-medium	=C-H (sp2 C-H)	can get bigger if lots of bonds present
3000-2900	weak-medium	-C-H (sp3 C-H)	can get bigger if lots of bonds present
2800 and 2700	medium	C-H in O=C-H	two peaks; "alligator jaws"
2250	medium	C≡N	
2250-2100	weak-medium	C≡C	stronger if near electronegative atoms
1800-1600	strong	C=O	lower frequency (1650-1550) if attached to O or N middle frequency if attached to C, H higher frequency (1800) if attached to Cl
1650-1450	weak-medium	C=C	lower frequency (1600-1450) if conjugated (i.e. C=C-C=C) often several if benzene present
1450	weak-medium	H-C-H bend	
1300 - 1000	medium-strong	C-O	higher frequency (1200-1300) if conjugated (i.e. O=C-O or C=C-O)
1250-1000	medium	C-N	
1000-650	strong	C=C-H bend	often several if benzene present

Note: strong, medium, weak refers to the length of the peak (in the y axis direction).

Note: spectra taken by ATR method (used at CSB/SJU) have weaker peaks between 4000-2500 cm^{-1} compared to reference spectra taken by transmittance methods (typical on SDBS and other sites).

Exercise 4.5.1

What wavenumber range would you predict the triple bond region to be?

Answer

2200 - 2500 cm^{-1}

Exercise 4.5.2

How could you determine the presence of an aldehyde and rule out a ketone?

Answer

The aldehyde would have peaks at 2700 and 2800 cm-1, whereas the ketone would lack these. The absorption is due to the the Csp^2-H bond.

Exercise 4.5.3

How can you tell the difference between and alcohol and a carboxylic acid?

Answer

Here the main point of difference is either the presence of a carbonyl (C=O) or its absence. The carboxylic acid contains a C=O, so you would expect a peak somewhere between 1800-1600 cm^{-1}, whereas an alcohol would not have a peak here.

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4.6: Interpretation

Learning Objectives

- After completing this section, you should be able to
- be able to read an IR spectrum
- understand where the different regions for bonds in the IR spectrum are
- determine what type of hydrocarbon you have in your molecule

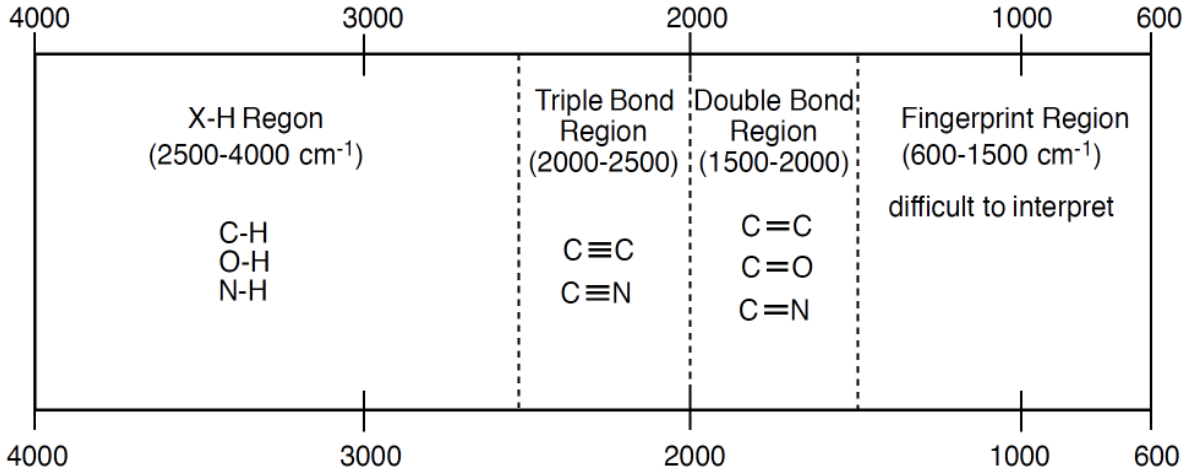
When analyzing IR spectra, there are a few things to remember:

1. You are looking to determine what functional groups are a part of a molecule. This is not a method for complete elucidation of a structure for the molecule.

2. You do NOT need to analyze every single peak. For example, the fingerprint region (1500 - 600 cm^{-1}) is a forest of peaks, so this region is often ignored in analysis.

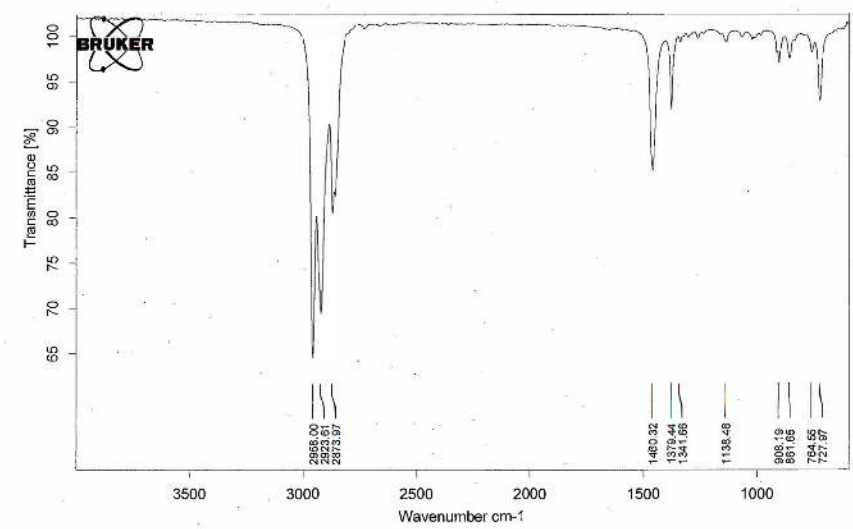
3. Remember, similar functional groups will have similar frequencies, which also indicates certain bonds will fall in the same region.

From this, different regions have been determined by previous research. The hydrogen bond region falls from 4000 to 2500 cm^{-1}. This is the area you will find all of your O-H, N-H, and C-H bonds that typically appear in organic molecules. The next region is the triple bond region (2500 - 2000 cm^{-1}), where the C≡C and C≡N bonds commonly found in organic molecules will absorb. The triple bond region leads into the double bond region (2000 - 1500 cm^{-1}). Here you will find the C=C, C=O, and C=N bonds. Finally, the fingerprint region is 1500 - 600 cm^{-1}, where all the single bonds will be found with the exception of some of the bonds to hydrogen that are found in the hydrogen bond region. Below is an image that summarizes what was just described. It is very helpful to have an idea of where these regions are when interpreting an IR spectrum, even with the data table in hand.

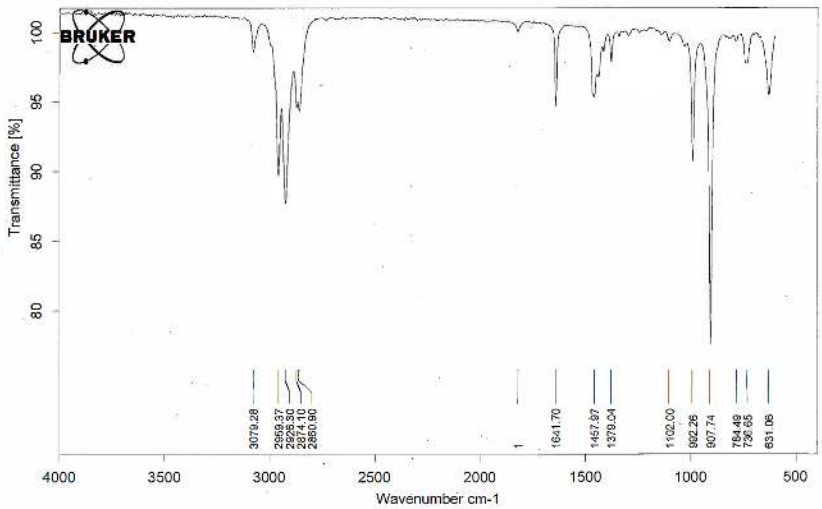


In alkanes, which have very few bands, each band in the spectrum can be assigned:

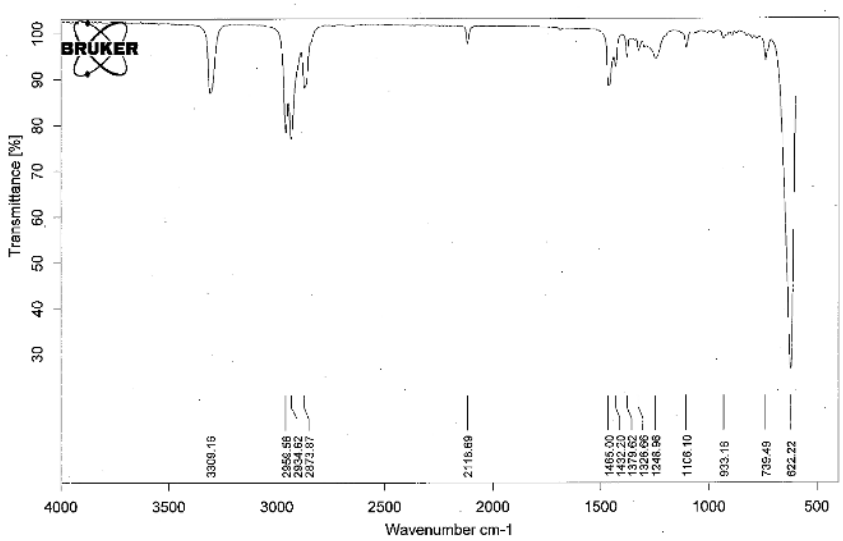
- Let's take a deeper look at pentane. Since most organic compounds have these features, these C-H vibrations are usually not noted when interpreting a routine IR spectrum, which appear at 2873 - 2958 cm^{-1} in this spectrum. Note that the change in dipole moment with respect to distance for the C-H stretching is greater than that for others shown, which is why the C-H stretch band is the more intense. The peak at 1460 cm^{-1}, is due to C-H scissoring. 1379 cm^{-1} is a methyl rock. The C-H scissoring and methyl rock an often get lost in the fingerprint region when looking at more complex molecules. Since so many molecules with have similar peaks to an alkane, we can consider these our baseline. Therefore, the regions that will be of interest will be the hydrogen bond region, triple bond region, and double bond region when determining what functional groups are present or if there are other characteristic functional groups present.



In spectrum of 1-hexene, a terminal alkene, is shown below. Here will will look for differences compared to pentane. For alkenes, there will be a Csp^2-H peak in the hydrogen bond region (if there are hydrogens attached to the double bond carbons as in this case) and the C=C bond. For 1-hexene, the Csp^2-H peak is at 3079 cm^{-1} and the C=C bond is at 1642 cm-1. At 992 cm^{-1} and 907 cm^{-1}, there are peaks due to the =C-H bend, but often get lost in the fingerprint region, so will not be a notable peak.



The spectrum of 1-hexyne, a terminal alkyne, is shown below. The notable peaks for the alkyne are the peak greater than 3000 cm^{-1} and the peak in the triple bond region. In 1-hexyne, there is a peak at 3309 cm^{-1}, which is due to the Csp-H bond. The other peak of note is at 2118 cm^{-1} for the C≡C. We can ignore the peaks at 2873 cm^{-1} to 2959 cm^{-1} because these are your Csp^3-H bonds, which are in so many organic molecules that they are not distinctive to the triple bond. This goes for the fingerprint region peaks as well.



Here, we have looked at hydrocarbons, but these are not the only functional groups to consider in organic molecules. In the next section, the focus will be on functional groups containing a heteroatom.

? Exercise 4.6.1

What regions of the IR would you focus on to determine if you have an alkane or alkene?

Answer

If we use the alkane as our baseline, the regions that would stick out for an alkene are the hydrogen bond region above 3000 cm^{-1} and the double bond region.

? Exercise 4.6.2

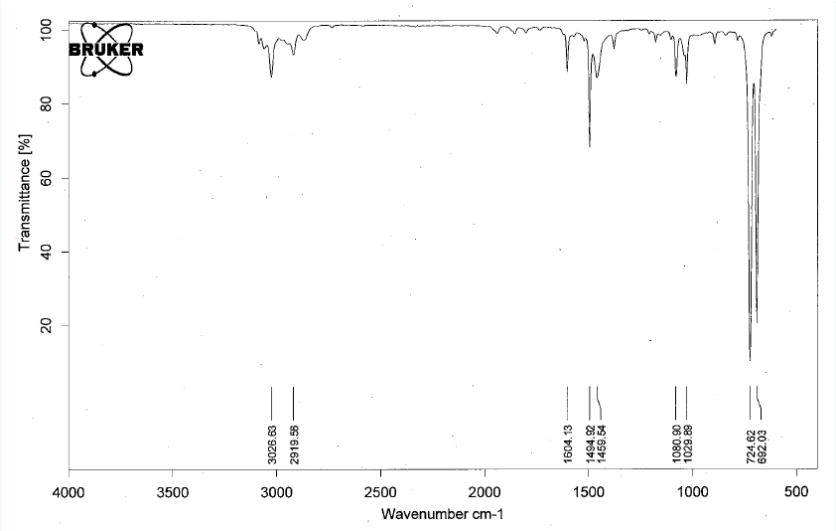
What two regions do you find the alkyne notable peaks?

Answer

The hydrogen bond region for the Csp-H bond and the triple bond region for the carbon-carbon triple bond.

? Exercise 4.6.3

Below is a spectrum of toluene. How does it differ from a plain alkene like 1-hexene?



Answer

Both still have a peak around 3000 cm^{-1} for the Csp2-H bond. However, due to conjugation the C=C shifts to a lower wavenumber in an aromatic molecule. It shifts to about 1600 cm^{-1} due to conjugation.

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4.7: 4.7 Identifying Characteristic Functional Groups

Learning Objectives

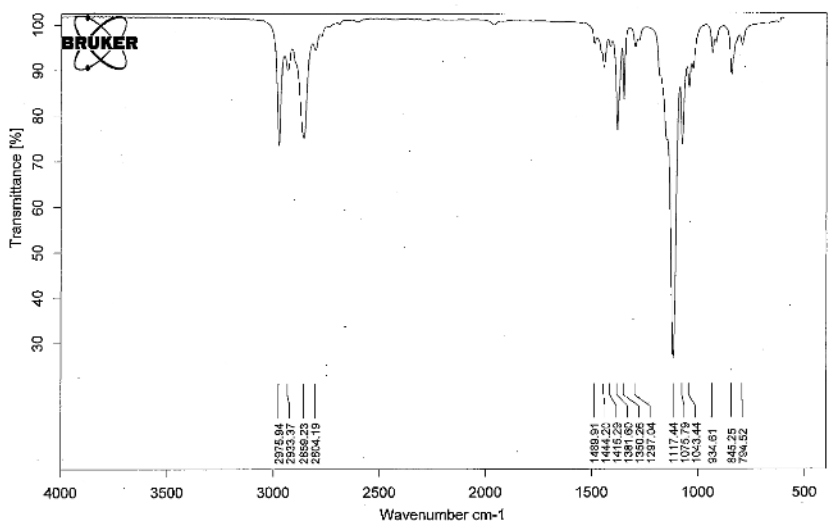
After completing this section, you should be able to

- describe how the so-called “fingerprint region” of an infrared spectrum can assist in the identification of an unknown compound.
- be able to use an infrared spectrum to determine the presence of functional groups, such as alcohols, amines and carbonyl groups, in an unknown compound, given a list of infrared absorption frequencies.
- identify the broad regions of the infrared spectrum in which occur absorptions caused by
  - N−H, C−H, and O−H
  - C≡C and C≡N
  - C=O and C=C

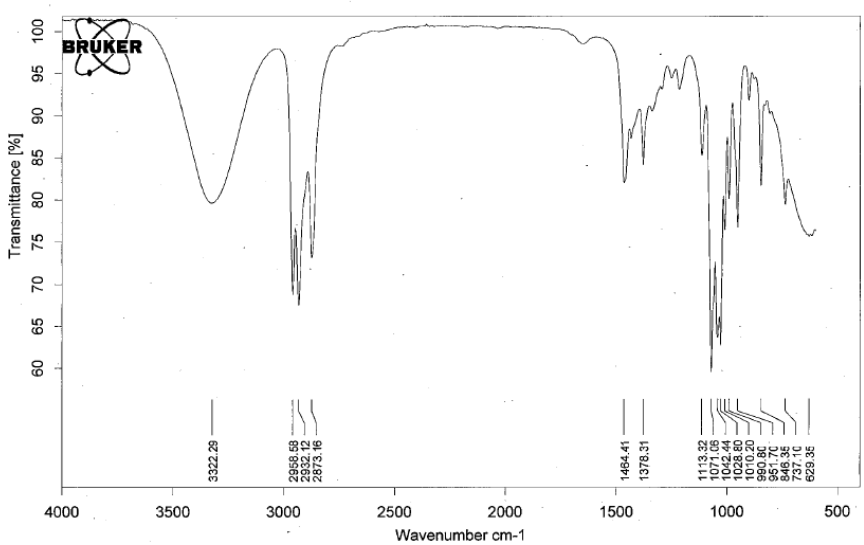
One of the most common application of infrared spectroscopy is to the identification of organic compounds. In this section, we will focus key IR peaks for common functional groups in organic chemistry. We will focus on functional groups with OH, NH, C-O, C=O, and C≡N. It is possible to identify functional groups such as tertiary amines and ethers, but the characteristic peaks for these groups are considerably more subtle and/or variable, and often are overlapped with peaks from the fingerprint region. This means you may or may not actually be able to determine if they are present as a functional group in your molecule.

Functional Groups Containing the C-O Bond

- Ethers have IR absorptions associated with both the C-O stretching vibrations.
  - The figure below shows the spectrum of diethyl ether.
  - Notable peak: C-O stretch at 1117 cm^{-1}. Note: Since this falls in the fingerprint region, it can be hard to interpret sometimes.

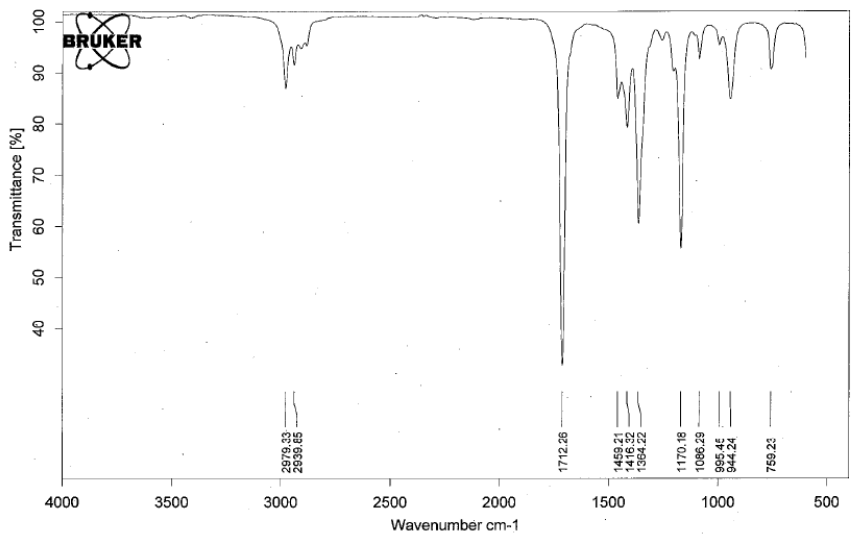


- Alcohols have IR absorptions associated with both the O-H and the C-O stretching vibrations.
  - The figure below shows the spectrum of ethanol.
  - Notable peaks: the very broad, strong band of the O–H stretch at 3322 cm^{-1} and C-O stretch at 1113 cm^{-1}.

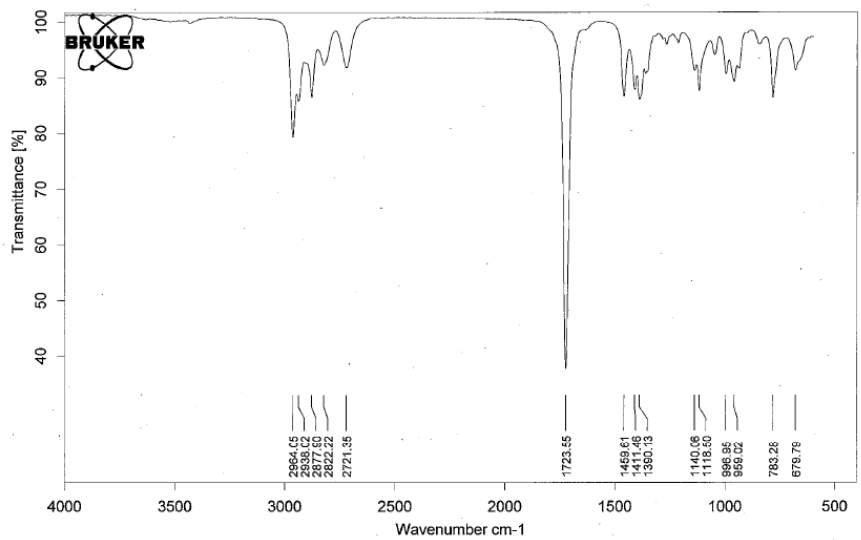


Functional Groups Containing the C=O Bond

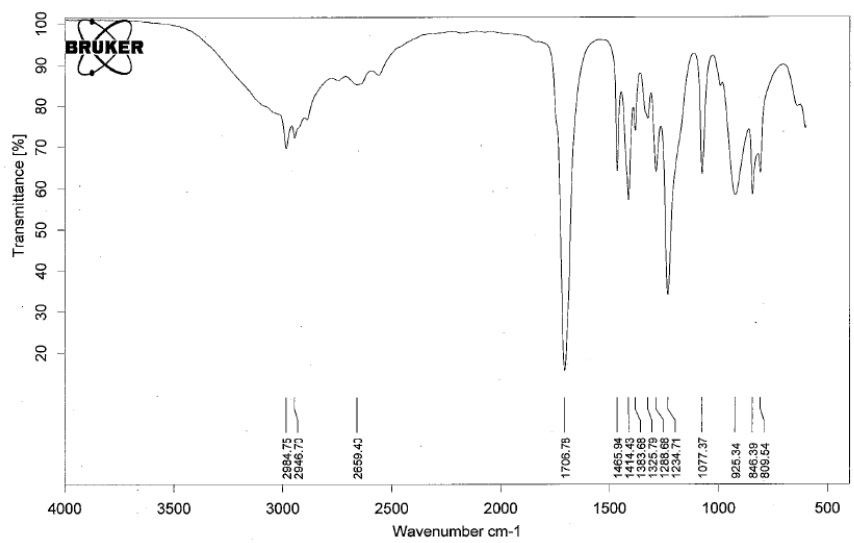
- Ketones have IR absorptions associated with the C=O bond.
  - Below is a spectrum of 2-butanone.
  - Notable peak: the strong band at 1712 cm^{-1} for the C=O.
  - Note: for conjugated ketones, the carbonyl peak will shift 20-30 cm^{-1} lower.



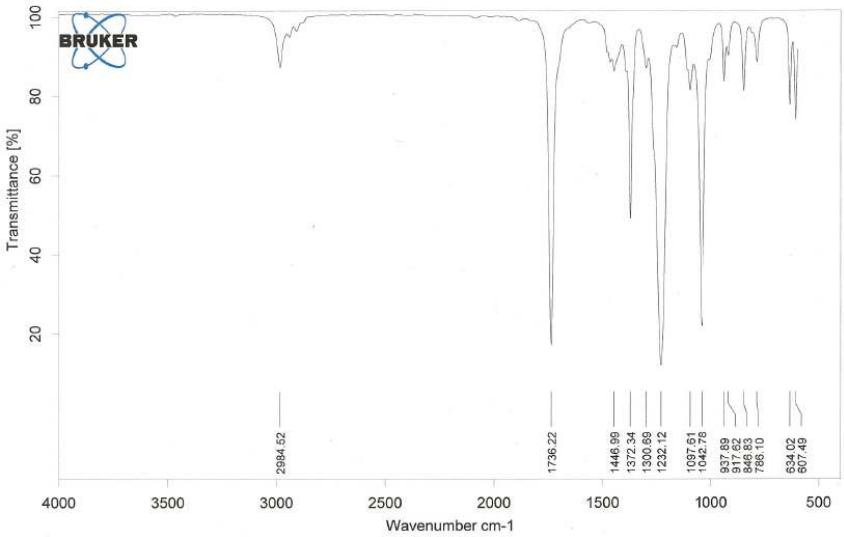
- Aldehydes have IR absorptions associated with the C=O bond and the aldehyldic proton.
  - Below is a spectrum of butanal.
  - Notable peaks: the strong band at 1723 cm^{-1} for the C=O and for the aldehyldic proton there are two peaks at 2822 cm^{-1} and 2721 cm^{-1}.
  - Note: for conjugated aldehydes, the carbonyl peak will shift 20-30 cm^{-1} lower.



- Carboxylic acids have IR absorptions associated with the C=O bond and the carboxylic acid proton.
  - Below is a spectrum of propanoic acid.
  - Notable peaks: the strong band at 1706 cm^{-1} for the C=O and for the carboxylic acid proton is very broad band from 3100 to 2800 cm^{-1}. The exact position of this broad band depends on whether the carboxylic acid is saturated or unsaturated, dimerized, or has internal hydrogen bonding.
  - Note: for conjugated carboxylic acids, the carbonyl peak will shift 20-30 cm^{-1} lower.

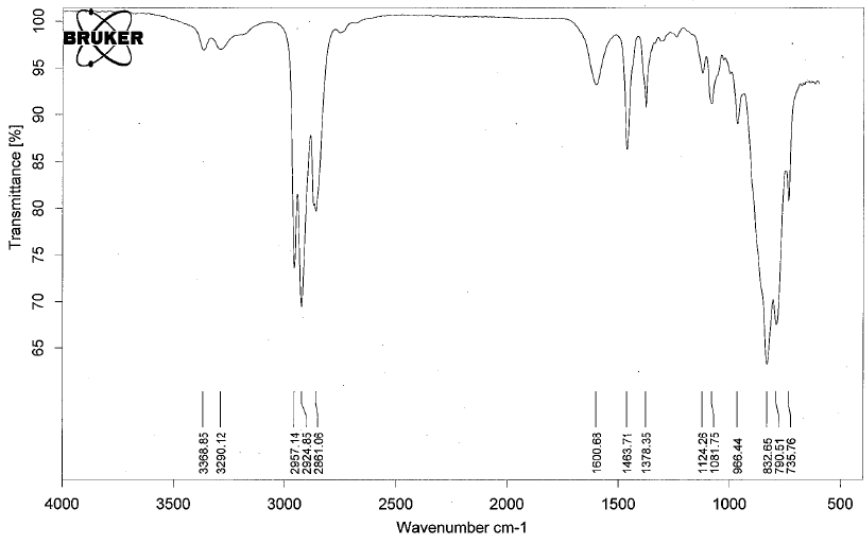


- Esters have IR absorptions associated with the C=O bond and the C-O bond.
  - Below is a spectrum of ethyl acetate.
  - Notable peaks: the strong band at 1736 cm^{-1} for the C=O and for the C-O bond is at 1232 cm^{-1}. Depending on the fingerprint region, it may be hard to determine the C-O bond peak.
  - Note: for conjugated esters, the carbonyl peak will shift 20-30 cm^{-1} lower.

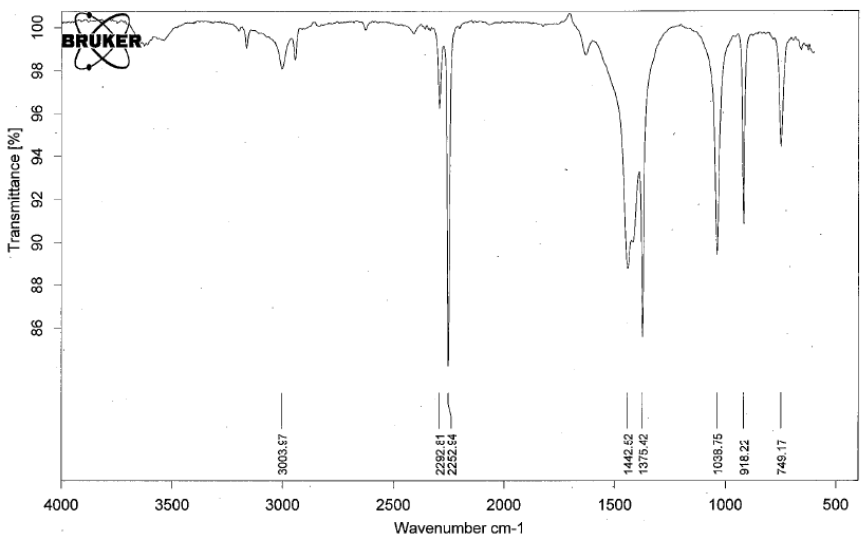


Organic Nitrogen Compounds

- Amines have IR absorptions associated with the N-H bond. There is a C-N peak as well, but it is often buried in the fingerprint region and difficult to discern.
  - Below is a spectrum of butylamine.
  - Notable peaks: the bands at 3368 cm^{-1} and 3290 cm^{-1}.
  - Note: 2 peaks in the range 3400 - 3300 cm^{-1} indicates a primary amine, 1 peak in this range indicates a secondary amine. A tertiary amine will not have a peak in this region due to the lack of a N-H bond.



- Nitriles have IR absorptions associated with the C≡N bond. There is a C-N peak as well, but it is often buried in the fingerprint region and difficult to discern.
  - Below is a spectrum of acetonitrile.
  - Notable peaks: the band at 2252 cm^{-1}.



Organic Compounds Containing Halogens

- Alkyl halides are compounds that have a C–X bond, where X is a halogen: bromine, chlorine, fluorene, or iodine.
  - The spectrum of propyl chloride is shown below.
  - There are stretches due to the C-Cl, but they are located in the fingerprint region and difficult to discern from other peaks.

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

? Exercise 4.7.1

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

A) 1700 cm^{-1}

B) 2250 cm^{-1}

C) 1700 cm^{-1} and 2510-3000 cm^{-1}

Answer

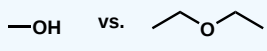
A) Carbonyl: C=O bond

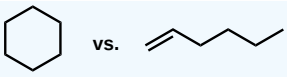
B) Nitrile: C≡N bond

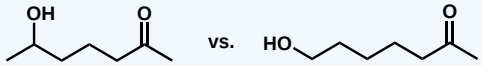
C) Carboxylic acid: for the C=O at 1700 cm^{-1} and the broad OH at 2510-3000 cm^{-1}

? Exercise 4.7.2

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

A) 

B) 

C) 

Answer

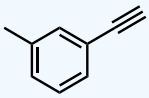
A) A OH peak will be present around 3300 cm^{-1} for methanol and will be absent in the ether.

B) 1-hexene will have a alkene peak around 1650 cm^{-1} for the C=C and there will be another peak around 3100 cm^{-1} for the sp^2 C-H group on the alkene, which will both be absent in cyclohexane

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

Exercise 4.7.3

3-Ethynyltoluene has the following spectrum. What notable peaks can you identify in the spectrum.



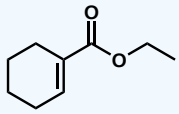
Source: SDBSWeb : http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, 2 December 2016)

Answer

Frequency (cm^{-1})	Functional Group
3200	C≡C-H
3050	Csp^2-H
2100	C≡C
1610	C=C

Exercise 4.7.4

What absorptions would the molecule below have in an IR spectrum?



Answer

Frequency (cm^{-1})	Functional Group
3000-3100	C=C-H
1710	C=O
1610	C=C
1100	C-O

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4.8: 4.8 Infrared Spectroscopy Problems

Learning Objectives

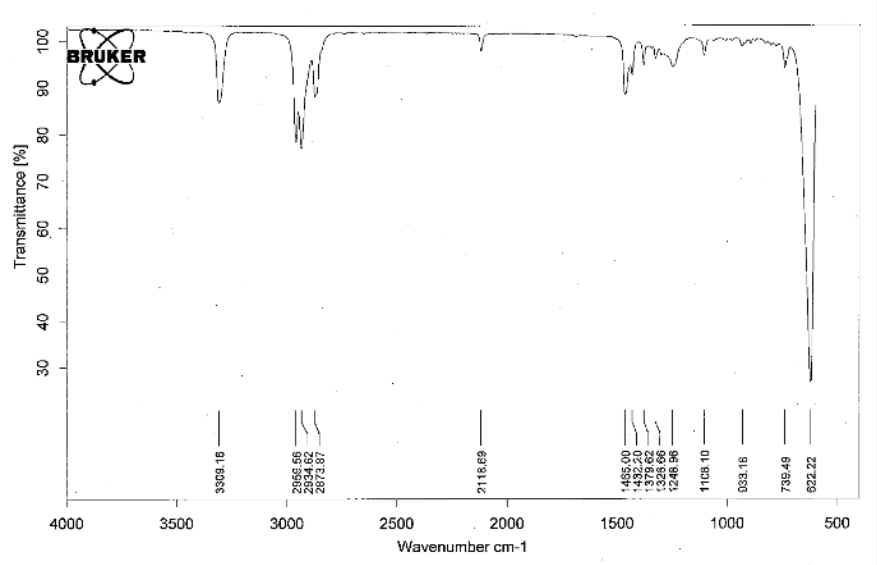
After completing this section, you should be able to

- determine functional groups in an IR spectrum

Here are some problems for IR analysis.

Exercise 4.8.1

What functional group is present in the spectrum below?

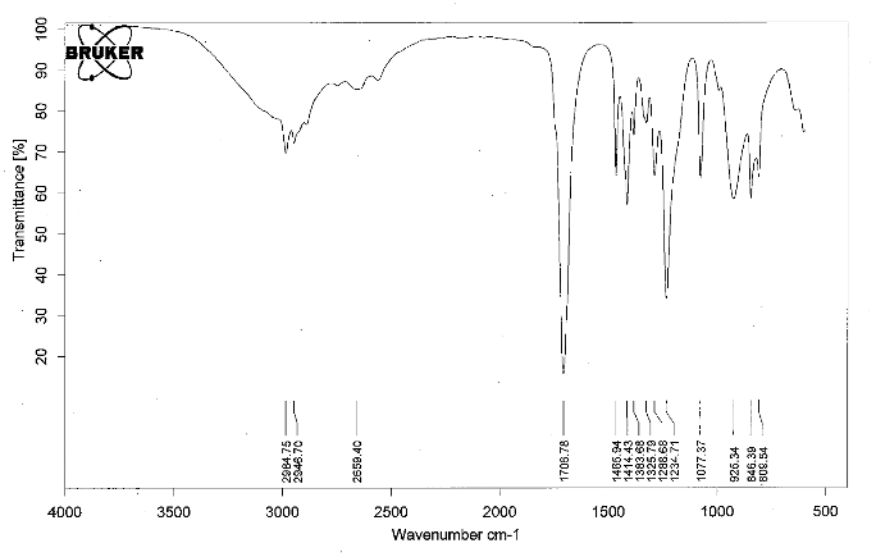


Answer

Alkyne

Exercise 4.8.2

What functional group is present in the spectrum below?

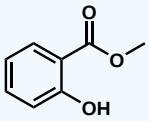


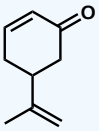
Answer

Carboxylic Acid

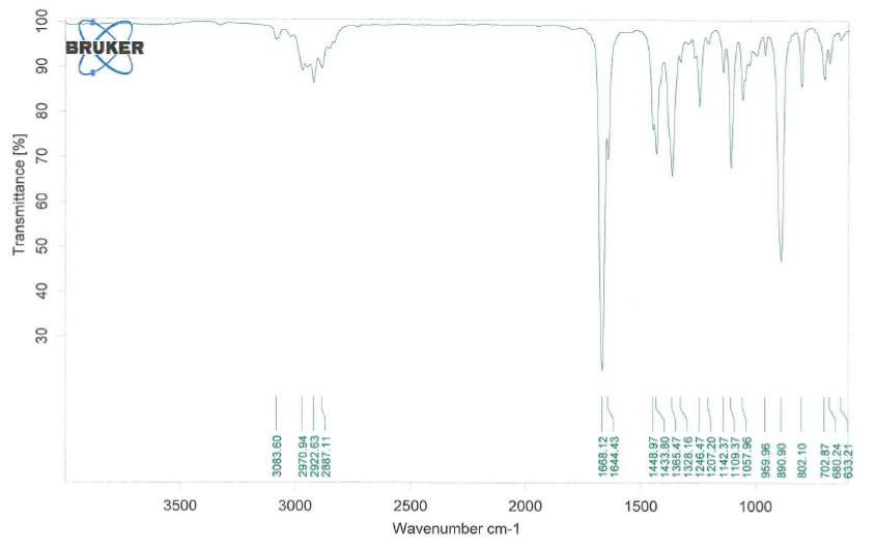
? Exercise 4.8.3

Which IR spectrum goes with which molecule below?

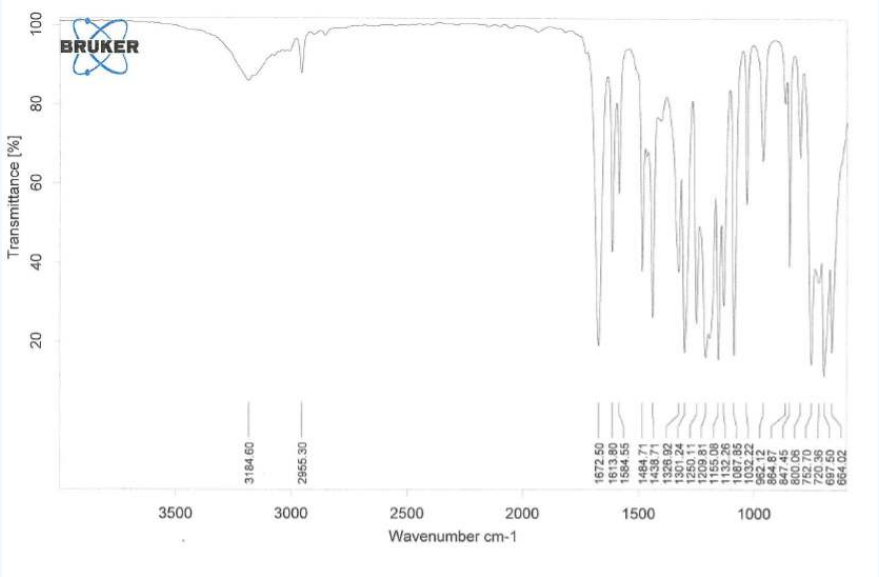
Molecule A: 

Molecule B: 

IR spectrum 1:



IR spectrum 2:



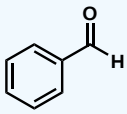
Answer

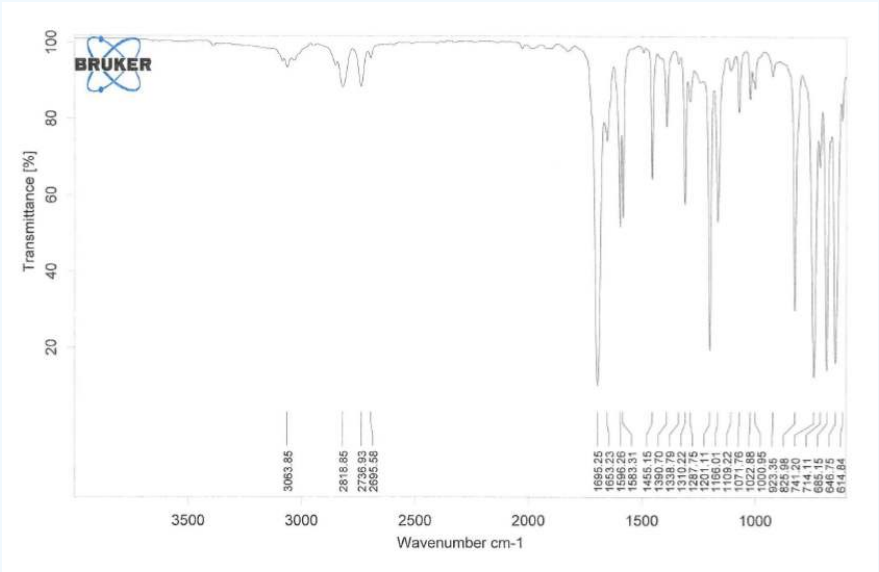
Molecule A is Spectrum 2.

Molecule B is Spectrum 1.

? Exercise 4.8.4

What notable peaks in the IR spectrum verify that benzaldehyde is present?





Answer

Frequency (cm^{-1})	Functional Group
3063	Csp2-H
2818 and 2736	aldehyldic proton
1695	C=O
1653-1455	aromatic ring

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4.9: Application

Learning Objectives

After completing this section, you should be able to

- who uses IR spectroscopy and why

Infrared spectroscopy, an analytical technique that takes advantage of the vibrational transitions of a molecule, has been of great significance to scientific researchers in many fields such as protein characterization, nanoscale semiconductor analysis and space exploration.

The most common application of IR spectroscopy is determining the functional groups present or absent in a molecule. Chemists often synthesize a molecule and need to determine if they made it or not and the presence or absence of a functional group could indicate whether or not the chemist made the molecule or not. For example, if one is performing a synthesis and oxidizes an alcohol to an aldehyde, the IR spectrum could help deduce quickly if you made the product or not. If the alcohol band disappears and the carbonyl band appears, this would be proof that the alcohol did in fact oxidize to the aldehyde. Since different molecules with different combination of atoms produce their unique spectra, infrared spectroscopy can be used to qualitatively identify substances. In addition, the intensity of the peaks in the spectrum is proportional to the amount of substance present, enabling its application for quantitative analysis.

Infrared spectroscopy is used across a wide variety of industries to monitor substances, since it is an simple and reliable technique. Environmental scientists use IR for detecting industrial pollutants. This can be to monitor air quality in big cities, such as Tokyo or London, to monitoring the methane levels in arctic circle. IR helps the environmental scientists study the pollutants or greenhouse gases and how it effects the everyday life.

In art conservation, IR spectroscopy is used to help identify what pigments, adhesives, fibers, plastics, and binders were used. The ability to know what molecular structures may be present in the artwork allows conservationists to determine the best way possible to preserve or clean the art. This helps the longevity of these important pieces of art and history persevere over time for many to enjoy and learn from.

Reference

1. Settle, F. A. *Handbook of instrumental techniques for analytical chemistry*; Prentice Hall PTR: Upper Saddle River, NJ, **1997**.
2. Heigl, J. J.; Bell, M.; White, J. U. *Anal. Chem.*1947, *19*, 293.
3. Baker, A. W. *J. Phys. Chem.* **1957**, *61*, 450.
4. Kamariotis, A.; Boyarkin, O. V.; Mercier, S. R.; Beck, R. D.; Bush, M. F.; Williams, E. R.; Rizzo, T. R. *J. Am. Chem. Soc.* **2006**, *128*, 905.
5. Stuart, B. *Infrared spectroscopy fundamentals and applications*; J. Wiley: Chichester, Eng.; Hoboken, N.J., **2004**.
6. Günzler, H.; Heise, H. M. *IR spectroscopy: an introduction*; Wiley-VCH: Weinheim, **2002**.
7. Wartewig, S. *IR and Raman spectroscopy: fundamental processin;* Wiley-VCH: Weinheim, **2003**.

Outside Links

- NIST Chemistry WebBook: http://webbook.nist.gov/
- Wikipedia: http://en.Wikipedia.org/wiki/Infrared_spectroscopy
- Labmate: https://www.labmate-online.com/news/...troscopy/57765

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4.10: 4.S Summary

Concepts & Vocabulary

4.2 Theory

- Molecules can absorb light energy by three different processes and IR absorptions occur with small differences between the rotational and vibrational modes.
- IR absorption is a net change in dipole moment in a molecule as it vibrates or rotates.
- The absorption of IR radiation by a molecule can be likened to two atoms attached to each other by a massless spring often based using Hooke's Law.
- The bond of a molecule experiences various types of vibrations and rotations since they are not stationary and to fluctuate continuously, which are defined by stretching and bending modes.
- A molecule consisting of (N) number of atoms has a total of 3N degrees of freedom, corresponding to the Cartesian coordinates of each atom in the molecule.
- The larger the molecule, the more complex the vibrational modes.

4.3 Instrumentation

- There are two types of instruments used to measure IR absorption: Fourier transform (FT) spectrometers and dispersive spectrometers.
- The basic components of a dispersive IR spectrometer include a radiation source, monochromator, and detector.
- Dispersive spectrometers have a double-beam design with two equivalent beams from the same source passing through the sample and reference chambers as independent beams.
- A common FTIR spectrometer consists of a source, interferometer, sample compartment, detector, amplifier, A/D convertor, and a computer.
- The major difference between an FTIR spectrometer and a dispersive IR spectrometer is the Michelson interferometer.
- The Michelson interferometer, which is the core of FTIR spectrometers, is used to split one beam of light into two so that the paths of the two beams are different.
- IR spectra can be obtained from solid, liquid, or gas samples.

4.4 The IR Spectrum

- The IR spectrum is a graph where the x-axis is frequency and is labeled as wavenumber (cm^{-1}).
- The y-axis is the amount of light absorbed and labeled as Transmittance (%).
- The spectrum is measuring how much light has been transmitted at a particular frequency.
- Bond strength and reduced mass are the two molecular properties determine the wavenumber at which a molecule will absorb infrared light.
- No two chemical substances in the universe have the same force constants and atomic masses, which is why the infrared spectrum of each chemical substance is unique.
- Peak intensity is determined by dipole moment and the concentration of the sample.
- The width of infrared bands for solid and liquid samples is determined by the number of chemical environments which is related to the strength of intermolecular interactions such as hydrogen bonding.
- An important observation made by early researchers is that many functional group absorb infrared radiation at about the same wavenumber, regardless of the structure of the rest of the molecule.

4.5 IR Data Table

- Since similar functional groups appear at similar frequencies, a data table was curated for scientists to use as a guide for where they would expect certain peaks.

4.6 Interpretation

- The hydrogen bond region falls from 4000 to 2500 cm^{-1}. This is the area you will find all of your O-H, N-H, and C-H bonds that typically appear in organic molecules.

- The next region is the triple bond region (2500 - 2000 cm^{-1}), where the C≡C and C≡N bonds commonly found in organic molecules will absorb.
- The double bond region (2000 - 1500 cm^{-1}). Here you will find the C=C, C=O, and C=N bonds.
- The fingerprint region is 1500 - 600 cm^{-1}, where all the single bonds will be found with the exception of some of the bonds to hydrogen that are found in the hydrogen bond region.
- You are looking to determine what functional groups are a part of a molecule.
- You do NOT need to analyze every single peak.

4.7 Identifying Characteristic Functional Groups

- Ethers have IR absorptions associated with both the C-O stretching vibrations.
- Alcohols have IR absorptions associated with both the O-H and the C-O stretching vibrations.
- Ketones have IR absorptions associated with the C=O bond.
- Aldehydes have IR absorptions associated with the C=O bond and the aldehydic proton.
- Carboxylic acids have IR absorptions associated with the C=O bond and the carboxylic acid proton.
- Esters have IR absorptions associated with the C=O bond and the C-O bond.
- Amines have IR absorptions associated with the N-H bond. There is a C-N peak as well, but it is often buried in the fingerprint region and difficult to discern.
- Nitriles have IR absorptions associated with the C≡N bond. There is a C-N peak as well, but it is often buried in the fingerprint region and difficult to discern.
- IR spectroscopy can prove to be a very valuable tool, given the information it provides about the presence or absence of key functional groups.

4.9 Application

- The most common application of IR spectroscopy is determining the functional groups present or absent in a molecule.
- Environmental scientists use IR for detecting industrial pollutants.
- In art conservation, IR spectroscopy is used to help identify what pigments, adhesives, fibers, plastics, and binders were used.
- IR spectroscopy is used in a wide variety of industries.

Skills to Master

- Skill 4.1 Distinguish between different types of stretching.
- Skill 4.2 Determine the number of vibrational modes molecules may have.
- Skill 4.3 Understand the instrumentation used to obtain IR spectra.
- Skill 4.4 Orient oneself with an IR spectrum.
- Skill 4.5 Be able to read a data table for IR spectroscopy.
- Skill 4.6 Determine functional groups present in the molecule based on an IR spectrum.

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CHAPTER OVERVIEW

5: Proton Nuclear Magnetic Resonance Spectroscopy (NMR)

5.1: Chapter Objectives and Preview of Nuclear Magnetic Resonance Spectroscopy
5.2: Theory of NMR
5.3: Instrumentation
5.4: Types of Protons
5.5: Chemical Shift
5.6: Integration of Proton Spectra
5.7: Spin-Spin Splitting in Proton NMR Spectra
5.8: More Complex Spin-Spin Splitting Patterns
5.9: Uses of Proton NMR Spectroscopy
5.10: Interpreting Proton NMR Spectra
5.11: Proton NMR problems
5.S: Summary

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5.1: Chapter Objectives and Preview of Nuclear Magnetic Resonance Spectroscopy

Objectives

After completing this chapter, you should be able to

- fulfill all of the detailed objectives listed under each individual section.
- solve road-map problems which may require the interpretation of ^{1}H NMR spectra in addition to other spectral data.
- define, and use in context, the key terms introduced in this chapter.

In the previous chapter, it was discussed that Infrared (IR) Spectroscopy gives information about the functional groups present in a molecule. Nuclear Magnetic Resonance (NMR) is another type of absorption spectroscopy similar to Ultraviolet-Visible spectroscopy (UV) or IR spectroscopy. In the presence of a magnetic field, a sample can absorb electromagnetic radiation, specifically in the radiofrequency (rf) region, based on the function of certain nuclei in the molecule. For organic chemists, NMR spectroscopy is an invaluable resource for determining the structure of molecules and often used first when analyzing a molecule. NMR spectroscopy complements IR spectroscopy because information on the hydrocarbon portion of the molecule can be obtained as well as additional information about the functional groups.

This chapter will focus on proton nuclear magnetic spectroscopy (^{1}H NMR). To start, some basic theory behind this technique will be discussed, followed by what type of information you can glean from spectra and finishing with interpretation of an NMR spectrum for the determination of a structure of a molecule.

Contributors and Attributions

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- Prof. Steven Farmer (Sonoma State University)

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5.2: Theory of NMR

Objectives

After reading this section, you should be able to

- understand why NMR works
- understand why different hydrogens do not all show up in the same location on a spectrum

Introduction

Nuclear magnetic resonance (NMR) plays an important role in the fields chemistry, materials science, physics and engineering. In 1946, NMR was co-discovered by Purcell, Pound and Torrey of Harvard University and Bloch, Hansen and Packard of Stanford University. The discovery first came about when it was noticed that magnetic nuclei, such as ^{1}H and ^{31}P (read: proton and Phosphorus 31) were able to absorb radiofrequency energy when placed in a magnetic field of a strength that was specific to the nucleus. Upon absorption, the nuclei begin to resonate and different atoms within a molecule resonated at different frequencies. This observation allowed a detailed analysis of the structure of a molecule. Since then, NMR has been applied to solids, liquids and gasses, kinetic and structural studies, resulting in 6 Nobel prizes being awarded in the field of NMR.

Nuclear magnetic resonance, NMR, is a physical phenomenon of resonance transition between magnetic energy levels, happening when atomic nuclei are immersed in an external magnetic field and an applied electromagnetic radiation with specific frequency. By detecting the absorption signals, one can acquire NMR spectrum. According to the positions, intensities and fine structure of resonance peaks, people can study the structures of molecules quantitatively. The size of molecules of interest varies from small organic molecules, to biological molecules of middle size, and even to some macromolecules such as nucleic acids and proteins. Apart from these commonly utilized applications in organic compounds, NMR also plays an important role in analyzing inorganic molecules, which makes NMR spectroscopy a powerful technique.

But the a major question still remains- Why does NMR work? Some types of atomic nuclei act as though they spin on their axis similar to the Earth. Since they are positively charged they generate an electromagnetic field just as the Earth does. In effect, they will act as tiny bar magnetics. Not all nuclei act this way, but fortunately both ^{1}H and ^{13}C do have nuclear spins and will respond to this technique.

The concept of spin is regularly addressed in subatomic particle physics. However, to most people spin seems like an abstract concept. This is due to the fact there is no macroscopic equivalent of what spin is. However, for those people who have taken an introduction to chemistry course have seen the concept of spin in electrons. Electrons are subatomic particles which have spin intrinsic to them. The nucleus is not much different. Spin is just another form of angular momentum. The nucleus consists of protons and neutrons and neutrons and protons are comprised of subatomic particles known as quarks and gluons. The neutron has 2 quarks with a -e/3 charge and one quark with a +2e/3 charge resulting in a total charge of 0. The proton however, has 2 quarks with +2e/3 charge and only one quark with a -e/3 charge giving it a net positive charge. Both protons and neutrons are spin=1/2.

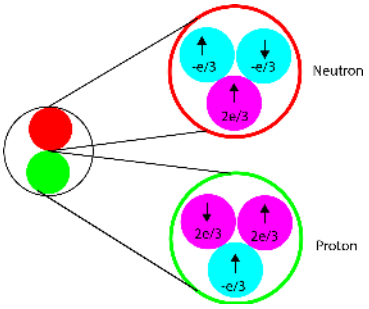


Figure **5.2.1**: The atomic nucleus (black) of ^{2}H. The proton (green) and neutron (red) are composed of quarks (purple and teal) which have a charge and spin (arrow).

For any system consisting of n multiple parts, each with an angular momentum the total angular momentum can be described by J where

$$J = |J_1 + J_2 + \ldots + J_n|, |J_1 + J_2 + \ldots + J_n| - 1, \ldots |J_1 - J_2 - \ldots - J_n| \tag{5.2.1}$$

$$a = mx^2 \tag{5.2.2}$$

Here are some examples using the isotopes of hydrogen

- ^{1}H = 1 proton so J=1/2
- ^{2}H= 1 proton and 1 neutron so $J = 1$ or 0.

For larger nuclei, it is not immediately evident what the spin should be as there are a multitude of possible values. For the remainder of the discussion we will attribute the spin of the nucleus, I, to be an intrinsic value. There are some rules that the nuclei do follow with respect to nuclear spin. They are summarized in the table below.

Table 5.2.1: General rules for determination of nuclear spin quantum numbers

Mass Number	Number of Protons	Number of Neutrons	Spin (I)	Example
Even	Even	Even	0	**^{16}O**
	Odd	Odd	Integer (1,2,...)	**^{2}H**
Odd	Even	Odd	Half-Integer (1/2, 3/2,...)	**^{13}C**
	Odd	Even	Half-Integer (1/2, 3/2,...)	**^{15}N**

Atomic nuclei with even numbers of protons and neutrons have zero spin and all the other atoms with odd numbers have a non-zero spin. Furthermore, all molecules with a non-zero spin have a magnetic moment, μ, given by

$$\mu = \gamma I \tag{5.2.3}$$

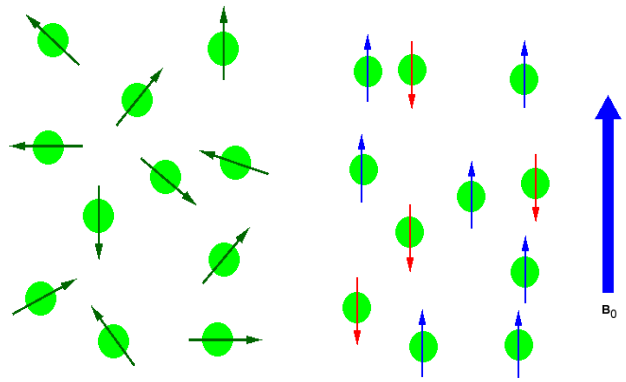
where γ is the gyromagnetic ratio, a proportionality constant between the magnetic dipole moment and the angular momentum, specific to each nucleus (Table 2). In other words, ^{1}H and ^{13}C are not unique in their ability to undergo NMR. All nuclei with an odd number of protons (^{1}H, ^{2}H, ^{14}N, ^{19}F, ^{31}P) or nuclei with an odd number of neutrons (*i.e.* ^{13}C) show the magnetic properties required for NMR. Only nuclei with even number of both protons and neutrons (^{12}C and ^{16}O) do not have the required magnetic properties.

Table 5.2.2: The gyromagnetic ratios for several common nuclei

Nuclei	Spin	Gyromagetic Ratio (MHz/T)	Natural Abundance (%)
^{1}H	1/2	42.576	99.9985
^{13}C	1/2	10.705	1.07
^{31}P	1/2	17.235	100
^{27}Al	5/2	11.103	100
^{23}Na	3/2	11.262	100
^{7}Li	3/2	16.546	92.41
^{29}Si	1/2	-8.465	4.68
^{17}O	5/2	5.772	0.038
^{15}N	1/2	-4.361	0.368

The magnetic moment of the nucleus forces the nucleus to behave as a tiny bar magnet. In the absence of an external magnetic field, each magnet is randomly oriented (as can be seen in the figure below on the left). During the NMR experiment the sample is placed in an external magnetic field, B_0, which forces the bar magnets to align with (low energy) or against (high energy) the B_0. The nuclear spins will adopt specific orientations like a compass needle responds to the Earth's magnetic field and aligns with it.

Two possible orientations are possible, with the external field (*i.e.* parallel to and in the same direction as the external field) or against the field (*i.e.* antiparallel to the external field) as can be seen in the figure below on the right.



(Left) Random nuclear spin without an external magnetic field. (Right) Ordered nuclear spin in an external magnetic field

If the ordered nuclei are now subjected to electromagnetic (EM) radiation, specifically radiofrequency, of the proper frequency the nuclei aligned with the field will absorb energy and "spin-flip" to align themselves against the field, a higher energy state. When this spin-flip occurs the nuclei are said to be in "resonance" with the field, hence the name for the technique, **N**uclear **M**agentic **R**esonance.

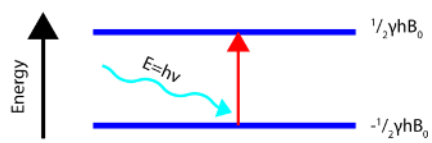


Figure 5.2.2: Absorption of radio frequency radiation to promote a transition between nuclear energy levels, called a spin flip.

In order for the NMR experiment to work, a spin flip between the energy levels must occur. The energy difference between the two states corresponds to the energy of the electromagnetic radiation that causes the nuclei to change their energy levels. For most NMR spectrometers, B_0 is on the order of Tesla (T) while γ is on the order of 10^7. Consequently, the electromagnetic radiation required is on the order of 100's of MHz and even GHz. The energy of a photon is represented by

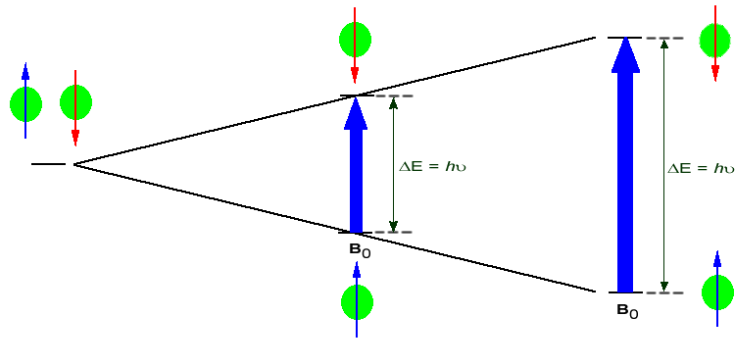
$$E = h\nu \tag{5.2.4}$$

and thus the frequency necessary for absorption to occur is represented as:

$$\nu = \frac{\gamma B_0}{2\pi} \tag{5.2.5}$$

For the beginner, the NMR experiment measures the resonant frequency that causes a spin flip. For the more advanced NMR users, the sections on NMR detection and Larmor frequency should be consulted.

The amount of energy, and hence the exact frequency of EM radiation required for resonance to occur is dependent on both the strength of the magnetic field applied and the type of the nuclei being studied. As the strength of the magnetic field increases the energy difference between the two spin states increases and a higher frequency (more energy) EM radiation needs to be applied to achieve a spin-flip (see image below).



Superconducting magnets can be used to produce very strong magnetic field, on the order of 21 tesla (T). Lower field strengths can also be used, in the range of 4 - 7 T. At these levels the energy required to bring the nuclei into resonance is in the MHz range and corresponds to radio wavelength energies, *i.e.* at a field strength of 4.7 T 200 MHz bring ^{1}H nuclei into resonance and 50 MHz bring ^{13}C into resonance. This is considerably less energy then is required for IR spectroscopy, ~10^{-4} kJ/mol versus ~5 - ~50 kJ/mol.

If all ^{1}H nuclei have the same gyromagnetic ratio, shouldn't all the ^{1}H absorb the same energy, so would all show up at the same spot? Luckily, no. The power of NMR is based on the concept of nuclear shielding, which allows for structural assignments. Every atom is surrounded by electrons, which orbit the nucleus. Charged particles moving in a loop will create a magnetic field which is felt by the nucleus. Therefore the local electronic environment surrounding the nucleus will slightly change the magnetic field experienced by the nucleus, which in turn will cause slight changes in the energy levels! This is known as shielding. Nuclei that experience different magnetic fields due to the local electronic interactions are known as nonequivalent nuclei ($B_{experienced} = B_0 - B_{isigma}$). The change in the energy levels requires a different frequency to excite the spin flip, which as will be seen below, creates a new peak in the NMR spectrum. The shielding allows for structural determination of molecules.

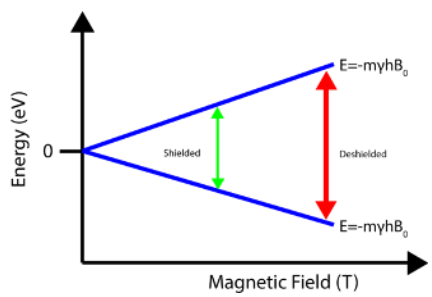


Figure 5.2.3: The effect that shielding from electrons has on the splitting of the nuclear energy levels. Electrons impart their own magnetic field which shields the nucleus from the externally applied magnetic field. This effect is greatly exaggerated in this illustration.

The shielding of the nucleus allows for chemically nonequivalent environments to be determined by Fourier Transforming the NMR signal. The result is a spectrum, shown below, that consists of a set of peaks in which each peak corresponds to a distinct chemical environment.

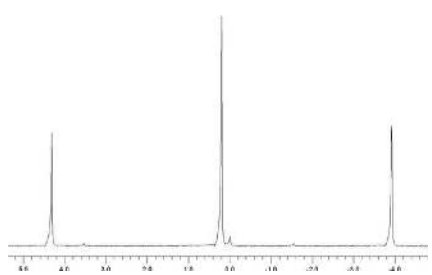
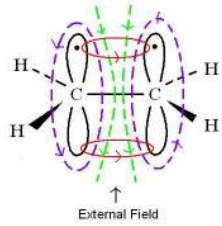


Figure 5.2.4: ^{31}P spectrum of phosphinic acid. Each peak corresponds to a distinct chemical environment while the area under the peak is proportional to the number of nuclei in a given environment.

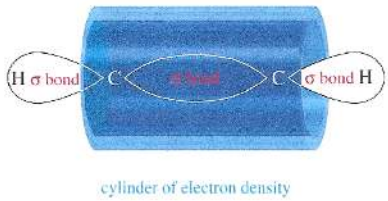
In ^{1}H NMR spectrum, hydrogen atoms bound to a carbon consisting of a double bond are typically found in low field of the NMR spectrum and the hydrogens are considered deshielded. The cause for this is due to the movement of the electrons in the pi bond of the carbon-carbon double bond and how the magnetic field effects the protons bound to the pi bond.



The pi system creates an external magnetic field that is perpendicular to the double bond axis and causes the electrons in the pi bond to enter a circular motion (shown in red). The circular motion actually reinforces the external field at the edge of the double bond on both sides of the pi bond but creates a local field (shown in purple and green) that opposes the external field in the center of the double bond. Because of this pulling force within the pi bond across the double bond which reinforces the regions occupied by alkenyl hydrogens, the alkenyl hydrogens are strongly deshielded.

$$B_{experienced} = B_0 - B_{isigma} + B_{ipi}$$

Unlike alkenyl hydrogens, alkynyl hydrogens give rise to shielded hydrogens, or relatively high field chemical shifts for H-NMR when subjected to an external magnetic field ($B_{experienced} = B_0 - B_{isigma} - B_{ipi}$). The molecules are tumbling all around in solution, but for the alkyne the triple bond has a cylindrical pi cloud around the carbon-carbon triple bond. When the two bonds are subjected to an external magnetic field, these electrons will enter into a cylindrical motion that results in this strong shielding effect with high field chemical shifts. This means that the alkynyl hydrogens will be experiencing less of the external magnetic field. This electron cloud can be seen in the figure below.



Relaxation

Relaxation refers to the phenomenon of nuclei returning to their thermodynamically stable states after being excited to higher energy levels. The energy absorbed when a transition from a lower energy level to a high energy level occurs is released when the opposite happens. This can be a fairly complex process based on different timescales of the relaxation. The two most common types of relaxation are spin lattice relaxation (T_1) and spin spin relaxation (T_2).

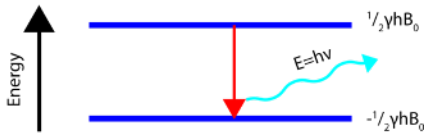


Figure 5.2.5: The process of relaxation

To understand relaxation, the entire sample must be considered. By placing the nuclei in an external magnetic field, the nuclei create a bulk magnetization along the z-axis. The spins of the nuclei are also coherent. The NMR signal may be detected as long as the spins are coherent with one another. The NMR experiment moves the bulk magnetization from the z-axis to the x-y plane, where it is detected.

- **Spin-Lattice Relaxation** (T_1): T_1 is the time it takes for the 37% of bulk magnetization to recovery along Z-axis from the x-y plane. The more efficient the relaxation process, the smaller relaxation time (T_1) value you will get. In solids, since motions between molecules are limited, the relaxation time (T_1) values are large. Spin-lattice relaxation measurements are usually carried out by pulse methods.

- **Spin-Spin Relaxation (T_2)**: T_2 is the time it takes for the spins to lose coherence with one another. T_2 can either be shorter or equal to T_1.

In the next sections, the topics to be discussed will build up to actually analyzing NMR spectra.

Exercise 5.2.1

Where is radiofrequency (RF) radiation on the energy scale of the electromagnetic spectrum?

Answer

Radiofrequency (RF) radiation, which includes radio waves and microwaves, is at the low-energy end of the electromagnetic spectrum. It is a type of non-ionizing radiation.

Exercise 5.2.2

If in a field strength of 4.7 T, ^{1}H requires 200 MHz of energy to maintain resonance. If atom X requires 150 MHz, calculate the amount of energy required to spin flip atom X's nucleus. Is this amount greater than the energy required for hydrogen?

Answer

$E = h\upsilon$

$E = (6.62 \times 10^{-34})(150 \text{ MHz})$

$E = 9.93 \times 10^{-26}$ J

The energy is equal to 9.93×10^{-26} J. This value is smaller than the energy required for hydrogen (1.324×10^{-25} J).

Exercise 5.2.3

Calculate the energy required to spin flip at 400 MHz. Does changing the frequency to 500 MHz decrease or increase the energy required? What about 300 MHz.

Answer

$E = h\upsilon$

$E = (6.62 \times 10^{-34})(400 \text{ MHz})$

$E = 2.648 \times 10^{-25}$ J

The energy would increase if the frequency would increase to 500 MHz, and decrease if the frequency would decrease to 300 MHz.

Exercise 5.2.4

What "things" in a molecule generate magnetic fields that will influence B_o for a particular hydrogen nucleus?

Answer

The electrons in bonds can generate magnetic fields that will influence B_O.

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5.3: Instrumentation

Objectives

After completing this section, you should be able to:

- have basic understanding of how the NMR works
- understand the basic components of the NMR spectrometer

NMR spectroscopy works by varying the machine's emitted frequency over a small range while the sample is inside a constant magnetic field. Most of the magnets used in NMR instruments are superconducting to create the magnetic field range from 6 to 24 T. The diagram below is of an NMR spectrometer. In a basic experiment, an organic sample is dissolved in a suitable solvent, which is often deuterated chloroform or another deuterated solvent, and placed in a thin glass tube. A reasonable concentration for your sample is 5 to 25 mg of desired compound dissolved in 0.6 to 1.0 mL of a suitable solvent, which should be free of particulate matter for solution NMR experiments. The sample is inserted through the NMR spinner and pneumatically lowered into the NMR probe, which is between two magnetic poles. The coils around the NMR tube in the diagram below is where the sample must be. NMR experiments require a uniform magnetic field over the whole of the NMR sample volume that sits within the detection coil. Deviation from this ideal introduces various line shape distortions, compromising both sensitivity and resolution.The strong magnetic field causes the ^{1}H nuclei (or other NMR active nuclei in other experiments) in a molecule to align in one of the two possible orientations. The sample is then subjected to a frequency from the radio wave source. A detector then interprets the results and sends it to the main console. Using a data analysis program, the free induction decay (FID) data is transformed into the spectrum typically shown in papers and books.

Diagram of NMR spectrometer

NMR Instrument

An NMR can be divided into three main components: the workstation computer where one operates the NMR instrument, the NMR spectrometer console, and the NMR magnet, which is shown in the picture below.

400 MHz NMR Spectrometer

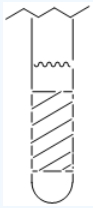
The NMR is layered with the superconducting magnet just outside the probe towards the center of the spectrometer (diagram below). The magnet only works if a coil is kept very cool, so it is immersed in the first layer inside the NMR, which is liquid helium (4.2 K). To reduce the boil off rate of the liquid helium, the next layer is filled with liquid nitrogen at 77 K. The liquid nitrogen reservoir space is mostly above the magnet. This way, it can act as a less expensive refrigerant to block infrared radiation

from reaching the liquid helium jacket. Aluminum and stainless steel are also used to contain the liquids and block infrared irradiation as well. All the layers are working to keep the magnet coil very cold.

Diagram of the main layers inside an NMR instrument

Exercise 5.3.1

Consider a sample in an NMR tube.The crosshatched region in the tube is the area over which signal is recorded.Why is it important that B_{APPL} be homogeneous over this entire region?



Answer

NMR experiments require a uniform magnetic field over the whole of the NMR sample volume that sits within the detection coil, which is represented by the crosshatched region. Deviation from this ideal introduces various line shape distortions, compromising both sensitivity and resolution.

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5.4: Types of Protons

Objectives

After completing this section, you should be able to:

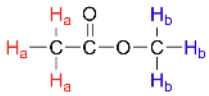
1. identify those protons which are equivalent in a given chemical structure.
2. use the ^{1}H NMR spectrum of a simple organic compound to determine the number of equivalent sets of protons present.

Key Terms

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

- diastereotopic
- enantiotopic
- homotopic

If all protons in all organic molecules had the same resonance frequency in an external magnetic field of a given strength, ^{1}H NMR would not be terribly useful to organic chemists. Fortunately for organic chemists, resonance frequencies are not uniform for all protons in a molecule. In an external magnetic field of a given strength, protons in different locations in a molecule have different resonance frequencies, because they are in non-identical electronic environments. In methyl acetate, below for example, there would be two peaks in the ^{1}H NMR spectrum, which means there are two types of protons. The three protons labeled H_a have a different - and easily distinguishable – resonance frequency than the three H_b protons, because the two sets of protons are in non-identical environments: they are, in other words, chemically nonequivalent.



On the other hand, the three H_a protons are all in the same electronic environment, and are chemically equivalent to one another. They have identical resonance frequencies. The same can be said for the three H_b protons.

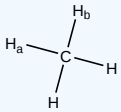
A good test to determine if hydrogens are chemically equivalent is by doing a thought exercise. In the thought exercise, you replace hydrogens by X to determine what the "thought molecules'" relationship would be to each other. If the protons in the two "thought molecules" are identical, then the protons are said to be **homotopic**. Homotopic protons are identical protons and will be chemically equivalent. This means that they will show up at the same location in the NMR spectrum.

Example 5.4.1

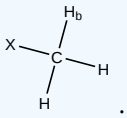
Are the protons in methane, CH_4, homotopic, enantiotopic, or diastereotopic?

Solution

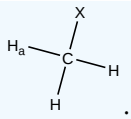
Let's do the thought experiment. Two of the hydrogens in methane have been labeled a and b.



Now exhange replace each with X to form two separate "thought molecules". If we exchange H_a for X, then the molecule would be

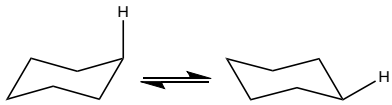


Doing the same with H_b, the resulting molecule is



The next step is to determine the relationship between these two molecules. Both "thought molecules" are identical, so the protons are homotopic.

You might expect that the equatorial and axial hydrogens in cyclohexane would be non-equivalent, and would have different resonance frequencies. In fact, an axial hydrogen *is* in a different electronic environment than an equatorial hydrogen. Remember, though, that the molecule rotates rapidly between its two chair conformations, meaning that any given hydrogen is rapidly moving back and forth between equatorial and axial positions. It turns out that, except at extremely low temperatures, this rotational motion occurs on a time scale that is much faster than the time scale of an NMR experiment.



In this sense, NMR is like a camera that takes photographs of a rapidly moving object with a slow shutter speed - the result is a blurred image. In NMR terms, this means that all 12 protons in cyclohexane are equivalent.

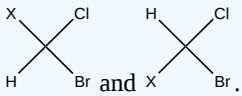
The next example we will consider is bromochloromethane. Are the protons of the CH_2 chemically equivalent?

Example 5.4.2

Are the protons in bromochloromethane, C_2H_4BrCl, homotopic, enantiotopic, or diastereotopic?

Solution

Start with the same thought experiment that we did with methane and exchange one of the hydrogens with X to make one "thought molecule" and then repeat with the other hydrogen. The two molecules you get are:



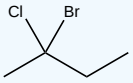
The relationship between the two molecules is that they are enantiomers. These protons are considered enantiotopic.

In Example 5.4.2, the "thought" molecules were enantiomers of each other. The hydrogens are termed **enantiotopic** and like enantiomers the protons are only different in the presence of something that is chiral. The solvents typically used for NMR spectroscopy are achiral. Therefore, the two methylene protons are equivalent protons and will have the same chemical shift. For bromochloromethane, one would expect there to be one NMR absorption for the CH_2 group. In summary, enantiotopic protons will be chemically equivalent. This means that they will show up at the same location in the NMR spectrum.

The final type of protons to discuss is diastereotopic protons.

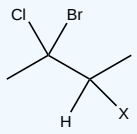
Example 5.4.3

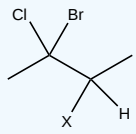
Are the methylene protons in 2-bromo-2-chlorobutane, C_4H_8BrCl, chemically equivalent?



Solution

Start with the same thought experiment that we did with methane and exchange one of the hydrogens with X to make one "thought molecule" and then repeat with the other hydrogen. The two "thought molecules" are:



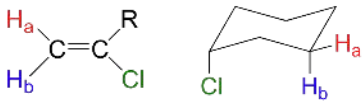
and


.

The relationship between these two molecules is diastereomers. These protons are considered diastereotopic protons. Diastereomers have different chemical properties, which means these protons are not chemically equivalent.

Overall, 2-bromo-2-chlorobutane will have four different types of hydrogens: the two methyl groups will be different giving two NMR absorptions and the CH_2 will give two NMR absorptions. In general, diastereotopic protons occur when there is a chirality center already present in the molecule. In summary, diastereotopic protons will be chemically different. This means that they will show up at different locations in the NMR spectrum.

When stereochemistry is taken into account, the issue of equivalence versus nonequivalence in NMR starts to get a little more complicated. It should be fairly intuitive that hydrogens on different sides of asymmetric ring structures and double bonds are in different electronic environments, and thus are nonequivalent and have different resonance frequencies. In the alkene and cyclohexane structures below, for example, H_a is *trans* to the chlorine substituent, while H_b is *cis* to chlorine. H_a and H_b in both the alkene and cyclohexane structures would give different absorptions in the NMR spectrum.

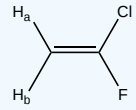


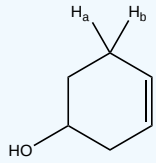
Most organic molecules have several sets of protons in different chemical environments, and each set, in theory, will have a different resonance frequency in ^{1}H-NMR spectroscopy. The ability to recognize chemical equivalency and nonequivalency among atoms in a molecule will be central to understanding NMR.

Exercise

? Exercise 5.4.2

Are the labeled protons homotopic, enantiotopic, or diastereotopic?

a. 

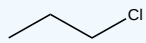
b. 

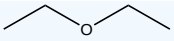
Answer

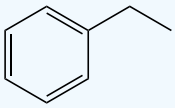
a. Diastereotopic
b. Diastereotopic

? Exercise 5.4.2

How many non-equivalent hydrogens are in the following molecules? How many different signals will you see in a ^{1}H NMR spectrum?

a. 

b. 

c. 

Answer

a. 1-chloropropane has three non-equivalent hydrogens and would have 3 signals in an ^{1}H NMR spectrum.

b. Diethylether has two non-equivalent hydrogens and would have 2 signals in an ^{1}H NMR spectrum.

c. Ethylbenzene has five non-equivalent hydrogens and would have 5 signals in an ^{1}H NMR spectrum.

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5.5: Chemical Shift

Objectives

After completing this section, you should be able to

- understand why the delta scale is used in NMR spectroscopy.
- explain how chemical environment of the proton is related to the chemical shift.
- understand how to read a table of the approximate chemical shift (δ) for protons
- predict the approximate chemical shifts of each of the protons in an organic compound, given its structure and a table of chemical shift correlations.

Key Terms

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

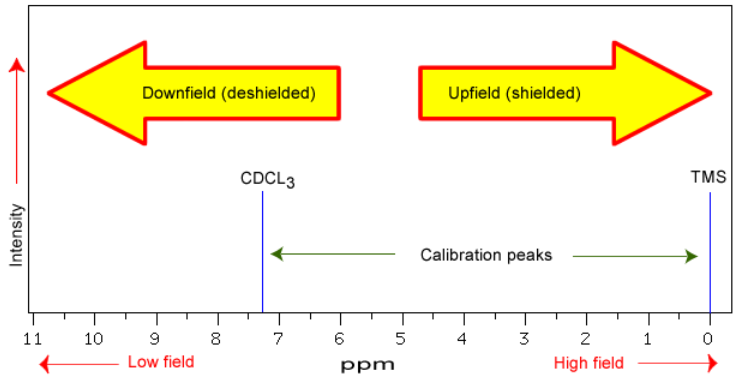
- chemical shift
- delta scale
- upfield/downfield

Study Notes

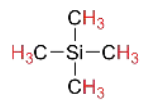
Although the calculations described in this section will help you understand the principles of NMR, it is the actual delta values, not the calculations, which are of greatest importance to the beginning organic chemist. Thus, we shall try to focus on the interpretation of NMR spectra, not the mathematical aspects of the technique.

You should not attempt to memorize the chemical shifts listed in the table of this section, you will refer to it quite frequently throughout your analysis of spectra. However, if you have an approximate idea of the chemical shifts of some of the most common types of protons, you will find the interpretation of ^{1}H NMR spectra less arduous than it might otherwise be.

NMR spectra are displayed on a plot that shows the applied field strength increasing from left to right. The left side of the plot is low-field or downfield and the right side of the plot is high-field or upfield. The different local chemical environments surrounding any particular nuclei causes them to resonate at slightly different frequencies. This is a result of a nucleus being more or less shielded than another. There are structural features of the molecule will have an effect on the exact magnitude of the magnetic field experienced by a particular nucleus causing an upfield or downfield shift. This means that nuclei which have different chemical environments will show up in different regions of the NMR plot or spectrum. This is what makes NMR so useful for structure determination in organic chemistry. There are three main features that will effect the shielding of the nucleus: 1) electronegativity, 2) magnetic anisotropy of π systems (Section 5.2) and 3) hydrogen bonding. The position on the spectrum at which a nucleus absorbs is called its chemical shift (δ).



The chemical shift is dependent on the applied field of the spectrometer and as discussed in Section 5.2, there are a variety of spectrometers. Therefore, if you were to run the same sample in a 300 MHz spectrometer and a 600 MHz spectrometer, the same proton would give a different chemical shift in Hertz (Hz). It would be inconvenient and confusing to always have to convert NMR data according to the field strength of the instrument used. Luckily, chemists report resonance frequencies not as absolute values in Hz, but rather as values relative to a common standard, generally the signal generated by the protons in tetramethylsilane (TMS). TMS (structure below) was chosen as a standard because it is chemically inert, symmetrical, volatile (bp = 27 C), and soluble in most organic solvents. Most importantly, it gives a single absorption peak and its protons are more shielded than almost all organic protons. Remember - more shielded means more toward the right of the spectrum and a lower chemical shift. With a standard in place, the units parts per million (ppm) comes in to play. Regardless of the magnetic field strength of the instrument being used, the resonance frequency of the 12 equivalent protons in TMS is defined as a zero point. The resonance frequencies of protons in the sample molecule are then reported in terms of how much higher they are, in ppm, relative to the TMS signal. Now whether a 300 MHz instrument was used or a 600 MHz instrument, the same peak report out at the same chemical shift in ppm. The equation below shows the conversion from Hertz (Hz) to part per million (ppm). Chemical shifts can be used to identify structural properties in a molecule based on our understanding of different chemical environments.



tetramethylsilane (TMS)

$$\delta = \frac{\text{frequency of signal - frequency of standard}}{\text{spectrometer frequency}} \times 10^6$$

Example 5.5.1

For $CHCl_3$, there is a peak at 1451 Hz in a H^1 NMR spectra from a 400 MHz spectrometer. Convert to δ (ppm) units.

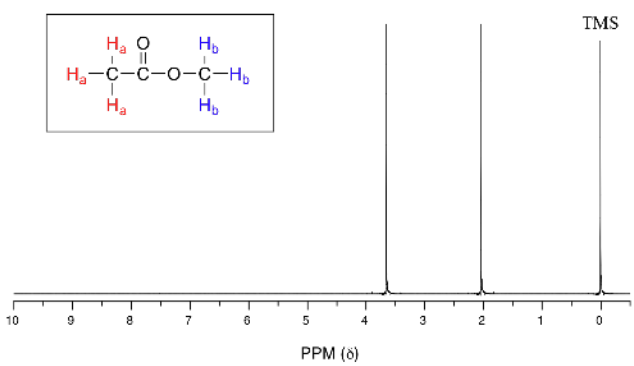
Solution

δ = ((1451 Hz - 0 Hz)/400,000,000 Hz) x 10^6 ppm = 3.627 ppm

Remember: TMS is our standard and is set to 0 Hz (or 0 ppm).

Chemical Shifts in ^{1}H NMR Spectroscopy

The NMR spectra is displayed as a plot of the applied radiofrequency versus the absorption. In ^{1}H NMR spectra, the typical range for protons is 0 to 14 ppm. Let's look at an actual ^{1}H-NMR plot for methyl acetate. Just as in IR and UV-Vis spectroscopy, the vertical axis corresponds to intensity of absorbance (typically not shown in an NMR spectrum) and the horizontal axis to frequency.



We see three absorbance signals: two of these correspond to H_a and H_b, while the peak at the far right of the spectrum corresponds to the 12 chemically equivalent protons in TMS. In the spectrum above, you can see that each methyl group has a different

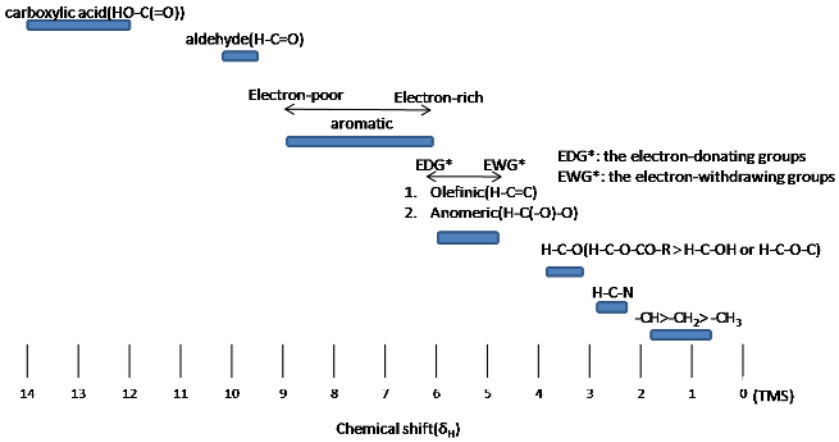
chemical shift, so the ^1H nuclei must be in different chemical environments. The two methyl groups are attached to different functionalities, which causes a difference in the shielding for each methyl group, creating the unique ^1H environments. The main difference is how close each methyl group is to an electronegative atom in methyl acetate.

Electronegativity

If you remember from Section 5.2, the electrons that surround the nucleus are in motion creating their own electromagnetic field. If this field opposes the the applied magnetic field, it reduces the magnetic field experienced by the nucleus. Thus the electrons are said to shield the nucleus. Since the magnetic field experienced at the nucleus defines the energy difference between spin states it also defines what the chemical shift will be for that nucleus. Electron with-drawing groups can decrease the electron density at the nucleus, deshielding the nucleus, resulting in a larger chemical shift. Let's look at some data in the table below.

Compound, CH_3X	**CH_3F**	**CH_3OH**	**CH_3Cl**	**CH_3Br**	**CH_3I**	**CH_4**	**$(CH_3)_4Si$**
Electronegativity of X	4.0	3.5	3.1	2.8	2.5	2.1	1.8
Chemical shift, δ (ppm)	4.26	3.4	3.05	2.68	2.16	0.23	0

As can be seen from the data, as the electronegativity of X increases the chemical shift, δ. This is an effect of the electronegative atom pulling the electron density away from the nuclei of ^1H atoms and exposing them more to the magnetic field, which "deshields" the nuclei and shifting the peak downfield. Looking back at the two methyl groups in methyl acetate, the methyl group directly attached to the oxygen atom brings that signal further downfield to about 3.6 ppm, while the methyl group attached to the carbonyl group, putting an additional carbon atom between the electron-withdrawing oxygen and the ^1H nuclei and thus there is less of an electron withdrawing effect on the nuclei, so they are more shielded. This leads the signal to be more upfield around 2 ppm. The diagram below shows where protons that are part of or near different organic functional groups generally show up on an NMR spectrum.



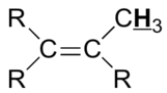
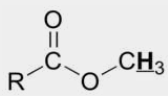
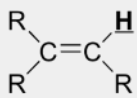
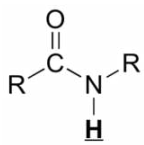
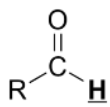
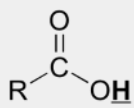
The effects of electron withdrawing groups are cumulative so the presence of more electron withdrawing groups will produce greater deshielding and therefore a larger chemical shift. As you can see in the table below, the more electronegative chlorine atoms present, increases the chemical shift. In general, the more electronegative atoms present in the environment, the more exposed the nuclei becomes and thus more deshielded.

Compound	**CH_4**	**CH_3Cl**	**CH_2Cl_2**	**$CHCl_3$**
δ (ppm)	0.23	3.05	5.30	7.27

These inductive effects are not only felt by the immediately adjacent atoms, but also the deshielding can occur further down the chain. The effect lessens the further away the nuclei is from the electronegative atom and after about three bonds away is not felt much any more. In the piece of a molecule below, you can see this trend. The protons closes to the bromine atom are more downfield at 3.30 ppm and an upfield shift occurs with the protons attached to carbons 2 bonds and 3 bonds away from the bromine.

NMR signal	$-CH_2-CH_2-CH_2Br$
δ (ppm)	1.25, 1.69, 3.30

Another way to view chemical shift data is in a table. You will notice that there are ranges. The range is where the proton peak may generally occur.

Hydrogen type	Chemical shift (ppm)
$RC\underline{\mathbf{H}}_3$	0.9 - 1.0
$RC\underline{\mathbf{H}}_2R$	1.2 - 1.7
$R_3C\underline{\mathbf{H}}$	1.5 – 2.3
	1.5 – 1.8
$RN\underline{\mathbf{H}}_2$	1 - 3
$ArC\underline{\mathbf{H}}_3$	2.2 – 2.4
$R{-}C{\equiv}C{-}\underline{\mathbf{H}}$	2.3 – 3.0
$ROC\underline{\mathbf{H}}_3$	3.2 – 3.8
	3.7 – 3.9
$RO\underline{\mathbf{H}}$	2 - 5
	5.0 – 6.5
	5 - 9
$Ar\underline{\mathbf{H}}$	6.0 – 8
	9 – 10.0
	10 - 13

Example 5.5.2

Calculate the chemical shift for the protons in ethanol (CH_3CH_2OH) using the table above.

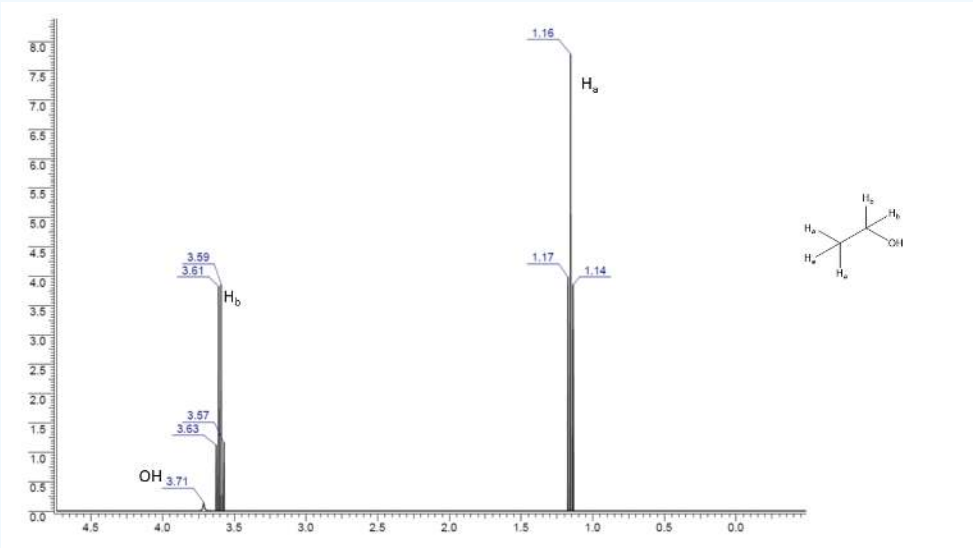
Solution

-OH proton = between 1-5 ppm

-CH_2- protons = 3.2-3.8 ppm

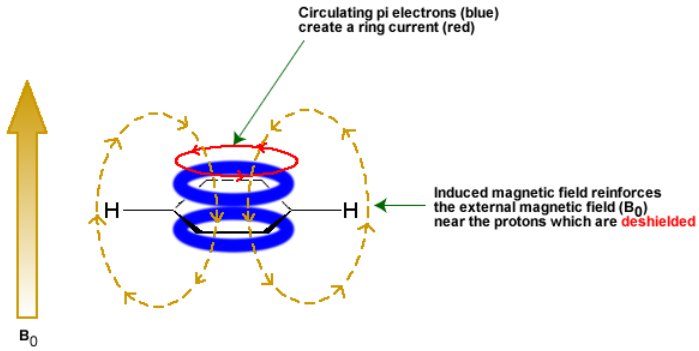
-CH_3 protons = > 0.9-1.0 ppm, since the methyl group is not directly attached to the electron-withdrawing group it will not feel the pull away of electron density as much as the methylene group, but it is still close enough to feel it a bit. This means the methyl group will be slightly higher than expected.

Below is an actual image of the NMR spectrum of ethanol. Our predicted values do align with the actual spectral data. The OH actually shows at 3.71 ppm, which is between 1-5ppm as predicted, the methylene occurs at 3.60 ppm also falls within the predicted rage of 3.2-3.8 ppm, and the methyl group does fall just higher than the predicted 0.9-1.0 ppm at 1.16 ppm.



Magnetic Anisotropy: π Electron Effects

The π electrons in a compound, when placed in a magnetic field, will move and generate their own magnetic field. The new magnetic field will have an effect on the shielding of atoms within the field. The best example of this is benzene (see the figure below). Also, see Section 5.2 for more details on generating magnetic fields.

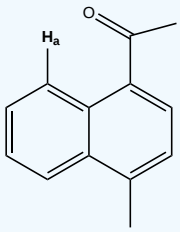


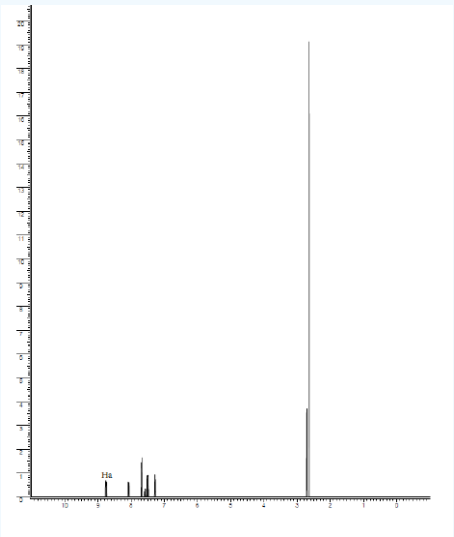
This effect is common for any atoms near a π bond.

Proton Type	Effect	Chemical shift (ppm)
C_6H_5-H	highly deshielded	6.5 - 8
C=C-H	deshielded	5 - 6.5
C≡C-H	shielded*	~2.5
O=C-H	very highly deshielded	9 - 10
* the acetylene H is shielded due to its location relative to the π system		

Example 5.5.3

The chemical shift for the highlighted proton $\mathbf{H_a}$ is 8.8 ppm, whereas the chemical shift for each of the other protons explicitly shown is between 7.3-8.0 ppm. Provide an explanation for this downfield shift of $\mathbf{H_a}$.





Solution

H_a feels the benzene pi system as do all the other hydrogens on naphthalene. The difference is that it also feels the pi system from the carbonyl as well, which brings H_a further downfield than the other hydrogens.

Hydrogen Bonding

Protons that are involved in hydrogen bonding (*i.e.*-OH or -NH) are usually observed over a wide range of chemical shifts. This is due to the deshielding that occurs in the hydrogen bond. Since hydrogen bonds are dynamic, constantly forming, breaking and forming again, there will be a wide range of hydrogen bonds strengths and consequently a wide range of deshielding. This exchange is faster than the time it takes to acquire a ^{1}H NMR spectrum. This, as well as, solvation effects, acidity, concentration and temperature make it very difficult to predict the chemical shifts for these atoms. The exchange process is facilitated by even traces of acid or base in the sample. The functional groups affected are alcohols, carboxylic acids, amines, and amides.

Experimentally -OH and -NH can be identified by carrying out a simple D_2O exchange experiment since these protons are exchangeable.

- run the normal H-NMR experiment on your sample
- add a few drops of D_2O
- re-run the H-NMR experiment

- compare the two spectra and look for peaks that have "disappeared"

Exercise

Exercise 5.5.1

The following peaks were from a ^{1}H NMR spectra from a 300 MHz spectrometer. Convert to δ units (ppm).

a) CH_3OH: 693 Hz

b) CH_2Cl_2: 1060 Hz

Answer

a) δ = ((693 Hz - x 0 Hz)/400,000,000 Hz) x 10^6 ppm = 1.73 ppm

b) δ = ((1060 Hz - x 0 Hz)/400,000,000 Hz) x 10^6 ppm = 2.65 ppm

Exercise 5.5.2

Butan-2-one shows a chemical shift around 2.1 on a 300 MHz spectrometer in the H^1 NMR spectrum.

a) How far downfield is this peak from TMS in Hz?

b) If the spectrum was done with a 400 MHz instrument, would a different chemical shift be seen?

c) On this new 400 MHz spectrum, what would be the difference in Hz from the chemical shift and TMS?

Answer

a) (2.1 ppm x 300000000 Hz)/10^6 ppm = 630 Hz The peak at 2.1 ppm would show at 630 Hz on a 300 MHz spectrometer. TMS is always at 0 Hz, so the peak would be 630 Hz downfield from TMS.

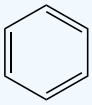
b) No, a different chemical shift would not be seen in ppm. The point of using the ppm scale is to be able to discuss the same peak at the same chemical shift unlike when using Hertz.

c) (2.1 ppm x 400000000 Hz)/10^6 ppm = 840 Hz The 2.1 ppm peak would show at 840 Hz on a 400 MHz spectrometer.

Exercise 5.5.3

The following have one H^1 NMR peak. In each case predict approximately where this peak would be in a spectra.

a)

b) 

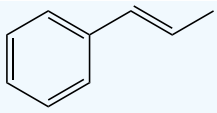
Answer

a) 1.2-1.7 ppm

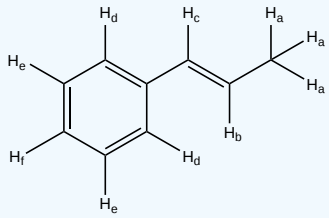
b) 6.0-8.0 ppm

Exercise 5.5.4

Identify the different equivalent protons in the following molecule and predict their expected chemical shift.



Answer

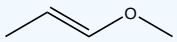


There are 6 different protons in this molecule.

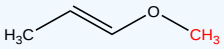
Proton	Predicted Chemical Shift (ppm) from Table	Actual Chemical Shift (ppm) Data
Ha	1.5-1.8	1.72
Hb	5.0-6.5	6.03
Hc	5.0-6.5	6.26
Hd	6.5-8	7.33
He	6.5-8	7.19
Hf	6.5-8	7.22

? Exercise 5.5.5

Which methyl group would you expect to be more downfield on the molecule below.



Answer



The methyl group directly attached to the oxygen will be further downfield (predicted 3.2-3.8 ppm) versus the methyl group directly attached to a double bond (predicted 1.5-1.8 ppm).

Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Dr. Richard Spinney (The Ohio State University)

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5.6: Integration of Proton Spectra

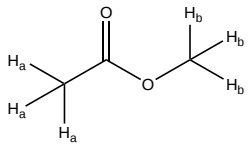
Objectives

After completing this section, you should be able to

1. explain what information can be obtained from an integrated ^{1}H NMR spectrum, and use this information in the interpretation of such a spectrum.
2. use an integrated ^{1}H NMR spectrum to determine the ratio of the different types of protons present in an organic compound.

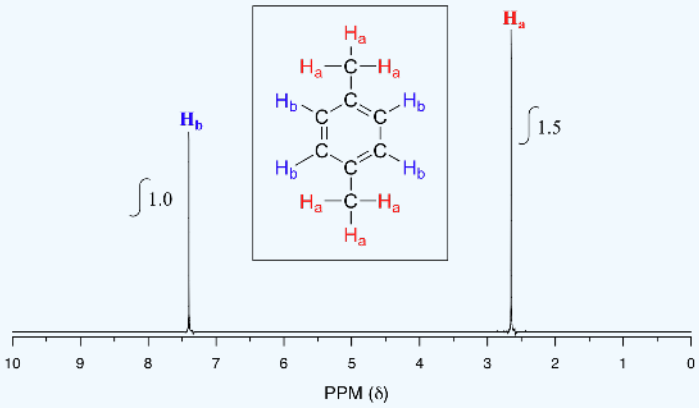
Integration

In a previous sections 5.4: Types of Protons and 5.5: Chemical Shift, equivalent and nonequivalent hydrogens were discussed as well as unique nonequivalent hydrogens having different chemical shifts. In this section, integration will let the researcher know how many hydrogens there are for each unique NMR absorption. The area of a peak in a ^{1}H NMR is proportional to the number of hydrogens to which the peak corresponds. This is very helpful when determining how many of each unique hydrogen exist and total number of hydrogens present in a molecule. The computer in an NMR instrument can be instructed to automatically integrate the area under a signal or group of signals, so it can be superimposed on the spectrum. The integration curve appears as a series of steps with the height being proportional to the area of the corresponding absorption peak, and the number of protons responsible for the absorption. In practice since it can be difficult to decide exactly where to start and stop, the ratios may not be exact whole numbers. If we look at methyl acetate (below), there are two types of protons that would give two separate peaks in an NMR spectrum. The peaks would integrate to approximately the same area, since both correspond to a set of three equivalent protons.



Example 5.6.1

If we look at a spectrum of para-xylene (common name) or 1,4-dimethylbenzene (IUPAC name), how many types of protons are there and what does the ratio mean?



Solution

There are still two signals like in methyl acetate indicating there are two types of hydrogens, but now instead of ratios being about 1 to 1, the ratio is 1 to 1.5. When we instruct the instrument to integrate the areas under the two signals, we find that the area under the peak at 2.6 ppm is 1.5 times greater than the area under the peak at 7.4 ppm. This molecule has two sets of protons: the six methyl (H_a) protons and the four aromatic (H_b) protons, which matches our 1:1.5 ratio since 6 is 1.5 times 4.

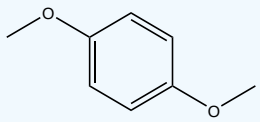
This (along with the actual chemical shift values, discussed in section 5.5: Chemical Shift) tells us which set of protons corresponds to which NMR signal. The aromatic protons (H_b) are at 7.4 ppm and the methyl protons, H_a, are at 2.6 ppm.

Integration can also be used to determine the relative amounts of two or more compounds in a mixed sample. If we have a sample that is a 50:50 (mole/mole) mixture of benzene and acetone, for example, the acetone signal should integrate to the same value as the benzene sample, because both signals represent six equivalent protons. If we have a 50:50 mixture of acetone and cyclopentane, on the other hand, the ratio of the acetone peak area to the cylopentane peak area will be 3:5 (or 6:10), because the cyclopentane signal represents ten protons.

Exercises

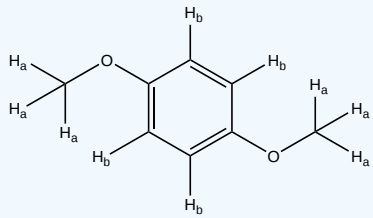
Exercise 5.6.1

Predict how many signals the following molecule would have and the integrations in ^{1}H NMR? Sketch the spectra and estimate the integration of the peaks.



Answer

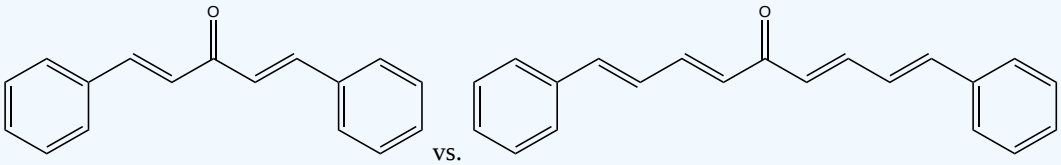
There would be two signals. One for H_a that would integrate to 6 and another for H_b that would integrate to 4.



Ideal general spectrum shown with integration (below).

Exercise 5.6.2

Using integration, how could you determine the difference between these two molecules.



Answer

The two will have very similar chemical shifts for their protons, but the total number of protons will be different. If you add up all the integrations, then you will get the total number of hydrogens for each molecule. The first molecule has 14 total protons, while the second molecule has 18 total protons.

? Exercise 5.6.3

You take the ^{1}H-NMR spectrum of a mixed sample of 36% *para*-xylene and 64% acetone in $CDCl_3$ solvent. How many peaks do you expect to see? What is the expected ratio of integration values for these peaks? (set the acetone peak integration equal to 1.0)

Answer

There are three peaks: two from para-xylene and one from acetone. The acetone peak and the para-xylene methyl peak both represent six protons, so the ratio of their integration values is simply 64 to 36 or 1 (64/64) to 0.56 (36/64). The ratio of the para-xylene methyl peak to the para-xylene aromatic peak is 6 to 4 (1.5: 1 ratio), or 0.56 to 0.37 (still 1.5: 1 ratio). So the final integral ratio of acetone:methyl:aromatic signals should be 1 to 0.56 to 0.37.

Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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5.7: Spin-Spin Splitting in Proton NMR Spectra

Objectives

After completing this section, you should be able to

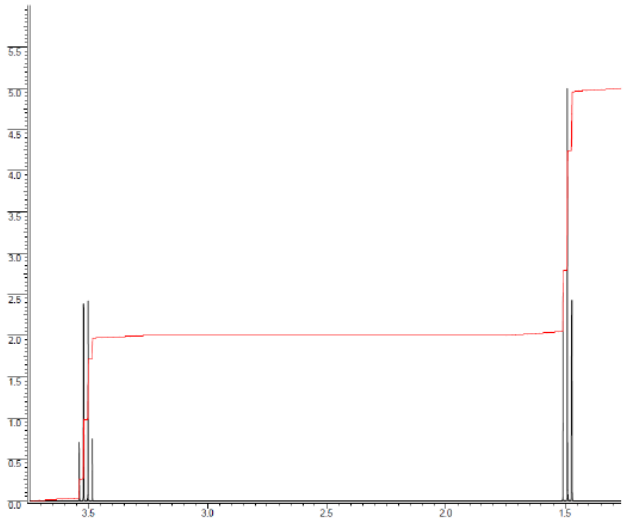
1. understand what spin-spin splitting is and what information it tells you
2. explain the spin-spin splitting pattern observed in the ^{1}H NMR spectrum of a simple organic compound.
3. interpret the splitting pattern of a given ^{1}H NMR spectrum.
4. determine the structure of a relatively simple organic compound, given its ^{1}H NMR spectrum and other relevant information.
5. use coupling constants to determine which groups of protons are coupling with one another in a ^{1}H NMR spectrum.
6. predict the splitting pattern which should be observed in the ^{1}H NMR spectrum of a given organic compound.

Key Terms

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

- coupling constant
- multiplet
- quartet
- triplet
- doublet

From what we have learned about ^{1}H NMR spectra so far, we might predict that the spectrum of 1-chloroethane, CH_3CH_2Cl, would consist of two peaks—one, at about 0.9 δ, expected for CH_3 and one shifted downfield because of the presence of an additional electronegative chlorine atom on the second carbon. However, when we look at the spectrum (below) it appears to be much more complex. True, we see absorptions in the regions we predicted, but instead of the single peak we have seen thus far, these absorptions appear as a group of three peaks (a *triplet*) and a group of four peaks (a *quartet*). This complication is in fact very useful to the organic chemist, and adds greatly to the power of NMR spectroscopy as a tool for the elucidation of chemical structures. The split peaks (*multiplets*) arise because the magnetic field experienced by the protons of one group is influenced by the spin arrangements of the protons in an adjacent group.

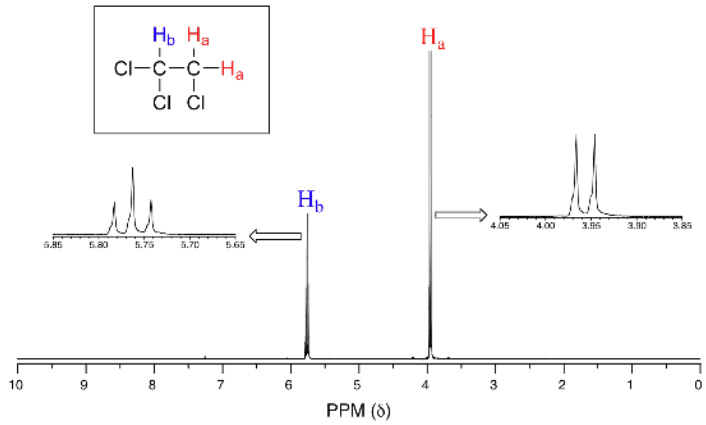


The source of spin-spin coupling

The ^{1}H-NMR spectra that we have seen so far (of methyl acetate and *para*-xylene) are somewhat unusual in the sense that in both of these molecules, each set of protons generates a single NMR signal. In fact, the ^{1}H-NMR spectra of most organic molecules

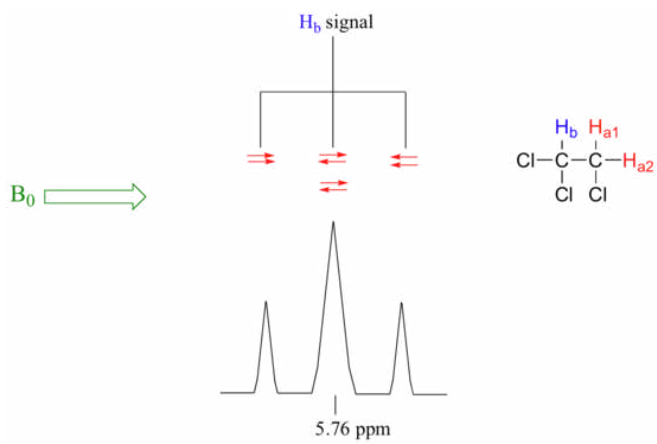
contain proton signals that are split into two or more sub-peaks. This splitting behavior actually provides us with more information about our sample molecule.

Consider the spectrum for 1,1,2-trichloroethane. In this and in many spectra to follow, enlargements of individual signals will be shown so that the signal splitting patterns are recognizable.



The signal at 3.96 ppm, corresponding to the two H_a protons, is split into two subpeaks of equal height (and area) – this is referred to as a **doublet**. The two H_b protons at 5.76 ppm, on the other hand, is split into three sub-peaks, with the middle peak higher than the two outside peaks - if we were to integrate each subpeak, we would see that the area under the middle peak is twice that of each of the outside peaks. This is called a **triplet**.

The source of signal splitting is a phenomenon called **spin-spin coupling**, a term that describes the magnetic interactions between neighboring, non-equivalent NMR-active nuclei. In our 1,1,2--trichloroethane example, the H_a and H_b protons are spin-coupled to each other. Here's how it works, looking first at the H_b signal. The magnetic environment experienced by H_b is influenced by the fields of both neighboring H_a protons, which we will call H_{a1} and H_{a2}. There are four possibilities here, each of which is equally probable. First, the magnetic fields of both H_{a1} and H_{a2} could be aligned with B_0, which would deshield H_b, shifting its NMR signal slightly downfield. Second, both the H_{a1} and H_{a2} magnetic fields could be aligned opposed to B_0, which would shield H_b, shifting its resonance signal slightly upfield due to being more shielded. Third and fourth, H_{a1} could be with B_0 and H_{a2} opposed, or H_{a1} opposed to B_0 and H_{a2} with B_0. In each of the last two cases, the shielding effect of one H_a proton would cancel the deshielding effect of the other, and the chemical shift of H_b would be unchanged. These ideas an be illustrated by a **splitting diagram**, as shown below.



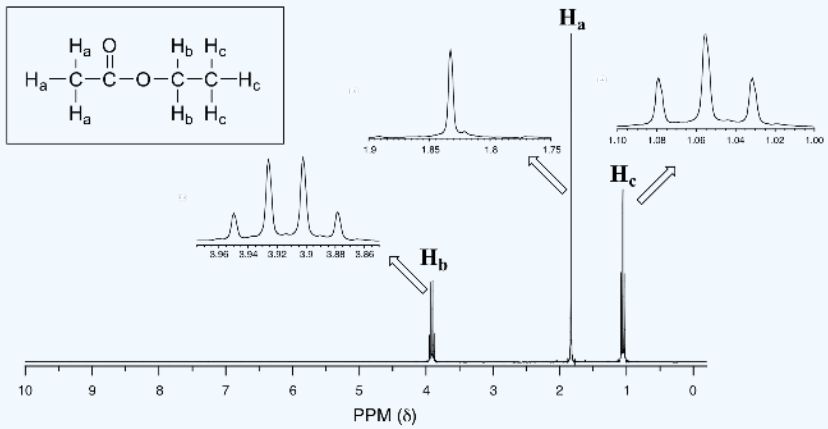
So in the end, the signal for H_b is a **triplet**, with the middle peak twice as large as the two outer peaks because there are *two* ways that H_{a1} and H_{a2} can cancel each other out.

The H_a hydrogens give rise to a **doublet** signal at 3.96 ppm – notice that the two peaks are equal in height to one another. This splitting pattern results from the spin-coupling effect of the one H_b hydrogen next door, and can be explained by an analysis similar

to that which we used to explain the triplet pattern above. The proton could be aligned with the magnetic field, which would deshield H_a or it could oppose the magnetic field, which would shield H_a.

Example 5.7.1

Now, consider the spectrum for ethyl acetate:



Explain the splitting patterns of H_a, H_b, and H_c in ethyl acetate.

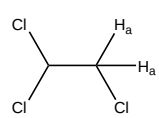
Solution

We see an unsplit singlet peak at 1.83 ppm that corresponds to the acetyl (H_a) hydrogens. This signal is unsplit because there are no hydrogens on the adjacent carbon. The signal at 1.055 ppm for the H_c hydrogens is split into a triplet by the two H_b hydrogens next door. The explanation here is the same as the explanation for the triplet peak we saw previously for 1,1,2-trichloroethane.

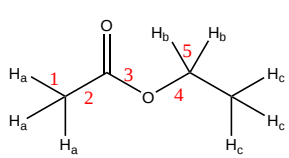
The H_b hydrogens give rise to a quartet signal at 3.91 ppm – notice that the two middle peaks are taller then the two outside peaks. This splitting pattern results from the spin-coupling effect of the three H_c hydrogens next door, and can be explained by an analysis similar to that which we used to explain the doublet and triplet patterns previously discussed.

Instead of drawing a splitting diagram for every molecule, there is a recognizable pattern which is usually referred to as the ***n* + 1 rule**: if a set of hydrogens has *n* neighboring, non-equivalent hydrogens, it will be split into *n* + 1 subpeaks. This is very useful information if we are trying to determine the structure of an unknown molecule: if we see a triplet signal, we know that the corresponding hydrogen or set of hydrogens has two neighboring hydrogens. When we begin to determine structures of unknown compounds using ^{1}H-NMR spectral data, it will become more apparent how this kind of information can be used.

Three important points need to be emphasized here. First, signal splitting only occurs between non-equivalent hydrogens – in other words, H_{a1} in 1,1,2-trichloroethane is not split by H_{a2}, and vice-versa.

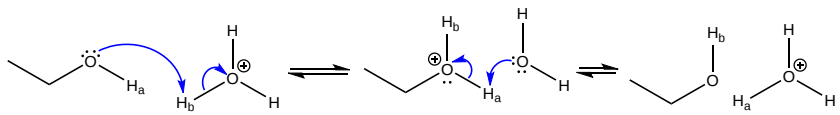


Second, splitting occurs primarily between hydrogens that are separated by three bonds. This is why the H_a hydrogens in ethyl acetate form a singlet– the nearest hydrogen neighbors are five bonds away (count the bonds between hydrogen to hydrogen), too far for coupling to occur.



Occasionally we will see four-bond and even 5-bond splitting, but in these cases the magnetic influence of one set of hydrogens on the other set is much more subtle than what we typically see in three-bond splitting (more complex coupling interactions is provided in section 5.8).

Finally, splitting is most noticeable with hydrogens bonded to carbon. Hydrogens that are bonded to heteroatoms (alcohol or amino hydrogens, for example) are coupled weakly - or not at all - to their neighbors. This has to do with the fact that these protons exchange rapidly with solvent or other sample molecules, which is greatly enhanced by even traces of acid or base (see mechanism with ethanol below). Remember, NMR is like a camera that takes photographs of a rapidly moving object with a slow shutter speed - the result is a blurred image. This blurred image here creates a broader singlet for exchanging protons, even if there are neighboring hydrogens.



To see the splitting of exchangeable protons, the NMR experiment needs to be carried out as low temperatures.

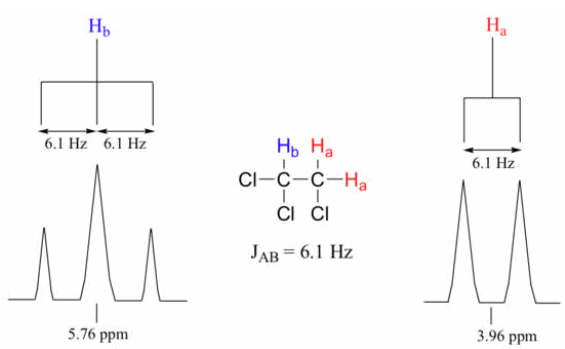
Multiplicity in Proton NMR

The number of lines in a peak is always one more (n+1) than the number of hydrogens on the neighboring carbon. This table summarizes coupling patterns that arise when protons have different numbers of neighbors.

# of lines	ratio of lines	term for peak	# of neighbors
1	-	singlet	0
2	1:1	doublet	1
3	1:2:1	triplet	2
4	1:3:3:1	quartet	3
5	1:4:6:4:1	quintet	4
6	1:5:10:10:5:1	sextet	5
7	1:6:15:20:15:6:1	septet	6
8	1:7:21:35:35:21:7:1	octet	7
9	1:8:28:56:70:56:28:8:1	nonet	8

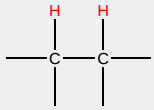
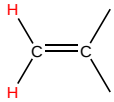
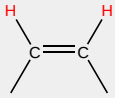
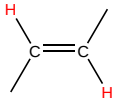
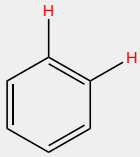
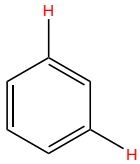
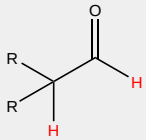
Coupling constants

Chemists quantify the spin-spin coupling effect using something called the **coupling constant**, which is abbreviated with the capital letter *J*. The coupling constant is simply the difference, expressed in Hz (not ppm), between two adjacent sub-peaks in a split signal. For our triplet in the 1,1,2-trichloroethane spectrum, for example, the three subpeaks are separated by 6.1 Hz, and thus we write $^3J_{a\text{-}b}$ = 6.1 Hz.



The superscript 3 tells us that this is a three-bond coupling interaction, and the a-b subscript tells us that we are talking about coupling between H_a and H_b. Unlike the chemical shift value, the coupling constant, expressed in Hz, is the same regardless of the applied field strength of the NMR magnet. This is because the strength of the magnetic moment of a neighboring proton, which is the source of the spin-spin coupling phenomenon, does not depend on the applied field strength. Also, the coupling constant $^3J_{a\text{-}b}$ quantifies the magnetic interaction between the H_a and H_b hydrogen sets, and this interaction is of the same magnitude in either direction. In other words, H_a influences H_b to the same extent that H_b influences H_a. When looking at more complex NMR spectra (Section 5.8), this idea of reciprocal coupling constants can be very helpful in identifying the coupling relationships between proton sets.

Similar types of bonds lead to similar coupling constants and this has resulted in a range for particular types of hydrogens interacting through a particular bond. For example, coupling constants between proton sets on neighboring sp^3-hybridized carbons (3 bonds) is typically in the region of 6-8 Hz. The table below lists typical three-bond coupling constant values for different types of bonds. Remember, chemically equivalent protons do not couple with one another to give spin-spin splitting.

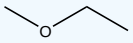
Type of bond	Image of type of bond	Coupling constant (Hz)
Standard three bond coupling		6-8
Vinylic geminal coupling		0-3
Vinylic cis coupling		6-15
Vinylic trans coupling		11-18
Benzylic ortho coupling		6-10
Benzylic meta coupling*		0-4
Aldehydic proton coupling		2-3

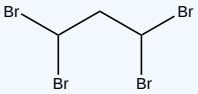
*Actually 4-bond coupling.

Exercise

Exercise 5.7.1

Predict the splitting patterns of the following molecules:

a) 

b) 

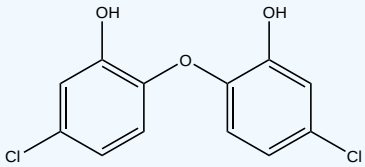
Answer

a) There are three types of protons, so there will be three peaks. The methyl directly attached to the oxygen will be a singlet. The methylene will be split into a quartet by the neighboring methyl group. The other methyl group will be split into a triplet by the neighboring $-CH_2-$.

b) This molecule is symmetrical, which leads to two types of hydrogens and therefore two peaks. The methylene will be split into a triplet by the two neighboring hydrogens on either side. The -CH- peak will be split into a triplet as well due to the neighboring $-CH_2-$.

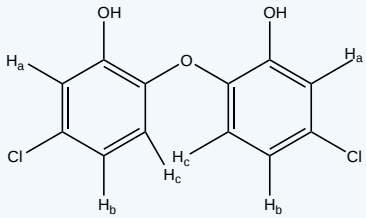
Exercise 5.7.2

How many proton signals would you expect to see in the ^{1}H-NMR spectrum of the structure shown below? For each of the proton signals, predict the splitting pattern. Assume that you see only 3-bond coupling.



Answer

Because of the symmetry in the molecule, there are only four proton signals.



OH proton = singlet

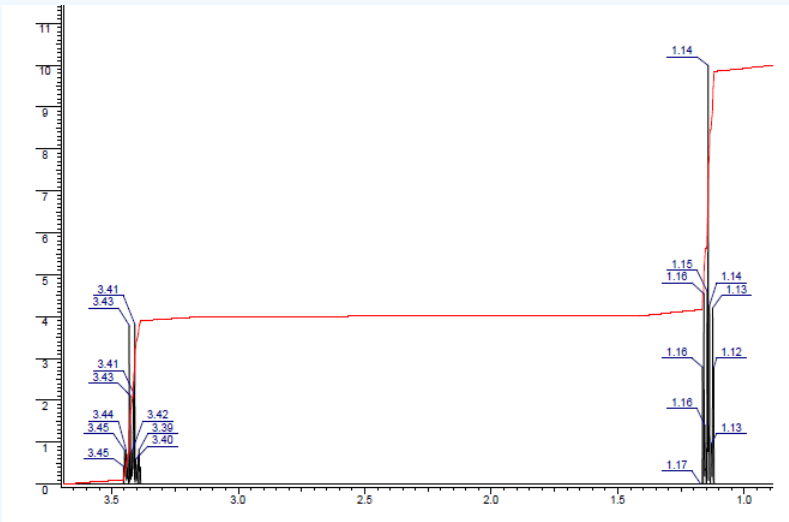
H_a = singlet

H_b = doublet

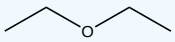
H_c = doublet

Exercise 5.7.3

The following spectrum is for $C_4H_{10}O$. Determine the structure. The ratio of integrals from left to right is 2:3.



Answer



The total number of hydrogens is 2+3 = 5. All the hydrogens are not accounted for since we need a total of 10 hydrogens. This means there is symmetry in the molecule. Ten is divisible by five. If we multiply each in the 2:3 ratio, then we get 4:6, which does add to 10.

Typically, integrations of 3 or multiples of 3 are methyl groups. The peak at 1.14 ppm is a methyl group with two neighbors, since the peak is split into a triplet. n +1 = 3, n = 2, n = number of neighbors. The first fragment is a $-CH_2-CH_3$. There are two of these fragments, since there are actually 6 total methyl protons.

The peak at 3.43 ppm integrates to 4 and is a quartet. The integration indicates it is a methylene group and since it is a quartet, it must have three neighbors. So far, the fragment would be $-CH_2-CH_3$. It is also very far downfield for a proton just bonded to other carbons with hydrogens, which would typically be around 1.2-1.7 ppm (see the table in Section 5.5). This means it must be attached to an electron withdrawing group. The electron withdrawing group in this molecule is the -O-. Our final fragment is CH_3-CH_2-O-.

If we look at all of our fragments, we can begin to put them together. Let's take the two fragments ($-CH_2-CH_3$ and $-O-CH_2-CH_3$), each makes one more bond. If you connect them, then you would get $CH_3-CH_2-O-CH_2-CH_3$. The molecule is symmetrical with two types of protons with teh 4:6 (or 2:3) ratio and correct splitting pattern. This spectrum correlates to diethyl ether.

Contributors and Attributions

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- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

5.7: Spin-Spin Splitting in Proton NMR Spectra is shared under a not declared license and was authored, remixed, and/or curated by Lauren Reutenauer.

5.8: More Complex Spin-Spin Splitting Patterns

Objectives

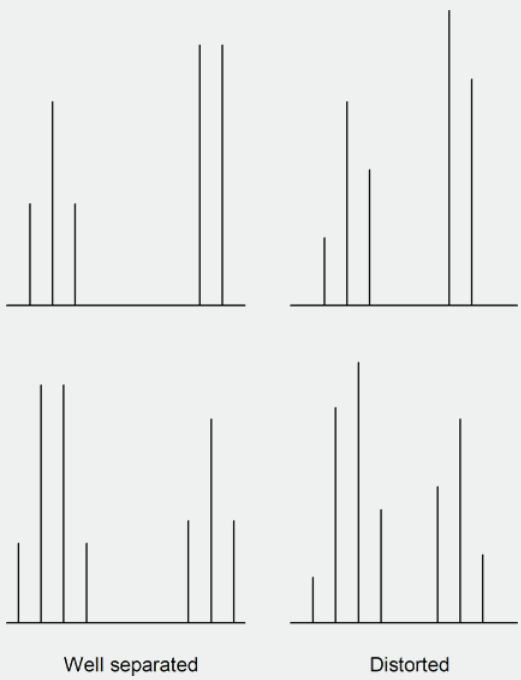
After completing this section, you should be able to

1. explain how multiple coupling can give rise to complex-looking ^{1}H NMR spectra.
2. predict the splitting pattern expected in the ^{1}H NMR spectrum of an organic compound in which multiple coupling is possible.
3. interpret ^{1}H NMR spectra in which multiple coupling is evident.

Study Notes

Another effect that can complicate a spectrum is the "closeness" of signals. If signals accidently overlap they can be difficult to identify. You can try this yourself by drawing a tree diagram. Keep this point in mind when interpreting real ^{1}H NMR spectra.

Also, when multiplets are well separated, they form patterns. However, when multiplets approach each other in the spectrum they sometimes become distorted. Usually, the inner peaks become larger than the outer peaks. Note the following examples:



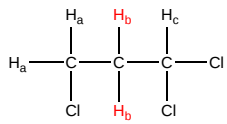
Complex coupling

In all of the examples of spin-spin coupling that we have seen so far, the observed splitting has resulted from the coupling of one set of hydrogens to *just one* neighboring set of hydrogens. What happens if there are hydrogens on both sides?

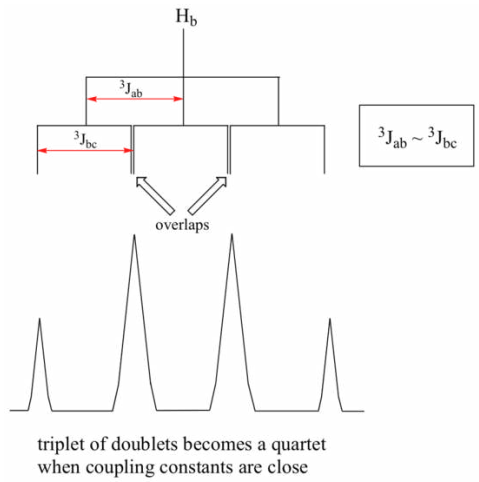
Similar Coupling Constants

When a proton is coupled to two different neighboring proton sets with identical or very close coupling constants, the splitting pattern that emerges often appears to follow the simple `$n$ + 1 rule` of non-complex splitting. Looking at 1,1,3-trichloropropane below, H_a and H_c only have H_b as neighbors. Remember, splitting occurs primarily between hydrogens that are separated by three bonds. This means that H_a would be a triplet as would H_c. However, H_b has two sets of neighboring protons (H_a and H_c). Each follows the simple spin-spin coupling patterns, since they each just have one neighboring set of hydrogens (H_b). However with H_b, it has neighboring hydrogens on both sides. There are two H_a neighbors and there is one H_c neighbor. It turns out that since the

types of interveneing bonds between H_a and H_b are the same as H_b and H_c, the coupling constants will be very similar. H_a and H_c are not equivalent (their chemical shifts are different), but it turns out that $^3J_{ab}$ is very close to $^3J_{bc}$.



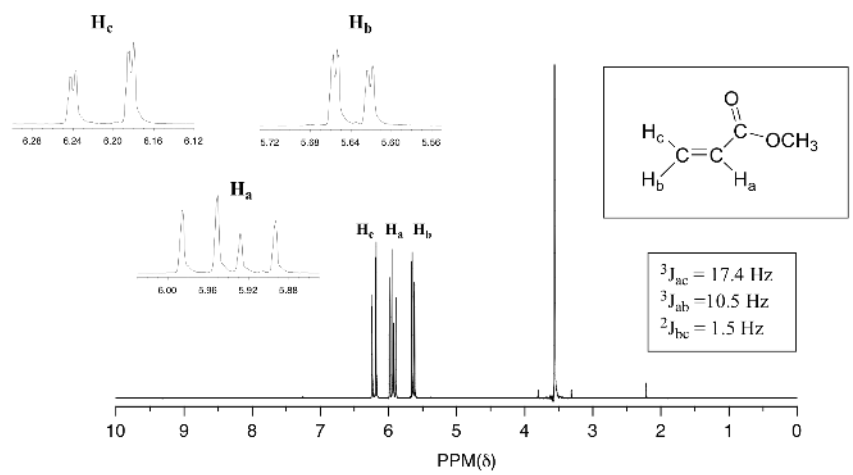
If we perform a splitting diagram analysis for H_b, we see that, due to the overlap of sub-peaks, the signal appears to be a quartet, and for all intents and purposes follows the *n* + 1 rule.



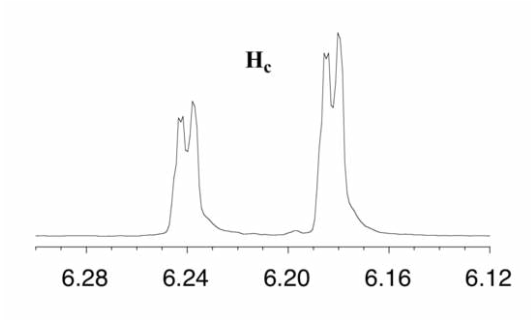
Therefore, we can still use the n + 1 rule when the coupling constants are similar and making it easier for organic chemists.

Different Coupling Constants

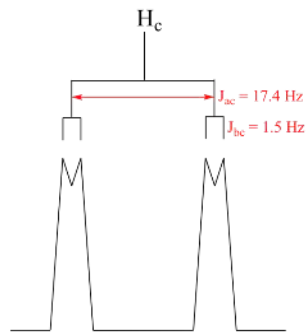
When a set of hydrogens is coupled to *two or more* sets of nonequivalent neighbors, the result is a phenomenon called **complex coupling**. A good illustration is provided by the ^{1}H-NMR spectrum of methyl acrylate:



First, let's first consider the H_c signal, which is centered at 6.21 ppm. Here is a closer look:

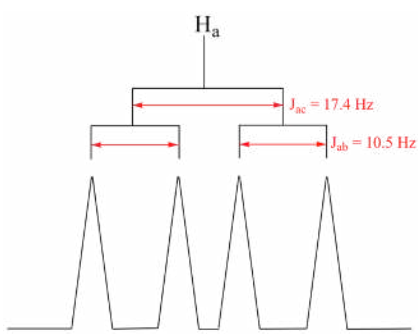


With this enlargement, it becomes evident that the H_c signal is actually composed of four sub-peaks. Why is this? H_c is coupled to both H_a and H_b , but with *two different coupling constants*. Once again, a splitting diagram (or tree diagram) can help us to understand what we are seeing. H_a is *trans* to H_c across the double bond, and splits the H_c signal into a doublet with a coupling constant of $^3J_{ac}$ = 17.4 Hz. In addition, each of these H_c doublet sub-peaks is split again by H_b (*geminal* coupling) into two more doublets, each with a much smaller coupling constant of $^2J_{bc}$ = 1.5 Hz.

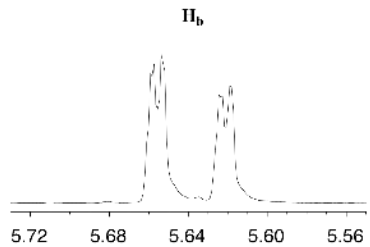


The result of this $doub \leq spli \in g$ is a pattern referred to as a **doublet of doublets**, abbreviated **dd**.

The signal for H_a at 5.95 ppm is also a doublet of doublets, with coupling constants $^3J_{ac}$= 17.4 Hz and $^3J_{ab}$ = 10.5 Hz. We know it is not a quartet because the intensity of the lines is the same for each like a doublet, whereas for a quartet the ratio of the lines is 1:3:3:1 where the outside lines would be shorter.



The signal for H_b at 5.64 ppm is split into a doublet by H_a, a *cis* coupling with $^3J_{ab}$ = 10.4 Hz. Each of the resulting sub-peaks is split again by H_c, with the same *geminal* coupling constant $^2J_{bc}$ = 1.5 Hz that we saw previously when we looked at the H_c signal. The overall result is again a doublet of doublets, this time with the two $\subset - doub \leq ts$ spaced slightly closer due to the smaller coupling constant for the *cis* interaction. Here is a blow-up of the actual H_b signal:



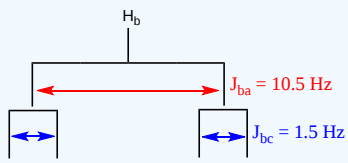
You may have noticed in the splitting diagram, the larger of coupling constant came first followed by the smaller or finer coupling constant.While it does not matter which coupling constant you start with, it is usually easier to construct the splitting diagram for analysis of complex coupling patterns if you begin with the larger coupling constant. However, the end result will be the same regardless of how you begin.

Example \PageIndex1

Construct a splitting diagram for the H_b signal in the ^{1}H-NMR spectrum of methyl acrylate. Show the chemical shift value for each sub-peak, expressed in Hz (assume that the resonance frequency of TMS is exactly 300 MHz).

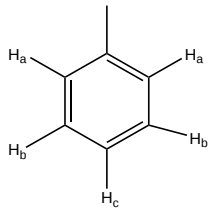
Solution

The coupling tree for H_b is:



The complex coupling pattern would be a doublet of doublets (dd).

In many cases, it is difficult to fully analyze a complex splitting pattern. Aromatic ring protons quite commonly have overlapping signals and multiplet distortions. Sometimes you cannot distinguish between individual signals, and one or more messy multiplets often appear in the aromatic region. In the spectrum of toluene, for example, if we consider only 3-bond coupling we would expect the signal for H_a to be a doublet, H_b a triplet, and H_c a triplet.



In practice, however, all three aromatic proton groups have very similar chemical shifts and their signals overlap substantially, making such detailed analysis difficult. In this case, we would refer to the aromatic part of the spectrum (~7.0 ppm) as a **multiplet**.

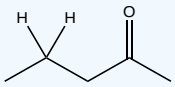
When we start trying to analyze complex splitting patterns in larger molecules, we gain an appreciation for why scientists are willing to pay large sums of money (hundreds of thousands of dollars) for higher-field NMR instruments. Quite simply, the stronger our magnet is, the more resolution we get in our spectrum. In a 100 MHz instrument (with a magnet of approximately 2.4 Tesla field strength), the 12 ppm frequency 'window' in which we can observe proton signals is 1200 Hz wide. In a 500 MHz (~12 Tesla) instrument, however, the window is 6000 Hz - five times wider. In this sense, NMR instruments are like digital cameras and HDTVs: better resolution means more information and clearer pictures (and higher price tags!).

It is much easier to rationalize the observed ^{1}H NMR spectrum of a known compound than it is to determine the structure of an unknown compound from its ^{1}H NMR spectrum. However, rationalizations can be a useful learning technique as you try to improve your proficiency in spectral interpretation. Remember that when a chemist tries to interpret the ^{1}H NMR spectrum of an unknown compound, he or she usually has additional information available to make the task easier. For example, the chemist will almost certainly have an infrared spectrum of the compound and possibly a mass spectrum too. Details of how the compound was synthesized may be available, together with some indication of its chemical properties, its physical properties, or both.

Exercises

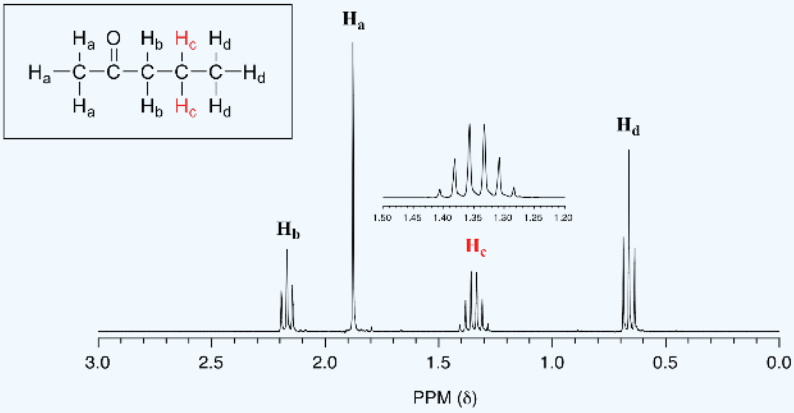
? Exercise \PageIndex1

The molecule below is 2-pentanone, what would the splitting pattern be for the two hydrogens explicitly indicated (below) in an ^{1}H NMR spectrum.



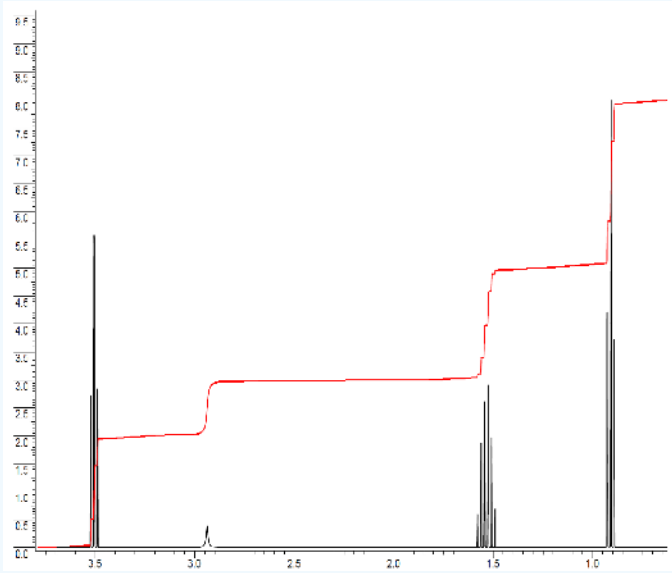
Answer

The indicated hydrogens (H_c below) in the spectrum of 2-pentanone appears as a sextet. They would be split by the five combined protons (H_b and H_d below). Since the intervening bonds are the same, J_{bc} and J_{cd} would be very similar and the n+1 rule can be followed. Technically, this 'sextet' could be considered to be a 'triplet of quartets' with overlapping sub-peaks.

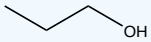


? Exercise \PageIndex2

The following spectrum is for C_3H_8O. Determine the structure. The ratio of integrals from left to right is 2:1:2:3.



Answer



The total number of hydrogens is 2+1+2+3 = 8. All the hydrogens are accounted for.

Typically, integrations of 3 or multiples of 3 are methyl groups. The peak at 0.9 ppm is a methyl group with two neighbors, since the peak is split into a triplet. n +1 = 3, n = 2, n = number of neighbors. The first fragment is a $-CH_2-CH_3$.

The peak just above 1.5 ppm integrates to 2 protons and is a sextet (split into 6 peaks). The integration of 2 indicates this is a methylene group ($-CH_2-$) and the spin-spin splitting pattern tells us that there are 5 neighbors. A methylene makes two more bonds, so one side must be the methyl group and the other side must be another methylene in order to have 5 total neighbors. The next fragment is $-CH_2-CH_2-CH_3$.

The peak just below 3.0 ppm is a broad singlet. Broad singlets typically come from exchangeable protons like an -OH or -NH-. In our molecular formula we have no N, but we do have an O, so this peak must be due to the -OH.

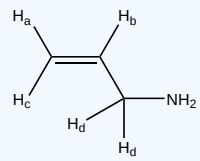
The final peak at 3.5 ppm integrates to 2 and is a triplet. The integration indicates it is another methylene group and since it is a triplet, it must have two neighbors. So far, the fragment would be $-CH_2-CH_2-$. It is also very far downfield for a proton just bonded to other carbons with hydrogens, which would typically be around 1.2-1.7 ppm (see the table in Section 5.5).

This means it must be attached to an electron withdrawing group. The electron withdrawing group in this molecule is the -OH. Our final fragment is $-CH_2-CH_2-OH$.

If we look at all of our fragments, we can see that it is too many carbons and hydrogens if they all represented a separate piece to include. However, spin-spin splitting is the information from neighboring hydrogens. This means that the fragments overlap each other. Let's take the first two fragments ($-CH_2-CH_3$ and $-CH_2-CH_2-CH_3$). The integration information indicates that there is only one peak that integrates to 3, so there is only one methyl group, not two. This means one of the methyl groups is a duplicate and there is actually only one methyl group. In the second fragment, the splitting pattern indicated that there must be a neighboring methyl group, but the information is actually about the central methylene in that fragment. Considering this, the molecule must be $HO-CH_2-CH_2-CH_3$. It has four different types of hydrogens, with the correct ratios as well as splitting pattern.

? Exercise \PageIndex3

For the molecule below, what would the coupling pattern be in a ^1H NMR spectrum?



Answer

H_b would be a doublet of doublet of triplets. H_c splits H_b by trans coupling into a doublet. H_a splits H_b by cis coupling into a doublet. The two H_d protons split H_b into a triplet. All of the J coupling constants are different, so you cannot use the n+1 rule.

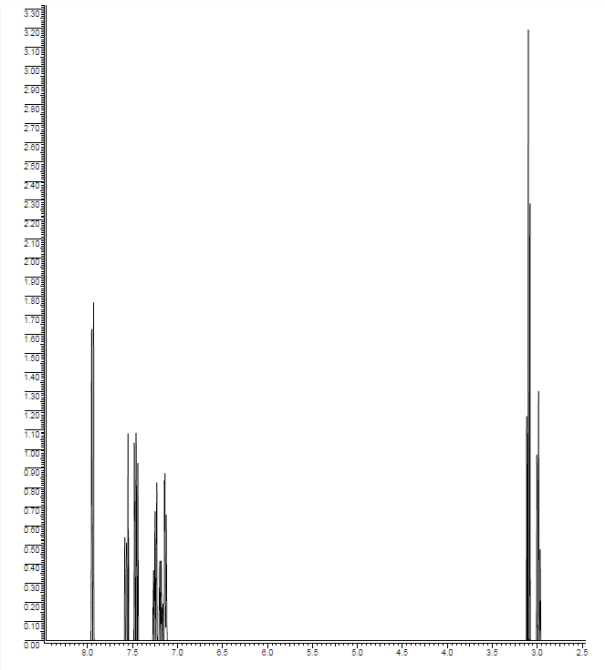
? Exercise \PageIndex4

Unknown compound *D* ($C_{15}H_{14}O$) has the following spectral properties.

Infrared spectrum:

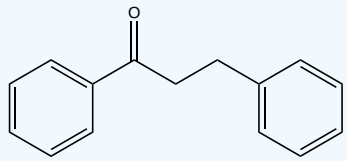
3010 cm^{-1} (medium)
1715 cm^{-1} (strong)
1610 cm^{-1} (strong)
1500 cm^{-1} (strong)

^1H NMR spectrum:



δ (ppm)	Relative Area	Multiplicity
3.00	2	triplet
3.07	2	triplet
7.1-7.9	10	Multiplets

Answer



Contributors and Attributions

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- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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5.9: Uses of Proton NMR Spectroscopy

Objective

After completing this section,

- understand how ^{1}H NMR data can be used to distinguish between two (or more) possible structures for an unknown organic compound
- determine if your reaction went to completion based on how clean the ^{1}H NMR spectrum is
- understand how the ratio of mixtures can be obtained

The two major areas where NMR has proven to be of critical importance is in the fields of medicine and chemistry, with new applications being developed daily.

Nuclear magnetic resonance imaging, better known as magnetic resonance imaging (MRI) is an important medical diagnostic tool used to study the function and structure of the human body. It provides detailed images of any part of the body, especially soft tissue, in all possible planes and has been used in the areas of cardiovascular, neurological, musculoskeletal and oncological imaging. Unlike other alternatives, such as computed tomography (CT), it does not used ionized radiation and hence is very safe to administer.

Figure **5.9.1**: ^{1}H MRI of a human head showing the soft tissue such as the brain and sinuses. The MRI also clearly shows the spinal column and skull.

In many laboratories today, chemists use nuclear magnetic resonance to determine structures of important chemical and biological compounds. In NMR spectra, different peaks give information about different atoms in a molecule according specific chemical environments and bonding between atoms. The most common isotopes used to detect NMR signals are ^{1}H and ^{13}C but there are many others, such as ^{2}H, ^{3}He, ^{15}N, ^{19}F, etc., that are also in use.

NMR has also proven to be very useful in other area such as environmental testing, petroleum industry, process control, earth's field NMR and magnetometers. Non-destructive testing saves a lot of money for expensive biological samples and can be used again if more trials need to be run. The petroleum industry uses NMR equipment to measure porosity of different rocks and permeability of different underground fluids. Magnetometers are used to measure the various magnetic fields that are relevant to one's study.

^{1}H NMR spectroscopy provides a lot of information. Each signal in the spectrum is a unique proton(s). Chemical shift indicates the type of environment protons are in. Integration tells how many of the unique protons there are. Spin-spin coupling tells how many neighbors a particular proton has. Each adding a bit more complexity, but how can ^{1}H NMR be used?

1) There will be cases in which you already know what the structure might be. In these cases:

- You should draw attention to pieces of data that most strongly support your expected structure. This approach will demonstrate evaluative understanding of the data; that means you can look at data and decide what parts are more crucial than others.
- You should also draw attention to negative results: that is, peaks that might be there if this spectrum matched another, possible structure, but that are in fact missing.

2) One of the most complicated problems to deal with is the analysis of a mixture. This situation is not uncommon when running a reaction in lab.

- Sometimes the spectra shows a little starting material mixed in with the product

- Sometimes the spectra shows a little starting material mixed in with the product.
- Sometimes solvents show up in the spectrum.
- As you might expect, the minor component usually shows up as smaller peaks in the spectrum. If there are fewer molecules present, then there are usually fewer protons to absorb in the spectrum.
- In this case, you should probably make two completely separate sets of data tables for your analysis, one for each compound, or else one for the main compound and one for impurities.

It can be helpful to either take a ^{1}H NMR spectrum of your starting materials or look it up in a database, which can be used as a reference for the product ^{1}H NMR.

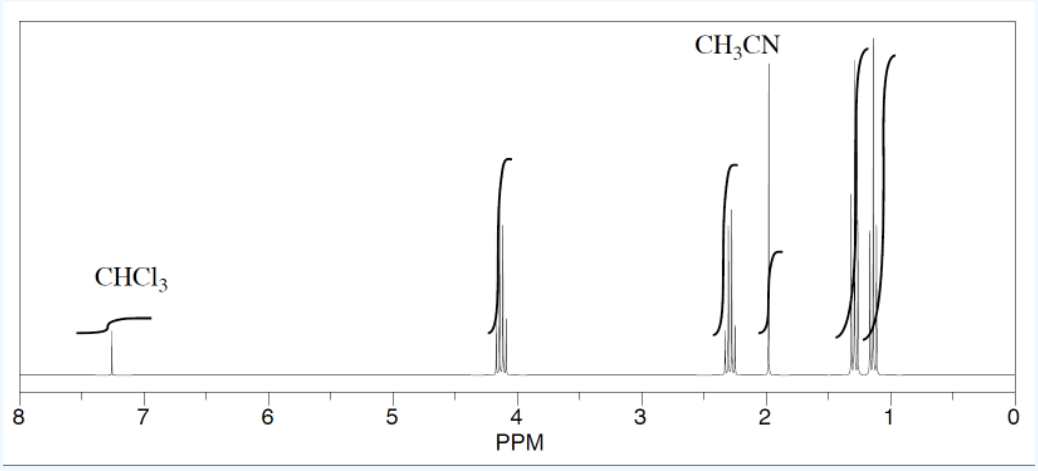
3) Remember that integration ratios are really only meaningful within a single compound. If your NMR sample contains some benzene (C_6H_6) and some acetone (CH_3COCH_3), and there is a peak at 7.15 that integrates to 1 proton and a peak at 2.10 ppm integrating to 6 protons, you may think it might mean there are 6 protons in acetone and 1 in benzene, but you can tell that isn't true by looking at the structures. Both benzene and acetone have six protons. In benzene, they should all show up near 7 ppm and in acetone they should all show up near 2 ppm. Assuming that small integral of 1H for the benzene is really supposed to be 6H, then the large integral of 6H for the acetone must also represent six times as many hydrogens, too. It would be 36 H. There are only six hydrogens in acetone, so it must represent six times as many acetone molecules as there are benzene molecules.

Similarly, if you have decided that you can identify two sets of peaks in the ^{1}H spectrum, such as starting material and product, analyzing them in different tables makes it easy to keep the integration analysis completely separate too; 1 H in one table will not be the same size integral as 1 H in the other table unless the concentrations of the two compounds in the sample are the same. Comparing the ratio of two integrals for two different compounds can give you the ratio of the two compounds in solution, just as we could determine the ratio of benzene to acetone in the mixture described above.

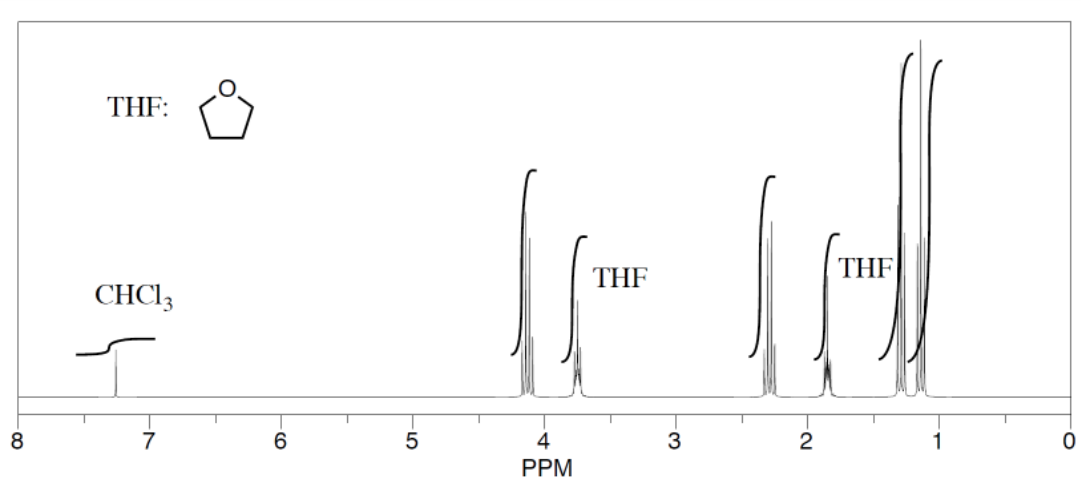
Example 5.9.1

Three students performed a synthesis of a fragrant ester, ethyl propanoate, $CH_3CH_2CO_2CH_2CH_3$. During their reactions, they each used a different solvent (acetonitrile, tetrahydrofuran, and dichloromethane). Did any of the students see just ethyl propanoate?

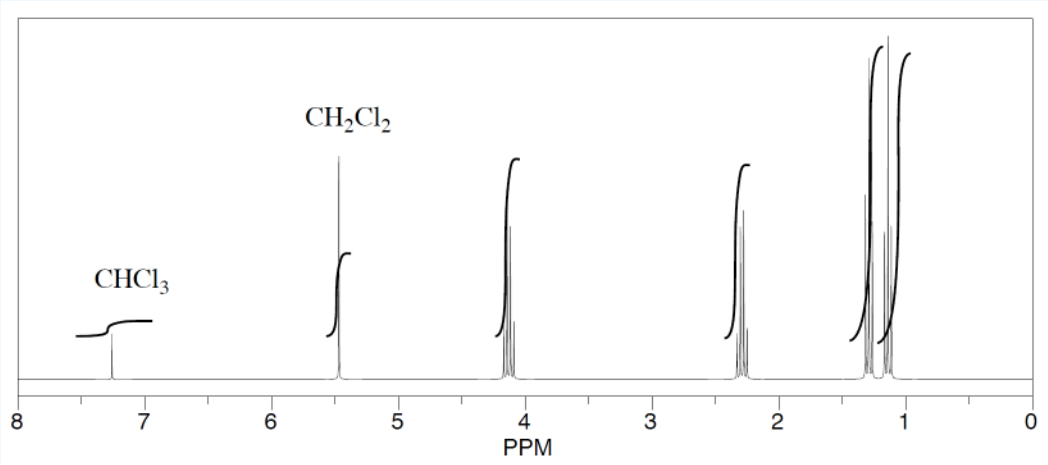
See the first student's spectrum:



See the second student's spectrum:



See the third student's spectrum:



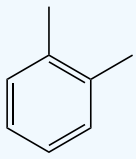
Solution

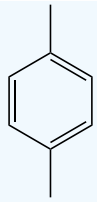
The students saw peaks in the NMR spectrum for ethyl propanoate, chloroform ($CHCl_3$, in the $CDCl_3$ they used to make their NMR samples), and trace amounts of solvent from running the reaction. They were also able to determine that they had some leftover solvent in their samples by consulting a useful table of solvent impurities in NMR (which they found in Goldberg et. al., Organometallics 2010, 29, 2176-2179).

Exercises

? Exercise 5.9.1

How could you tell the difference between *o*-xylene and *p*-xylene in $_1$H NMR?

o-xylene: 

p-xylene: 

Answer

There are a variety of ways to determine the difference between these two molecules. In *o*-xylene, there are 3 types of protons and in *p*-xylene there are two types of protons. There will be spin-spin splitting in the o-xylene aromatic protons, since there are two types of aromatic protons and the protons are neighbors. *p*-Xylene will show now splitting in the aromatic protons, since there is just one type of aromatic proton with no neighbors.

Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
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5.10: Interpreting Proton NMR Spectra

Objectives

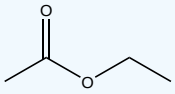
- understand how chemical shift, integration, spin-spin splitting all come together to solve ^{1}H NMR problems.
- solve unknown ^{1}H NMR problems given the molecular formula.

This page is devoted to explaining solved ^{1}H NMR problems to help guide you through different scenarios. The first will be a case in which you know the structure of the product you are synthesizing, but need to prove you did indeed make it. Your strategy should be:

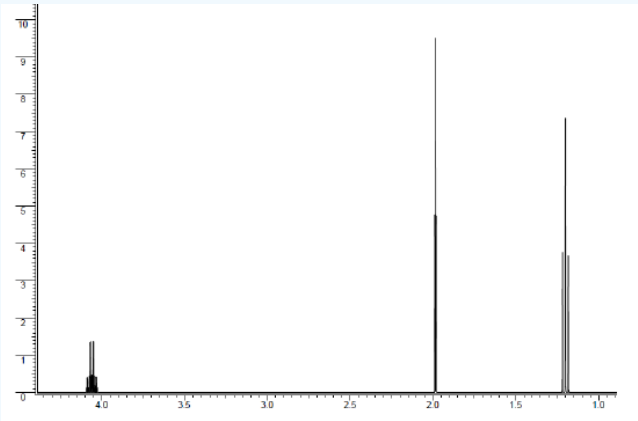
- Draw your attention to pieces of data that most strongly support your expected structure. A skill necessary for this will be your ability to demonstrate evaluative understanding of the data. In other words, you can look at the data and decide what parts are more important than other parts.
- Draw you attention to negative results: what peaks might be there if the spectrum matched another possible structure, but is missing.

Example 5.10.1

In the laboratory, you performed an esterification to make ethyl acetate. Based on the ^{1}H NMR spectrum, did you make your desired product?

Expected Product: 

^{1}H NMR: The ratio of protons is 2:3:3.



Solution

Yes, ethyl acetate was synthesized. First, the ratio of protons equals the number of protons in our expected product.

The peak at 1.20 ppm is a triplet that integrates to 3 protons. The integration indicates that the peak corresponds to a methyl group. The splitting pattern of a triplet indicates that there are two neighboring. All of this information together gives the piece $-CH_2CH_3$.

The peak at 1.98 ppm is a singlet that integrates to 3 protons. The integration tells us the peak corresponds to a methyl group. The splitting pattern of a singlet indicates that there are no neighbors. The chemical shift is quite far downfield at 1.98 ppm (a methyl group attached to another carbon would be at about 0.9 ppm). Being further downfield means that the methyl group is attached to an electron-withdrawing group, which could be directly to an oxygen or the carbonyl carbon. All of this information together gives the piece $-EWG-CH_3$. EWG = Electron-Withdrawing Group

The peak at 4.06 ppm is a quartet that integrates to 2 protons. The integration tells us the peak corresponds to a methylene group (-CH_2-). The splitting pattern of a quartent indicates that there are 3 neighbors. The chemical shift is quite far downfield at 4.06 ppm (a methylene group attached to another carbon would be at about 1.2 ppm). Being the furthest downfield, the methylene group needs to be attached to the electron-withdrawing group that will be the most deshielding for the protons (Chemical Shift information). This is the proton must be directly attached to the oxygen. All of this information together gives the piece -O-CH_2CH_3, which means the methyl group at 1.98 ppm is directly attached to the carbonyl carbon.

From this analysis, it can be concluded that yes, ethyl acetate was synthesized as expected.

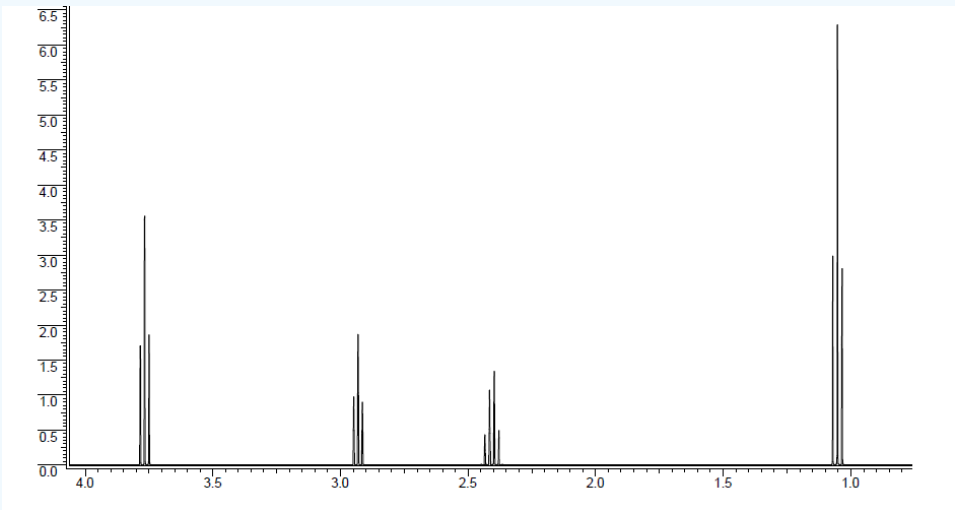
Next, we will look at a ^{1}H NMR spectrum of an unknown and determine its structure.

Example 5.10.2

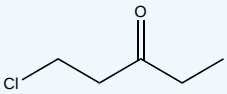
Using the chemical formula and ^{1}H NMR spectrum, determine the structure of your unknown molecule.

Chemical Formula: C_5H_9ClO

Unknown molecule ^{1}H NMR spectrum: The ratio of protons is 2:2:2:3.



Solution

Unknown molecule: 

First, if the molecular formula is known, then start by calculating the degree of unsaturation (DU), which will tell how many double bond, triple bond, or rings are present in the molecule. A double bond is a DU = 1. A ring is a DU = 1. A triple bond is a DU = 2. The degree of unsaturation for C_5H_9ClO is 1. Therefore, the molecule either contains a ring or a double bond.

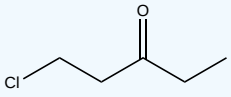
The peak at 1.05 ppm is a triplet that integrates to 3 protons. The integration indicates that the peak corresponds to a methyl group. The splitting pattern of a triplet indicates that there are two neighboring. All of this information together gives the piece -CH_2CH_3.

The peak at 2.40 ppm is a quartet that integrates to 2 protons. The integration tells us the peak corresponds to a methylene group. The splitting pattern of a quartet indicates that there are 3 neighboring protons. The chemical shift is quite far downfield at 2.40 ppm (a methylene group attached to another carbon would be at about 1.2 ppm). Being further downfield means that the methylene group is attached to an electron-withdrawing group, which could be directly to the chlorine or carbonyl carbon. All of this information together gives the piece -EWG-CH_2CH_3. EWG = Electron-Withdrawing Group

The peak at 2.90 ppm is a triplet that integrates to 2 protons. The integration tells us the peak corresponds to a methylene group. The splitting pattern of a triplet indicates that there are 2 neighboring protons. The chemical shift is quite far downfield

at 2.90 ppm. Being further downfield means that the methylene group is attached to an electron-withdrawing group, which could be directly to the chlorine or carbonyl carbon. All of this information together gives the piece -EWG-CH_2CH_2-.

The peak at 3.77 ppm is a triplet that integrates to 2 protons. The integration tells us the peak corresponds to a methylene group. The splitting pattern of a triplet indicates that there are 2 neighbors. The chemical shift is quite far downfield at 3.77 ppm. Being the furthest downfield, the methylene group needs to be attached to the electron-withdrawing group that will be the most deshielding for the protons (Chemical Shift information). This is the proton must be directly attached to the chlorine. All of this information together gives the piece Cl-CH_2CH_2-, which means the methylene groups at 2.40 and 2.90 ppm are directly attached to the carbonyl carbon, since the chlorine only makes one bond.

All of this information yields the unknown molecule structure to be 

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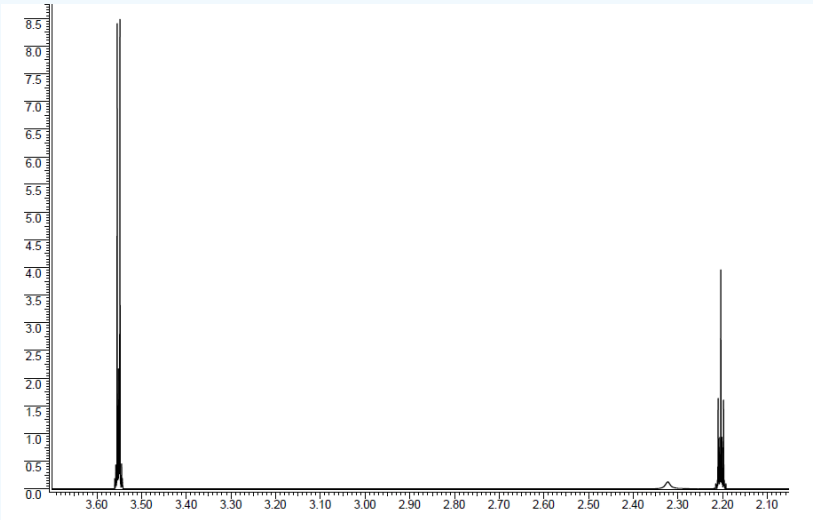
In the example just discussed, the number of hydrogens in the spectrum was equal the number of hydrogens in the molecular formula. What if this is not the case? Symmetry in a molecule can complicate your ability to determine a structure because the ^{1}H NMR spectrum seems more simple than expected.

Example 5.10.3

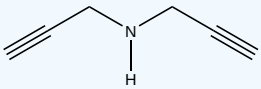
Using the chemical formula and ^{1}H NMR, determine the structure of the unknown molecule.

Molecular formula: C_6H_7N

Unknown molecule ^{1}H NMR spectrum: The ratio is 1:1:2.



Solution

Unknown molecule: 

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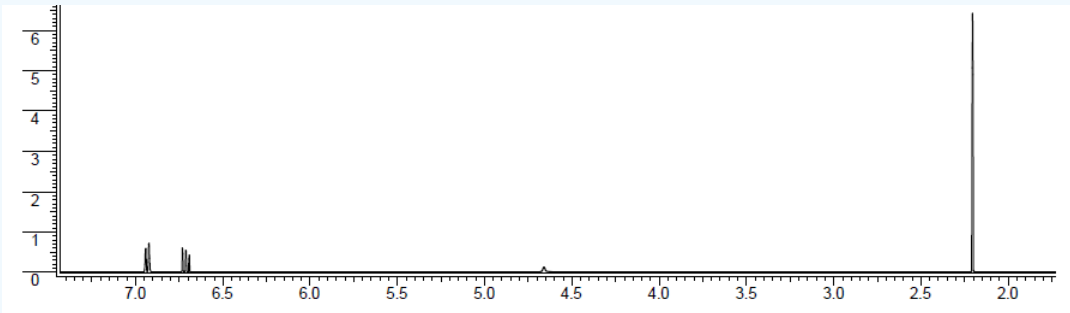
Thus far, we have not needed to use the J-coupling constants from the splitting patterns, because the constants would have all been very similar of about 7 Hz. However, they can be very useful in determining your final product and ruling out other possibilities.

Example 5.10.4

Using the chemical formula and the ^{1}H NMR spectrum, determine the structure of the unknown molecule.

Molecular formula: $C_8H_{10}O$.

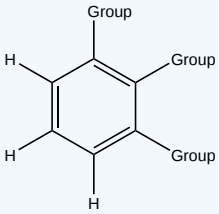
Unknown molecule ^{1}H NMR spectrum: The proton ratio is 2:1:1:6. The coupling constant for the doublet (6.93 ppm) and triplet (6.71 ppm) is 8 Hz.



Solution

DU = 4. Anytime there is a DU of at least 4, it is often an aromatic ring. Each double bond is 1 DU and the ring is 1 DU, so 3(1) + 1 = 4.

To double check this, look to see if there are any protons in the aromatic proton region (6.5 ppm - 8 ppm). This spectrum does in fact have aromatic protons, so there must be an aromatic ring. There is a total of 3 protons in the aromatic region, which means that there are three hydrogens coming of the aromatic ring and three groups coming off the aromatic ring. The coupling constant of 8 Hz indicates that the aromatic protons are ortho to one anther. The piece from this information is

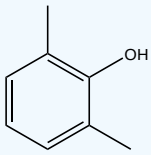


.

For the groups, since there are only two types of aromatic protons, this means that the groups ortho to the hydrogens must be the same.

The peak at 4.66 ppm is broad and small and integrates to one proton. Broad peaks typically are from exchangeable protons attached to oxygen or nitrogen. Since our molecular formula contains an O, this must be a hydroxyl group (-OH).

The singlet at 2.20 ppm integrates to 6 protons. The most common way to have 6 equivalent protons is that there are two methyl groups with no neighbors. Two methyl groups would be two of the same group and therefore are the groups ortho to the protons on the aromatic ring.

All of this information yields the unknown molecule structure to be 

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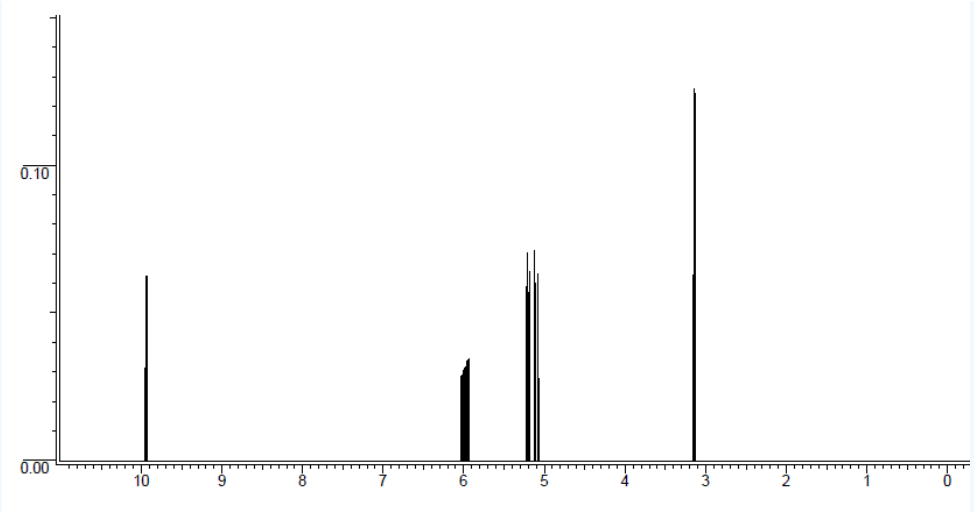
The final example brings in a more complex splitting pattern.

Example 5.10.5

Using the chemical formula and the ^{1}H NMR spectrum, determine the structure of the unknown molecule.

Molecular formula: C_4H_6O.

Unknown molecule ^{1}H NMR spectrum: The proton ratio is 1:1:1:1:2. The coupling constant for the doublet of doublet of triplets (5.93 ppm) has three coupling constants which are 17 Hz, 10 Hz, and 7 Hz. and triplet (6.71 ppm) is 8 Hz. The doublet of doublets at 5.20 ppm has coupling constants of 10 Hz and 2 Hz and the doublet of doublets at 5.10 ppm has coupling constants of 17 Hz and 2 Hz. The doublet at 3.12 ppm has a coupling constant of 7 Hz.



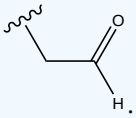
Solution

DU = 2. Therefore, there is either a double bond or a ring. If we look at chemical shifts, there are peaks in the double bond region, so the molecule has at least one double bond.

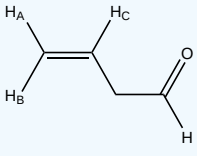
Another thing to note is that the ratio of protons equals our total number of protons of 6. Therefore, all the protons are accounted for and there is not integration of 3, so this molecule has NO methyl groups.

The peak out at 10 ppm is an aldehyde proton. Very few peaks show up that far downfield and using the chemical shift table, it indicates that it is an aldehydic proton. An aldehyde contains a carbonyl (C=O), which is our second degree of unsaturation.

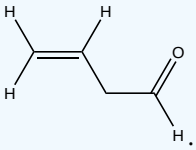
The peak at 3.12 ppm is a methylene ($-CH_2-$) group, since the integration is 2. It is quite far downfield, so it must be near an electron-withdrawing group. So far, there is an aldehyde, which would be an "end" to the molecule much like a methyl group.

The fragment piece could be 

.

This brings us to the double bond region. In total, there are three double bond protons, which means we have a terminal double bond. There is only one way to have a double bond with three protons, but let's consider the splitting. If we combine the double bond with the fragment we have, then our molecule would be 

. H_A is a doublet of doublets. It is split by cis coupling to H_c of 10 Hz and geminal coupling to H_B of 2 Hz, which yields a doublet of doublets. H_B is a doublet of doublets. It is split by trans coupling to H_c of 17 Hz and geminal coupling to H_A of 2 Hz, which yields a doublet of doublets. The doublet of doublet of triplets is H_c. As we just discussed, it couples through cis bonding to H_A (10 Hz) and trans to H_B (17 Hz). The triplet comes from regular 3-bond coupling to the methylene group, which is J = 7 Hz.

All of this information yields the unknown molecule structure to be 

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The next section will have problems for you to solve.

5.10: Interpreting Proton NMR Spectra is shared under a not declared license and was authored, remixed, and/or curated by Lauren Reutenauer.

5.11: Proton NMR problems

Objectives

- Solve unknown problems using ^{1}H NMR spectra and molecular formula.

Note

Helpful resources for solving these types of problems:

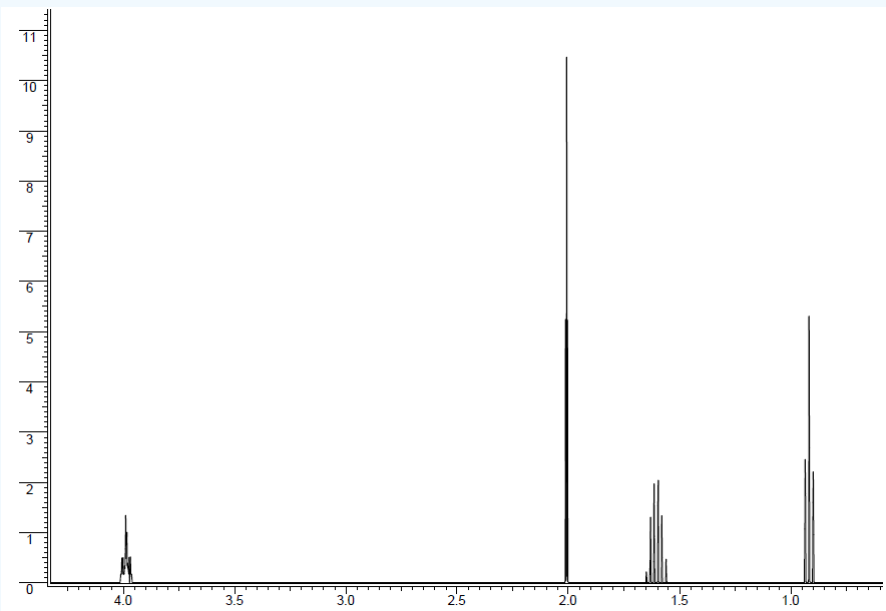
1. Degree of Unsaturation Equation
2. Chemical Shift Data Table
3. Coupling Constant Data Table
4. IR Data Table

You may also want to read through some worked problems on how to solve unknown structure determination problems (Section 5.10).

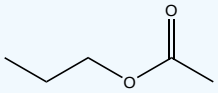
Exercise 5.11.1

Determine the structure for the unknown molecule with the molecular formula of $C_5H_{10}O_2$.

^{1}H NMR: The ratio of protons is 2:3:2:3. J = 7 Hz for all coupling.



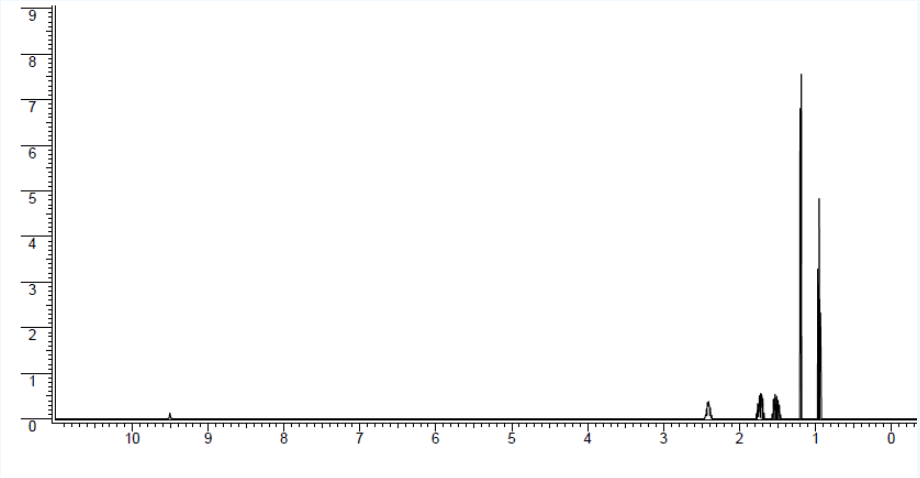
Answer



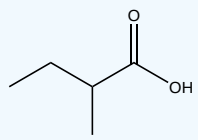
Exercise 5.11.2

Determine the structure for the unknown molecule with the molecular formula of $C_5H_{10}O_2$.

^{1}H NMR: The ratio of protons is 1:1:1:1:3:3. The peak at 9.5 ppm is a singlet. The peak at 2.41 ppm is sextet (J = 7 Hz). The peak at 1.72 ppm is a multiplet (J = 7Hz, 25 Hz). The peak at 1.53 ppm is a multiplet (J = 7 Hz, 25 Hz). The peak at 1.20ppm is a doublet (J = 7 Hz). The peak at 0.95 ppm is a triplet (J = 7 Hz).



Answer

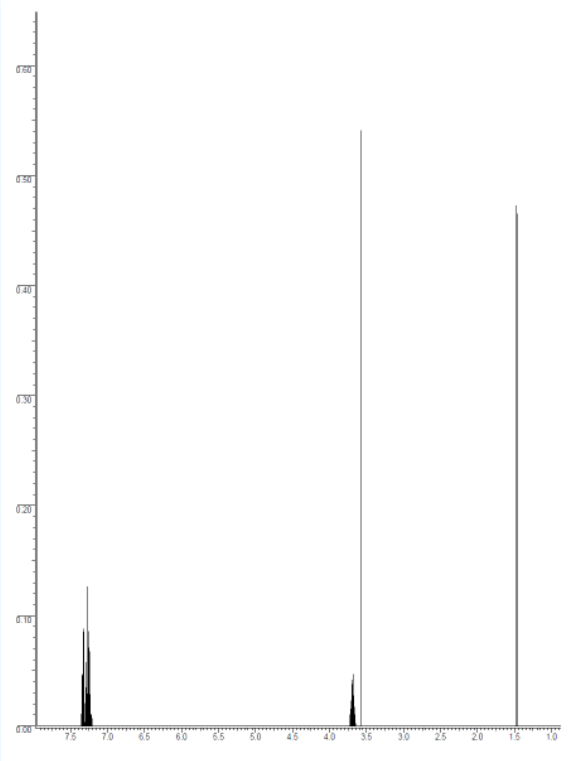


Note: The -CH_2- protons are diastereotopic, so they show up differently in ^{1}H NMR spectra.

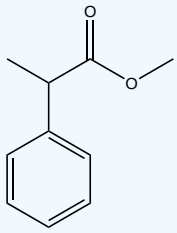
Exercise 5.11.3

Determine the structure for the unknown molecule with the molecular formula of $C_{10}H_{12}O_2$.

^{1}H NMR: The ratio of protons is 5:1:3:3. The peak at 7.5 ppm is a multiplet. The peak at 3.70 ppm is quartet (J = 7 Hz). The peak at 3.58 ppm is a singlet. The peak at 1.48 ppm is a doublet (J = 7 Hz).



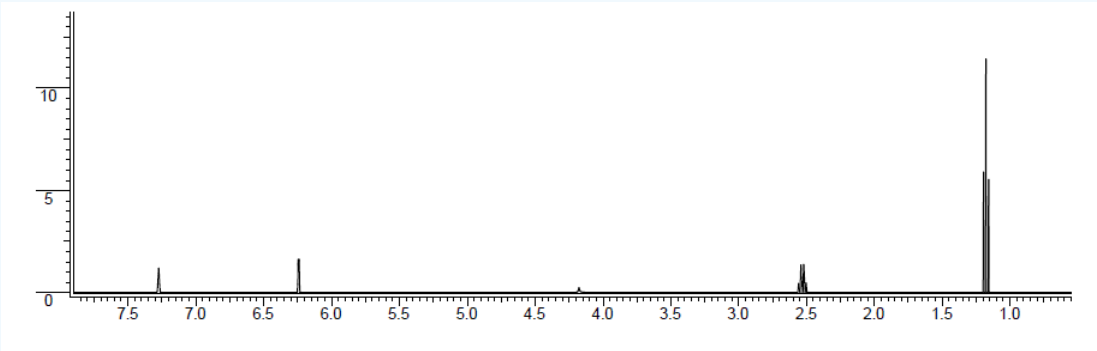
Answer



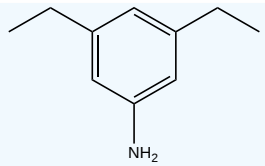
Exercise 5.11.4

Determine the structure for the unknown molecule with the molecular formula of $C_{10}H_{15}N$.

^{1}H NMR: The ratio of protons is 1:2:2:4:6. The peak at 7.3 ppm is a triplet (J = 2Hz) and the peak at 6.24 ppm is a doublet (J = 2 Hz).



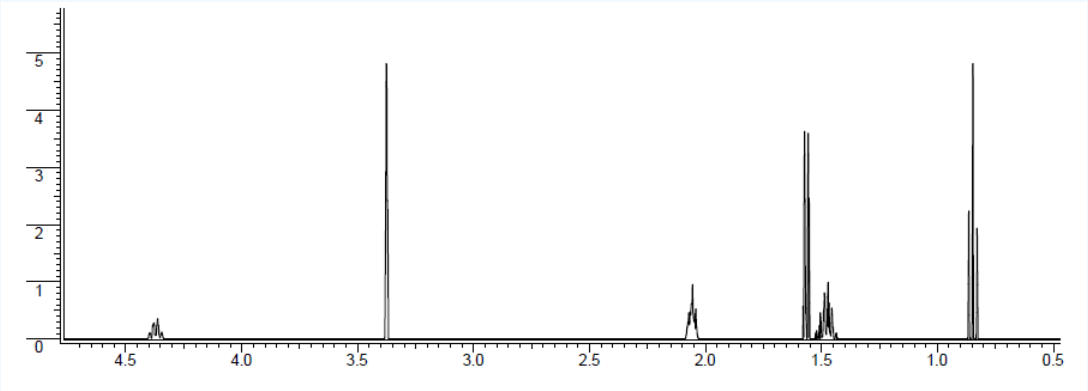
Answer



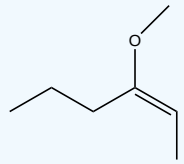
Exercise 5.11.5

Determine the structure for the unknown molecule with the molecular formula of $C_7H_{14}O$.

^{1}H NMR: The ratio of protons is 1:3:2:3:2:3. The peak at 4.36 ppm is a triplet of quartets (J = 17 Hz and 7Hz). The peak at 3.37 ppm is a singlet. The peak at 2.04 ppm is a doublet of triplets (J = 17 Hz and 7Hz). The peak at 1.56 ppm is a doublet (J = 7 Hz). The peak at 1.48 ppm is a sextet (J = 7 Hz). The peak at 0.85 ppm is a triplet (J = 7 Hz).



Answer



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5.S: Summary

Concepts & Vocabulary

5.1: Chapter Objectives and Preview of Nuclear Magnetic Resonance Spectroscopy

- Nuclear magnetic resonance spectroscopy is based on the function of nuclei as they interact with a magnetic field.

5.2 Theory of NMR

- Some types of atomic nuclei act as though they spin on their axis similar to the Earth.
- Atomic nuclei with even numbers of protons and neutrons have zero spin and all the other atoms with odd numbers have a non-zero spin.
- The magnetic moment of the nucleus acts as a tiny bar magnet.
- In the absence of an external magnetic field, each magnet is randomly oriented. However in the presence of an external magnetic field, the nuclear spins will either align with the magnetic field or oppose it.
- In order for the NMR experiment to work, a spin flip between the energy levels must occur.
- The local electronic environment surrounding the nucleus will slightly change the magnetic field experienced by the nucleus, which in turn will cause slight changes in the energy levels.
- Hydrogens attached to single or triple bonds are more shielded than alkenyl hydrogens due to position of induced magnetic fields of the electrons.
- Relaxation refers to the phenomenon of nuclei returning to their thermodynamically stable states after being excited to higher energy levels.

5.3 Instrumentation

- NMR spectroscopy works by varying the machine's emitted frequency over a small range while the sample is inside a constant magnetic field.
- The magnets used by NMR instruments are superconducting to create the magnetic field range from 6 to 24 T.
- A sample is inserted into the NMR probe, which sits in a uniform magnetic field, and is irradiated by radio wave frequency. A detector interprets the results.

5.4 Types of Protons

- There are homotopic, enantiotopic, and diastereotopic protons.
- Homotopic protons are identical protons and will be chemically equivalent. These will show up at the same location in NMR spectroscopy.
- Enantiotopic protons are chemically equivalent. These will show up at the same location in NMR spectroscopy.
- Diastereoptopic protons are different protons and will be chemically nonequivalent. These will show up at different locations in NMR spectroscopy.

5.5 Chemical Shift

- NMR spectra are displayed on a plot that shows the applied field strength increasing from left to right.
- The left side of the plot is low-field or downfield and the right side of the plot is high-field or upfield.
- The different local chemical environments surrounding any particular nuclei causes them to resonate at slightly different frequencies. This means that nuclei which have different chemical environments will show up in different regions of the NMR plot or spectrum.
- Chemical shift is dependent on the applied field of the spectrometer, so TMS is used as a standard in order to use the units parts per million (ppm). This allows scientists to talk about the same peak in the same units regardless of field strength.
- The main "things" that effect the shielding of a nucleus are electronegative of atoms, magnetic anisotropy of pi systems, and hydrogen bonding.
- Electron with-drawing groups can decrease the electron density at the nucleus, deshielding the nucleus, resulting in a larger chemical shift.
- The π electrons in a compound, when placed in a magnetic field, will move and generate their own magnetic field. The new magnetic field will have an effect on the shielding of atoms within the field.

- Protons that are involved in hydrogen bonding (*i.e.*-OH or -NH) are usually observed over a wide range of chemical shifts since hydrogen bonds are dynamic

5.6 Integration of Proton Spectra

- The area of a peak in a ^{1}H NMR is proportional to the number of hydrogens to which the peak corresponds.
- The integration curve appears as a series of steps with the height being proportional to the area of the corresponding absorption peak, and the number of protons responsible for the absorption.
- Integration can be used to determine the relative amounts of two or more compounds in a mixed sample.

5.7 Spin-Spin Splitting in Proton NMR spectra

- The split peaks (multiplets) arise because the magnetic field experienced by the protons of one group is influenced by the spin arrangements of the protons in an adjacent group.
- There is a recognizable pattern which is usually referred to as the n + 1 rule: if a set of hydrogens has n neighboring, non-equivalent hydrogens, it will be split into n + 1 subpeaks.
- Splitting occurs primarily between hydrogens that are separated by three bonds.
- The spin-spin coupling effect is quantified by the coupling constant, *J*. The coupling constant is simply the difference, expressed in Hz (not ppm), between two adjacent sub-peaks in a split signal.

5.8 More Complex Spin-Spin Splitting Patterns

- When a proton is coupled to two different neighboring proton sets with identical or very close coupling constants, the splitting pattern that emerges often appears to follow the simple `$n$ + 1 rule` of non-complex splitting.
- If the set of protons is coupled to two or more sets of nonequivalent neighbors, the result is complex coupling.
- Complex coupling occurs when the coupling constants are different from each other on the neighboring protons.
- The stronger our magnet is, the more resolution we get in our spectrum. This means a clearer picture to gather more information.

5.9 Uses of ^{1}H NMR Spectroscopy

- Nuclear magnetic resonance imaging (MRI) is an important medical diagnostic tool developed from NMR spectroscopy.
- Scientists use NMR spectroscopy to determine the structure of a molecule.

Skills to Master

- Skill 5.1 Distinguish between different types of protons in a molecule.
- Skill 5.2 Estimate the chemical shift of protons.
- Skill 5.3 Know which protons will be more downfield.
- Skill 5.4 Determine the ratio of different types of protons present in an organic compound.
- Skill 5.5 Provide a splitting diagram for a proton.
- Skill 5.6 Predict splitting patterns using a splitting diagram or the n + 1 rule.
- Skill 5.7 Interpret complex splitting in a spectrum.
- Skill 5.8 Solve unknown structure determination problems with ^{1}H NMR spectroscopy.

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CHAPTER OVERVIEW

6: Carbon-13 NMR Spectroscopy

6.1: Chapter Objectives and Preview of C-13 Nuclear Magnetic Resonance Spectroscopy
6.2: C-13 NMR Spectroscopy- Signal Averaging and FT-NMR
6.3: Characteristics of C-13 NMR Spectroscopy
6.4: DEPT C-13 NMR Spectroscopy
6.5: Interpreting C-13 NMR Spectra
6.6: Uses of C-13 NMR Spectroscopy
6.7: Structure Determination Problems with C-13 NMR and 1-H NMR
6.S: Summary

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6.1: Chapter Objectives and Preview of C-13 Nuclear Magnetic Resonance Spectroscopy

Learning Objectives

After completing this chapter, you should be able to

- fulfill all of the detailed objectives listed under each individual section.
- solve road-map problems which will require the interpretation of ^{13}C NMR spectra in addition to other spectral data.
- define, and use in context, the key terms introduced in this chapter.

In the previous chapter, ^{1}H Nuclear Magnetic Resonance (NMR) was discussed. The theory for NMR spectroscopy is the same for all NMR spectroscopy. In the presence of a magnetic field, a sample can absorb electromagnetic radiation, specifically in the radiofrequency (rf) region, based on the function of certain nuclei in the molecule. This chapter will focus on carbon nuclear magnetic spectroscopy (^{13}C NMR) and what type of information you can glean from spectra and how it complements ^{1}H NMR for the determination of a structure of a molecule.

6.1: Chapter Objectives and Preview of C-13 Nuclear Magnetic Resonance Spectroscopy is shared under a not declared license and was authored, remixed, and/or curated by Lauren Reutenauer.

- **Interpreting C-13 NMR Spectra** by Jim Clark is licensed CC BY-NC 4.0.

6.2: C-13 NMR Spectroscopy- Signal Averaging and FT-NMR

Learning Objectives

- Learn how ^{1}H NMR and ^{13}C NMR are similar and different.
- Understand the basics of how ^{13}C NMR works.

Why are we talking about ^{13}C NMR when the ^{12}C isotope of carbon - which accounts for up about 99% of the carbons in organic molecules? The ^{12}C isotope does not have a nuclear magnetic moment, and thus is NMR-inactive (cannot be seen by the NMR). Fortunately for organic chemists, however, the ^{13}C isotope, which accounts for most of the remaining 1% of carbon atoms in nature, has a magnetic moment just like protons, which is why we will be discussing ^{13}C NMR spectroscopy and not ^{12}C NMR spectroscopy. Most of what the theory we have learned about ^{1}H-NMR spectroscopy also applies to ^{13}C-NMR, although there are several important differences.

The basics of ^{13}C NMR spectroscopy

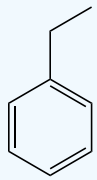
The magnetic moment of a ^{13}C nucleus is much weaker than that of a proton. This means that NMR signals from ^{13}C nuclei are inherently much weaker than proton signals. Combining the weaker magnetic moment with the low natural abundance of ^{13}C, means that it is much more difficult to observe carbon signals: more sample is required, and often the data from hundreds of scans must be averaged in order to bring the signal-to-noise ratio down to acceptable levels.

Chemical Shift

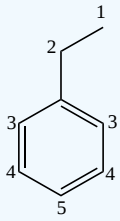
The resonance frequencies of ^{13}C nuclei are lower than those of protons in the same applied field - in a 7.05 Tesla instrument, protons resonate at about 300 MHz, while carbons resonate at about 75 MHz. This is fortunate, as it allows us to look at ^{13}C signals using a completely separate 'window' of radio frequencies. Just like in ^{1}H-NMR, the standard used in ^{13}C NMR experiments to define the 0 ppm point is tetramethylsilane (TMS), although of course in ^{13}C NMR it is the signal from the four equivalent *carbons* in TMS that serves as the standard. Chemical shifts for ^{13}C nuclei in organic molecules are spread out over a much wider range than for protons – up to 200 ppm for ^{13}C compared to 12 ppm for protons (see Table 3 for a list of typical ^{13}C NMR chemical shifts). This is also fortunate, because it means that the signal from each carbon in a compound can almost always be seen as a distinct peak, without the overlapping that often plagues ^{1}H NMR spectra. The chemical shift of a ^{13}C nucleus is influenced by essentially the same factors that influence a proton's chemical shift: bonds to electronegative atoms and diamagnetic anisotropy effects tend to shift signals downfield (higher resonance frequency). In addition, sp^2 hybridization results in a large downfield shift. The ^{13}C NMR signals for carbonyl carbons are generally the furthest downfield (170-220 ppm), due to both sp^2 hybridization and to the double bond to oxygen. Symmetry will also play a role in how many signals are observed on a ^{13}C NMR spectrum. If there is no symmetry, then each carbon should show up as a signal in the spectrum. If symmetry is present in the molecule, then there will be less than the total number of carbons in the molecule. Only non-equivalent carbons will appear as a signal in ^{13}C NMR.

Example 6.2.1

How many sets of non-equivalent carbons are there in ethyl benzene?



Solution



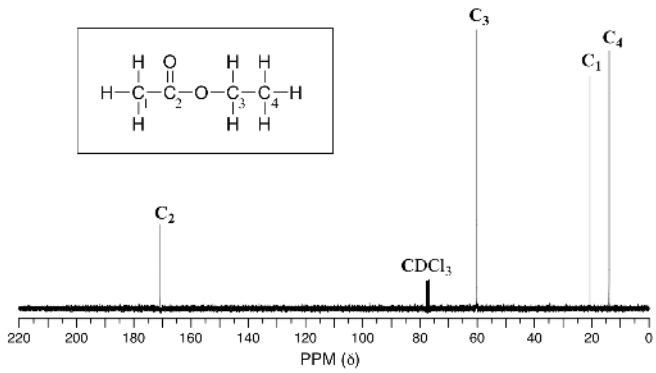
There are 5 different carbons in ethyl benzene. There is symmetry in ethyl benzene in the aromatic ring. On the labeled molecule, there are two carbon 3's and two carbon 4's due to the symmetry of the molecule.

Integration

Unlike ^{1}H NMR signals, the area under a ^{13}C NMR signal cannot be used to determine the number of carbons to which it corresponds. This is because the signals for some types of carbons are inherently weaker than for other types – peaks corresponding to carbonyl carbons, for example, are much smaller than those for methyl or methylene (CH_2) peaks. There are some quantitative ^{13}C NMR experiments that when enriched with ^{13}C can be integrated, but typically it is not done.

Spin-spin Splitting

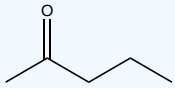
Because of the low natural abundance of ^{13}C nuclei, it is very unlikely to find two ^{13}C atoms near each other in the same molecule, which means that spin-spin coupling is not observed between neighboring carbons in a ^{13}C NMR spectrum. However,there is heteronuclear coupling between ^{13}C carbons and the hydrogens to which they are bound. Carbon-proton coupling constants are very large, on the order of 100 – 250 Hz. Proton-coupled ^{13}C spectra show complex overlapping multiplets, which makes for a very difficult interpretation. For clarity, chemists generally use a technique called broadband decoupling , which essentially 'turns off' C-H coupling, resulting in a spectrum where all carbon signals are singlets. Below is the proton-decoupled ^{13}C NMR spectrum of ethyl acetate, showing the expected four signals, one for each of the carbons with no spin-spin splitting.

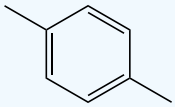


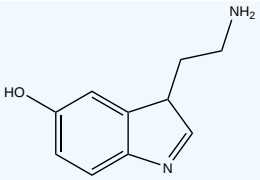
While broadband decoupling results in a much simpler spectrum, useful information about the presence of neighboring protons is lost. However, there are other ^{13}C NMR experiments that can give more information, such as Distortionless Enhancement by Polarization Transfer (DEPT) allows us to determine how many hydrogens are bound to each carbon.

? Exercise 6.2.1

How many sets of non-equivalent carbons are there in:

a. 2-pentanone: 

b. para-xylene: 

c. serotonin: 

Answer

a. 5 non-equivalent carbons

b. 3 non-eqivalent carbons

c. 10 non-equivalent carbons

Contributors and Attributions

- Prof. Steven Farmer (Sonoma State University)
- Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

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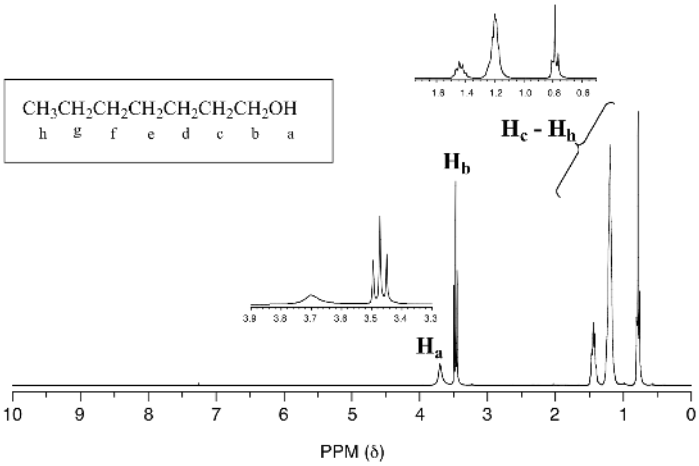
6.3: Characteristics of C-13 NMR Spectroscopy

Learning Objectives

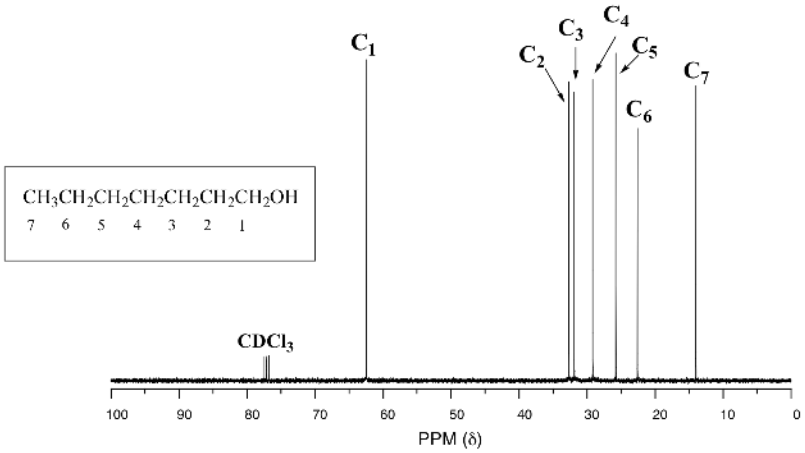
- Understand where different types of carbon appear on the spectrum

Simply, ^{13}C NMR allows you to determine how many different carbons are in a molecule. It will also be seen that information on functional groups present in a molecule can be determined using ^{13}C NMR. In a spectrum, each signal represents a resonance for a different carbon atom. The typical range for the resonance frequencies is 0 to 220 ppm from tetramethylsilane (TMS) reference. Like ^{1}H NMR, the chemical shift of ^{13}C nuclei is influenced by its chemical environment like the ^{1}H nuclei.

One of the greatest advantages of ^{13}C-NMR compared to ^{1}H-NMR is the breadth of the spectrum - carbons resonate from 0-220 ppm relative to the TMS standard, as opposed to only 0-12 ppm for protons. Because of this, ^{13}C signals rarely overlap, meaning we can almost always distinguish separate peaks for each carbon, even in a relatively large compound containing carbons in very similar environments. In a ^{1}H NMR spectrum of 1-heptanol, for example, many of the signals overlap and it becomes difficult to analyze, only the signals for the alcohol proton (H_a) and the two protons on the adjacent carbon (H_b) are easily analyzed.



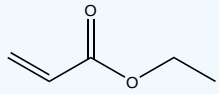
In the ^{13}C spectrum of 1-heptanol, we can easily distinguish each carbon signal, and we know from this data that our sample has seven non-equivalent carbons. (Notice also that, as we would expect, the chemical shifts of the carbons get progressively smaller as they get farther away from the deshielding oxygen.)



This property of ^{13}C NMR makes it very helpful in the elucidation of larger, more complex structures.

Example 6.3.1

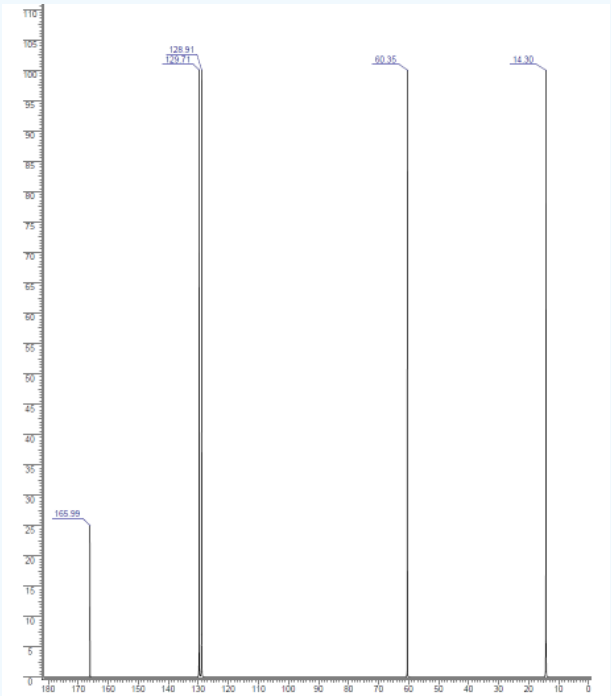
Predict the number of carbon resonances expected in a ^{13}C NMR spectrum of ethyl prop-2-enoate, $C_5H_8O_2$.



Solution

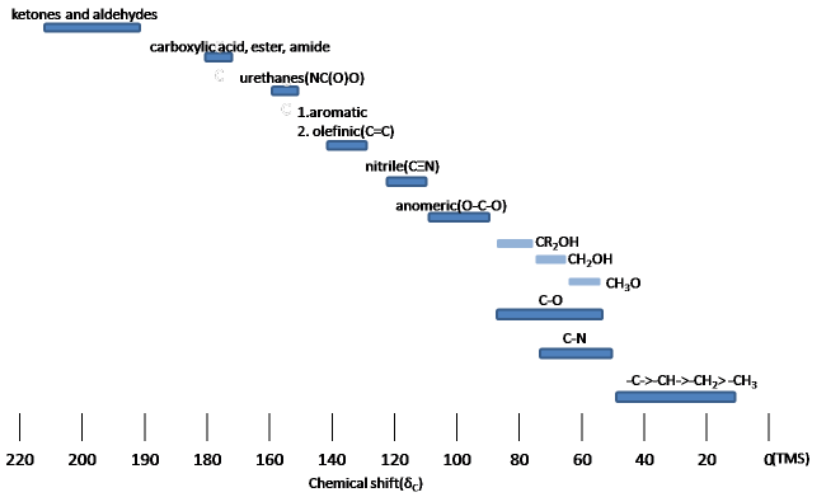
There is no symmetry in this molecule, so you would expect 5 resonances - one for each C in the molecule - in a ^{13}C NMR spectrum.

^{13}C NMR spectrum of ethyl prop-2-en-oate:



^{13}C NMR Chemical Shifts

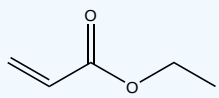
The ^{13}C NMR is used for determining functional groups based on characteristic shift values. ^{13}C chemical shifts are greatly affected by electronegative effects and magnetic anisotropy. If a H atom in an alkane is replaced by substituent X, electronegative atoms (O, N, halogen), ^{13}C signals for nearby carbons shift downfield (left; increase in ppm) with the effect diminishing with distance from the electron withdrawing group just as in ^{1}H NMR. Below, a typical ^{13}C chemical shift table shows the regions of some of the common organic functional groups.

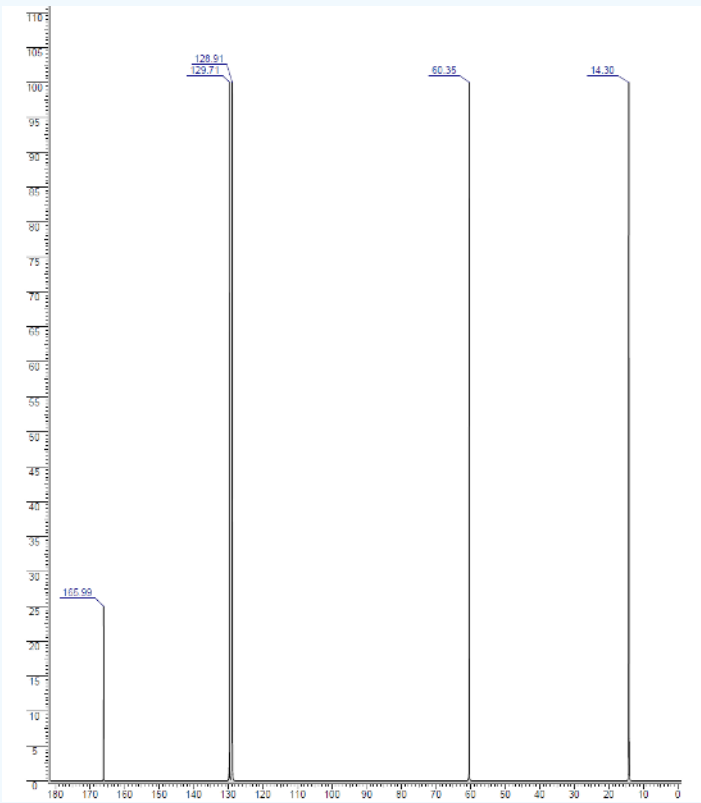


^{13}C Chemical shift range for organic compounds

Example 6.3.2

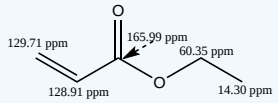
Assign the resonances in a ^{13}C NMR spectrum of ethyl prop-2-enoate, $C_5H_8O_2$.





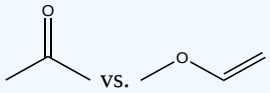
Solution

There are 5 carbons in the molecule, which equate to the 5 peaks in the ^{13}C NMR spectrum.



Exercise 6.3.1

Using ^{13}C NMR spectrum, how could you tell the difference between the isomers acetone and methoxy ethene?

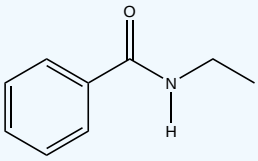


Answer

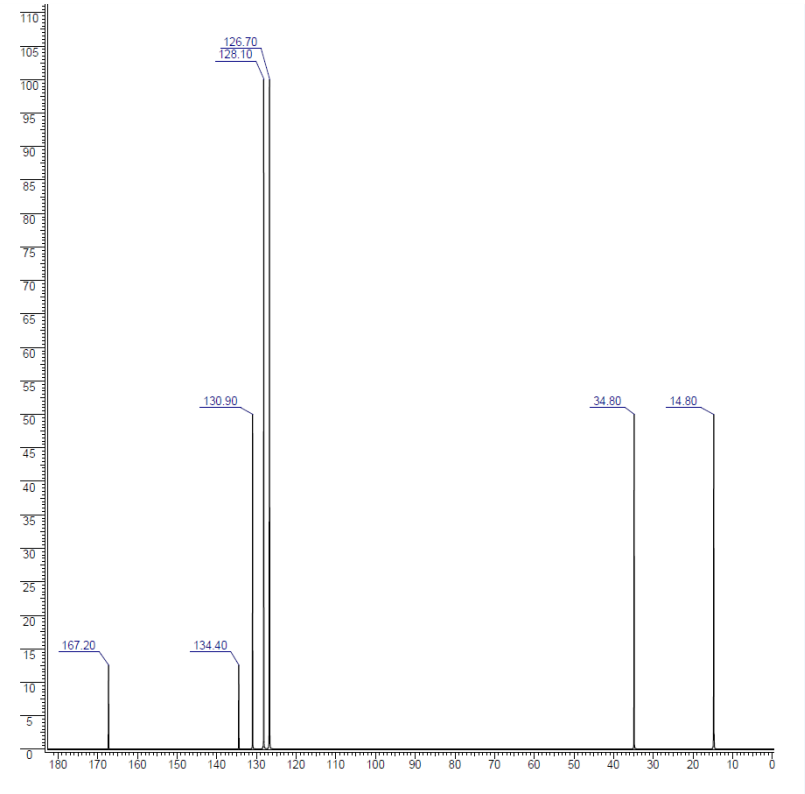
There are a few ways to tell the difference between the two molecules. Acetone would have 2 different resonances in a ^{13}C NMR spectrum due to the symmetry of the molecule. Acetone is a ketone and ketone carbons appear far downfield 180-220 ppm. Methoxy ethene is difunctional molecule with an ether and an alkene. It would show 3 resonances in the ^{13}C NMR spectrum, which all would be lower than the ketone resonance. Alkene resonances are 100-150 ppm and a C-O bond would be 40-85 ppm.

Exercise 6.3.2

Assign as many peaks as you can to the 13C NMR spectrum to specific carbons in the N-ethylbenzamide.

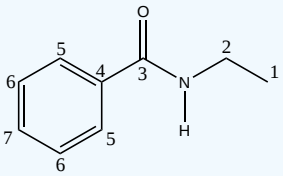


^{13}C NMR spectrum:



Answer

While there are 9 total carbons, there are only 7 non-equivalent carbons.



Labeled Carbon Number	Chemical Shift (ppm)
1	14.80
2	34.80
3	134.40
4	126.70
5	128.10
6	130.90
7	167.20

Contributors and Attributions

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- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

6.3: Characteristics of C-13 NMR Spectroscopy is shared under a not declared license and was authored, remixed, and/or curated by Lauren Reutenauer.

6.4: DEPT C-13 NMR Spectroscopy

Learning Objectives

- Understand the difference between 1D ^{13}C NMR and DEPT.
- Determine what information is gained when using DEPT

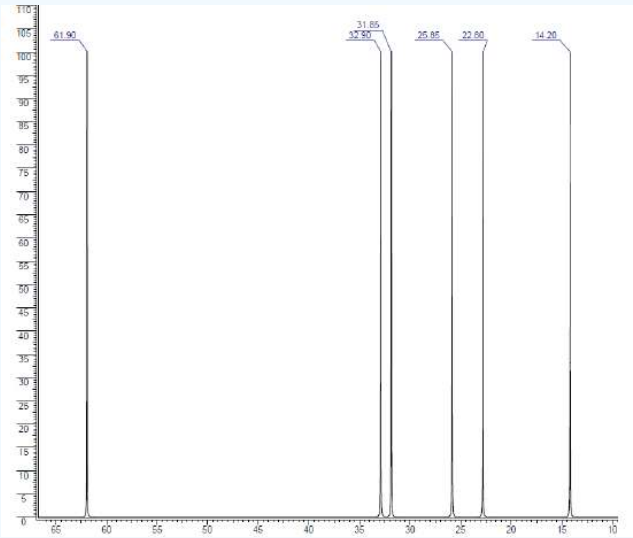
There are many types of experiments that can be run using the NMR spectrometer, including gathering information from ^{13}C NMR spectra and while broadband decoupling gives a simpler spectrum, it loses information about neighbors. Distortionless enhancement by polarization transfer, DEPT, is one of these techniques to gain this type of information back and making it possible to distinguish between methyl (CH_3), methylene (CH_2), methine (CH), and quaternary carbons. In other words, the number of hydrogens attached to a particular carbon can be determined. In DEPT, it takes advantage of the ^{13}C to ^{1}H coupling that is removed in broadband-decoupled ^{13}C spectra.

DEPT experiments often start by running an ordinary ^{13}C spectrum (typically broadband-decoupled spectrum). This allows one to know where the chemical shifts for the carbons in a molecule to be known. For a DEPT, there is a final step in the data acquisition that has a final flip angle of 90 or 135. During the experiment, polarization is transferred from one nuclei to another. Typically, the small gyromagnetic nuclei is observed, so the transfer would be from ^{1}H to ^{13}C. This allows for the DEPT to determine which carbons are attached to hydrogens. In a DEPT-135 spectrum, the CH_3 and CH resonances are upright or positive, the CH_2 resonances are inverted or negative, and quaternary carbons do not show up since these carbons are not directly attached to a hydrogen. Another DEPT experiment is the DEPT-90. While DEPT-135 showed all of the resonances of protonated carbons, DEPT-90 only shows CH peaks (upright/positive).

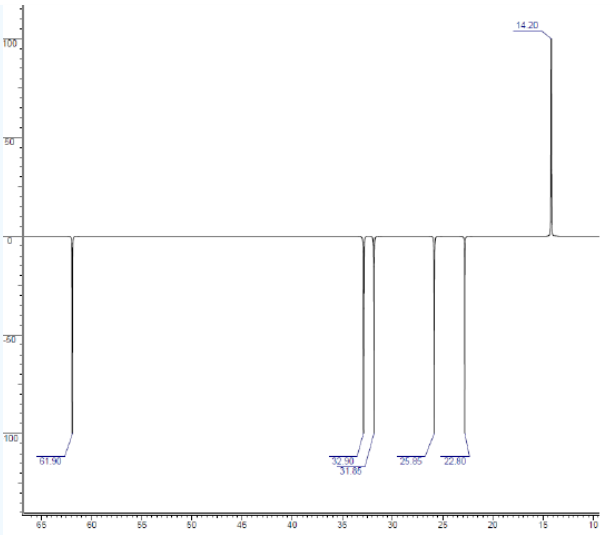
Example 6.4.1

Propose a structure for an alcohol, $C_6H_{14}O$, that has the following ^{13}C NMR spectral data.

Broadband-decoupled ^{13}C NMR spectrum:



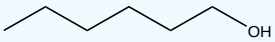
DEPT-135:



DEPT-90: No positive peaks.

Solution

From the ^{13}C NMR spectrum, the resonances inform that there are 6 distinct carbons. There are only 6 carbons in our molecular formula, therefore they are all different. Based on chemical shift, there are no multiple bonds in the molecule. You can also begin by calculating the degrees of unsaturation, which indicates know multiple bonds or rings. The DEPT-135 shows 5 negative peaks and 1 positive peak. The negative resonances are methylenes and the positive peak is either a methyl or methine. The DEPT-90 indicates that there are no CH peaks in the molecule. Therefore, the resonance at 14.20 ppm is a methyl group. Our structure is:

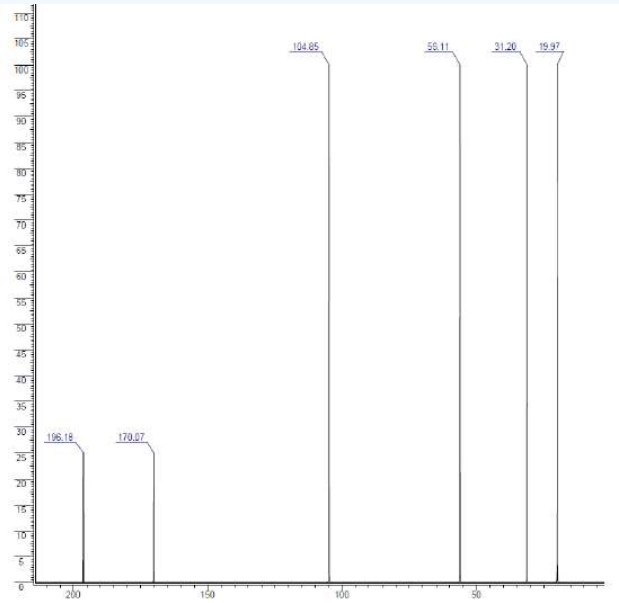


There are many more complicated experiments as well, but that is beyond the scope of this chapter.

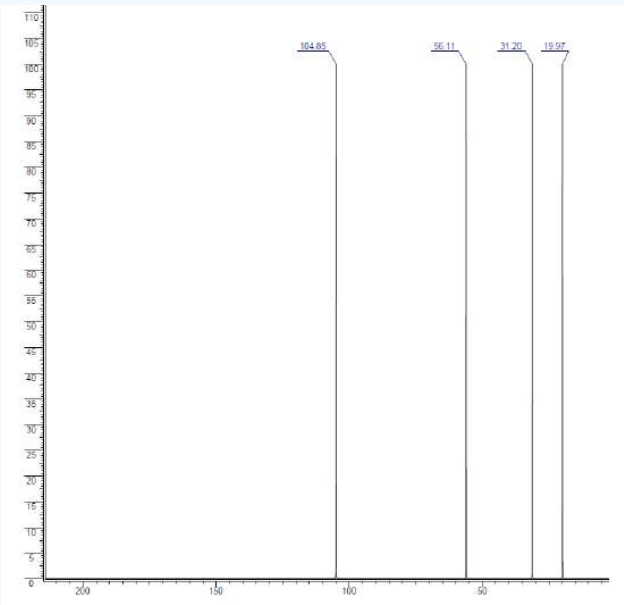
? Exercise 6.4.1

Propose a structure for an alcohol, $C_6H_{10}O_2$, that has the following ^{13}C NMR spectral data.

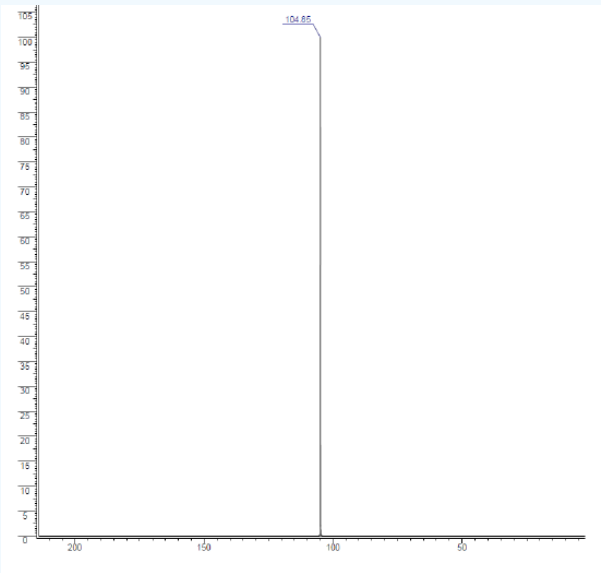
Broadband-decoupled ^{13}C NMR spectrum:



DEPT-135:

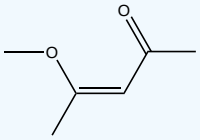


DEPT-90:



Answer

There are 2 degrees of unsaturation. The ^{13}C NMR spectrum indicates that all 6 carbons are different. The resonance at 196 ppm indicates a C=O based on chemical shift and the resonances at 170 and 104 ppm indicate a C=C bond. This would account for both degrees of unsaturation. The DEPT-135 shows no negative resonances, so there are no CH_2s. The loss of the resonances at 196 and 170 ppm means that they are quaternary carbons (not attached to hydrogen). The DEPT-90 shows one resonance at 104 ppm, which means it is a CH and before was indicated as part of a double bond. The peaks at 56, 31, and 20 ppm are all methyl groups. The one at 56 ppm must be attached to an electron withdrawing group, which in this example an O. The fragment is $-OCH_3$. To have a quaternary carbon that is not the carbonyl, there must be a methyl group attached to the one of the carbon of the C=C double bond. 196 ppm indicates a ketone, which would be where the last methyl group goes. The final structure based on chemical shift and DEPT is:



6.4: DEPT C-13 NMR Spectroscopy is shared under a not declared license and was authored, remixed, and/or curated by Lauren Reutenauer.

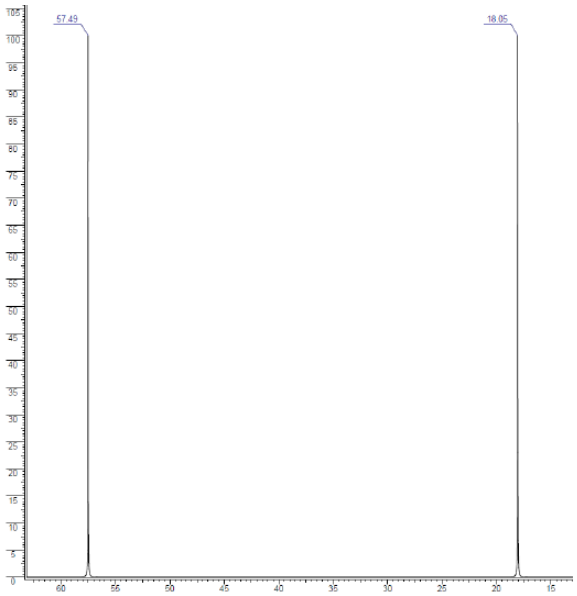
6.5: Interpreting C-13 NMR Spectra

Learning Objectives

- understand how chemical shift and number of peaks come together to determine functional groups.
- solve unknown ^{13}C NMR problems given the molecular formula.

This section will help identify how to interpret information from ^{13}C NMR spectra.

Starting with the ^{13}C NMR spectrum for ethanol, C_2H_6O.



Remember that each peak identifies a carbon atom in a different environment within the molecule. In this case there are two peaks because there are two different environments for the carbons. The carbon in the CH_3 group is attached to 3 hydrogens and a carbon. The carbon in the CH_2 group is attached to 2 hydrogens, a carbon and an oxygen. So which peak is which?

You might remember from Section 6.2 that the external magnetic field experienced by the carbon nuclei is affected by the electronegativity of the atoms attached to them. The effect of this is that the chemical shift of the carbon increases if you attach a more electronegative atom like oxygen to it. That means that the peak at about 60 (the larger chemical shift) is due to the CH_2 group because it has a more electronegative atom attached.

In principle, you should be able to work out the fact that the carbon attached to the oxygen will have the larger chemical shift. In practice, you always work from tables of chemical shift values for different groups (see below).

What if you needed to work it out? The electronegative oxygen pulls electrons away from the carbon nucleus leaving it more exposed to any external magnetic field. That means that you will need a smaller external magnetic field to bring the nucleus into the resonance condition than if it was attached to less electronegative things. The smaller the magnetic field needed, the higher the chemical shift.

A table of typical chemical shifts in ^{13}C NMR spectra

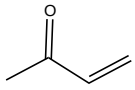
carbon environment	chemical shift (ppm)
C=O (in ketones)	205 - 220
C=O (in aldehydes)	190 - 200
C=O (in acids and esters)	170 - 185
C in aromatic rings	125 - 150
C=C (in alkenes)	115 - 140
RCH_2OH	50 - 65
RCH_2Cl	40 - 45
RCH_2NH_2	37 - 45
R_3CH	25 - 35
CH_3CO-	20 - 30
R_2CH_2	16 - 25
RCH_3	10 - 15

In the table, the "R" groups will not necessarily be simple alkyl groups. If a substituent is very close to the carbon in question, and very electronegative, that might affect the values given in the table slightly. For example, ethanol has a peak at about 60 because of the -CH_2OH group. No problem! It also has a peak due to the RCH_3 group. The "R" group this time is -CH_2OH. The electron pulling effect of the oxygen atom increases the chemical shift slightly from the one shown in the table to a value of about 18 ppm.

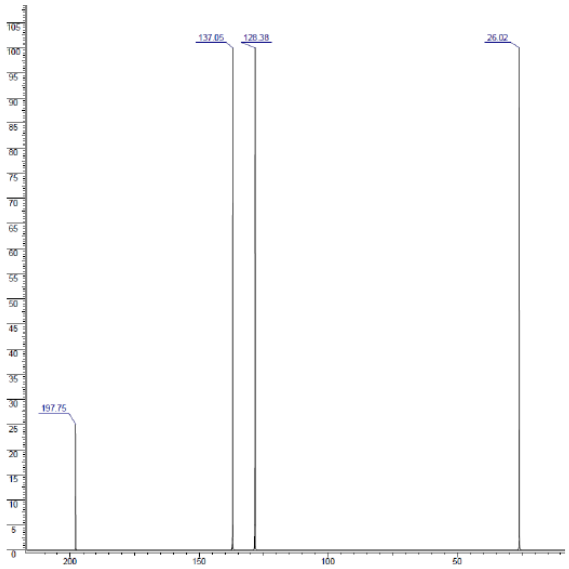
A simplification of the table:

carbon environment	chemical shift (ppm)
C-C	0 - 50
C-O	50 - 100
C=C	100 - 150
C=O	150 - 200

Now, we will look at 3-buten-2-one:

The structure for the compound is:  . This molecule has carbons and all four are in different chemical environments. Therefore, in the ^{13}C NMR spectrum there should be four signals.

The ^{13}C NMR spectrum for 3-buten-2-one is:



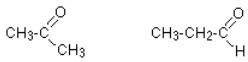
Using the table above, you can assign each peak to each carbon.

- The peak at just under 200 ppm is due to a carbon-oxygen double bond. The two peaks at 137 ppm and 129 ppm are due to the carbons at either end of the carbon-carbon double bond. And the peak at 26 is the methyl group which, of course, is joined to the rest of the molecule by a carbon-carbon single bond. If you want to use the more accurate table, you have to put a bit more thought into it - and, in particular, worry about the values which do not always exactly match those in the table!
- The carbon-oxygen double bond in the peak for the ketone group has a slightly lower value than the table suggests for a ketone. There is an interaction (resonance) between the carbon-oxygen and carbon-carbon double bonds in the molecule which affects the value slightly. This will be observed in many conjugated systems. Discrepencies can also happen in more complicated systems.
- The two peaks for the carbons in the carbon-carbon double bond are exactly where they would be expected to be. Notice that they aren't in exactly the same environment, and so do not have the same shift values. The one closer to the carbon-oxygen double bond has the larger value.
- And the methyl group on the end has exactly the sort of value you would expect for one attached to C=O. The table gives a range of 20 - 30, and that's where it is.

One final important thing to notice. There are four carbons in the molecule, but they aren't all the same height. In ^{13}C NMR, you **cannot** draw any simple conclusions from the heights of the various peaks.

Working out Structures from ^{13}C NMR Spectra

So far, the structures of them molecules have been known and we have just been trying to see the relationship between carbons in particular environments in a molecule and the spectrum produced. Now let's make it a little more difficult - by looking at isomers! How could you tell from just a quick look at a ^{13}C NMR spectrum whether you had propanone or propanal (assuming those were the only options)?

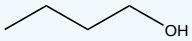


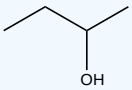
propanone propanal

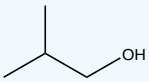
Because these are isomers, each has the same number of carbon atoms, but there is a difference between the environments of the carbons which will make a big impact on the spectra. In propanone, the two carbons in the methyl groups are in exactly the same environment, and so will produce only a single peak. That means that the propanone spectrum will have only 2 peaks - one for the methyl groups and one for the carbon in the C=O group. However, in propanal, all the carbons are in completely different environments, and the spectrum will have three peaks.

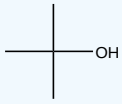
Example 6.5.1

There are four alcohols with the molecular formula $C_4H_{10}O$.

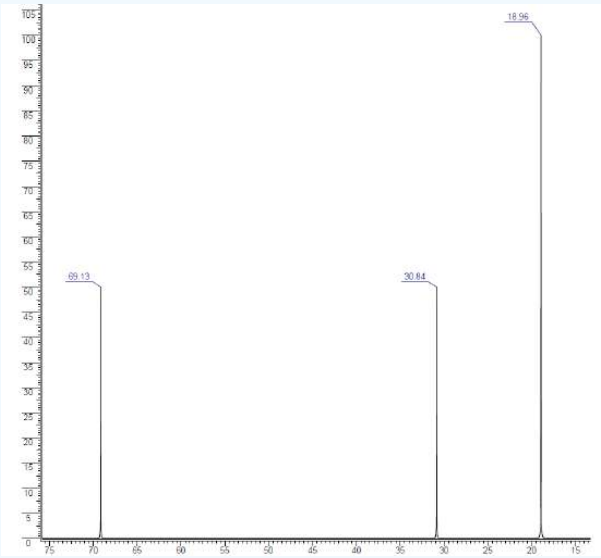
A. 

B. 

C. 

D. 

Which one produced the ^{13}C NMR spectrum below?



Solution

You can do this perfectly well without referring to chemical shift tables at all.

In the spectrum there are a total of three peaks - that means that there are only three different environments for the carbons, despite there being four carbon atoms.

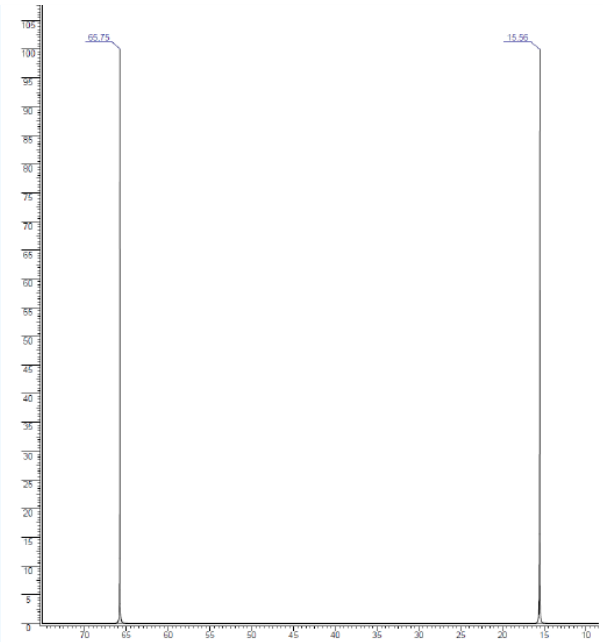
In A and B, there are four totally different environments. Both of these would produce four peaks.

In D, there are only two different environments - all the methyl groups are exactly equivalent. D would only produce two peaks.

That leaves C. Two of the methyl groups are in exactly the same environment - attached to the rest of the molecule in exactly the same way. They would only produce one peak. With the other two carbon atoms, that would make a total of three. The alcohol is C.

Example 6.5.2

This follows on from previous example, and also involves an isomer of $C_4H_{10}O$ but which isn't an alcohol. Its ^{13}C NMR spectrum is below. Work out what its structure is.



Solution

Because we do not know what sort of structure we are looking at, this time it would be a good idea to look at the shift values. The approximations are perfectly good, and we will work from this table:

carbon environment	chemical shift (ppm)
C-C	0 - 50
C-O	50 - 100
C=C	100 - 150
C=O	150 - 200

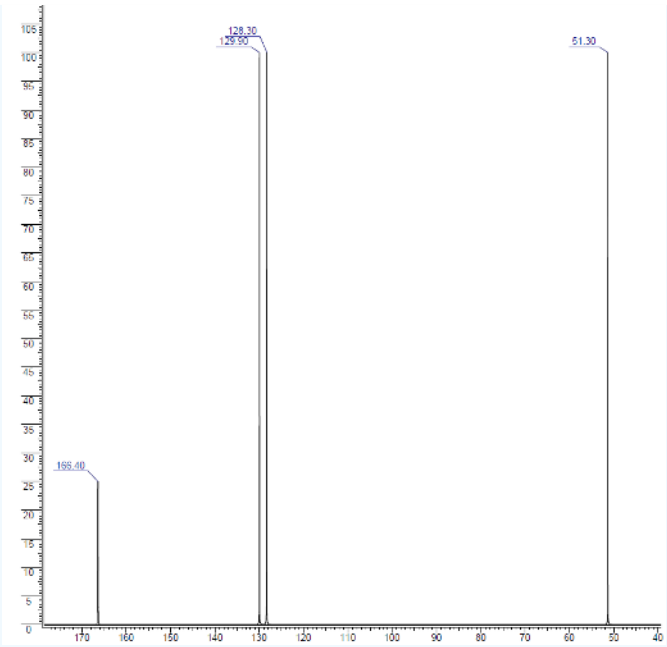
The peak at 66.75 ppm indicates there is a peak for carbon(s) in a carbon-oxygen single bond. The peak at 15.55 ppm indicates that there is a peak for carbon(s) in a carbon-carbon single bond. That would be consistent with C-C-O in the structure.

It is not an alcohol (you are told that in the question), and the molecular formula is $C_4H_{10}O$. With only two peaks, but four total carbons there must be symmetry in the carbons within the molecule. The only solution to that is to have two identical ethyl groups either side of the oxygen. The compound is ethoxyethane (diethyl ether), $CH_3CH_2OCH_2CH_3$.

Example 6.5.3

Using the simplified table of chemical shifts above, work out the structure of the compound with the following ^{13}C NMR spectrum. Its molecular formula is $C_4H_6O_2$.

^{13}C NMR Spectrum:

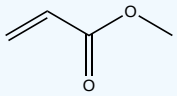


Solution

Let's sort out what we've got.

- There are four peaks and four carbons. No two carbons are in exactly the same environment, so all of our carbons are accounted for since there are only four in the molecular formula. This means no symmetry within the molecule.
- The peak at just over 50 must be a carbon attached to an oxygen by a single bond.
- The two peaks around 130 must be the two carbons at either end of a carbon-carbon double bond.
- The peak at just less than 170 is the carbon in a carbon-oxygen double bond.

Putting this together is a matter of playing around with the structures until you have come up with something reasonable. But you can't be sure that you have got the right structure using this simplified table. In this particular case, the spectrum was for the compound:



If you refer back to the more accurate table of chemical shifts towards the top of the page, you will get some better confirmation of this. The relatively low value of the carbon-oxygen double bond peak suggests an ester or acid rather than an aldehyde or ketone.

It can't be an acid because there has to be a carbon attached to an oxygen by a single bond somewhere - apart from the one in the -COOH group. We've already accounted for that carbon atom from the peak at about 170. If it was an acid, you would already have used up both oxygen atoms in the structure in the -COOH group. Without this information, though, you could probably come up with reasonable alternative structures. If you were working from the simplified table in an exam, your examiners would have to allow any valid alternatives.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

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6.6: Uses of C-13 NMR Spectroscopy

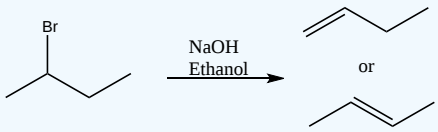
Learning Objectives

- understand how ^{13}C NMR data can be used to distinguish between two (or more) possible structures for an unknown organic compound
- determine if you made the correct product

^{13}C NMR spectroscopy derives information that is helpful for structure determination, especially when paired with ^{1}H NMR spectroscopy. ^{13}C allows the organic chemist a way to determine how many non-equivalent carbons are in a molecule of interest. This allows one to understand if there is symmetry in the molecule or not. The chemical shift of each of the resonances in ^{13}C NMR spectra gives information about the electronic environment, which can indicate what type of functional group is present or what type of bond is present. If you add in DEPT, then the organic chemist can determine how many hdyrogens are attached to each of the carbons.

Example 6.6.1

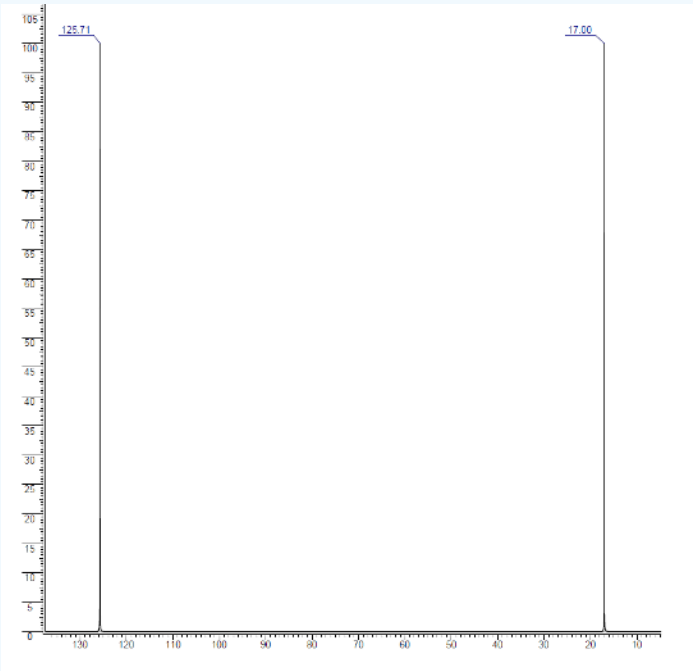
The E2 reaction follows Zaitsev's rule, but how do we know that? Let's consider the reaction below:



1) How can you tell the difference between 1-butene and 2-butene in a ^{13}C NMR spectrum?

2) Which product was made based on the ^{13}C NMR spectrum of the product?

^{13}C NMR spectrum of the product:



Solution

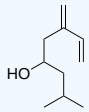
1) IR spectroscopy and mass spectrometry would not be helpful in elucidation of this problem. It is very difficult to address the structural differences in either of those spectroscopic methods. ^{1}H NMR could be used, but there would be overlapping peaks,

so it would again be difficult. In a ^{13}C NMR spectrum, 1-butene would have 4 different signals in the spectrum where as 2-butene would have 2 distinct signals in the spectrum.

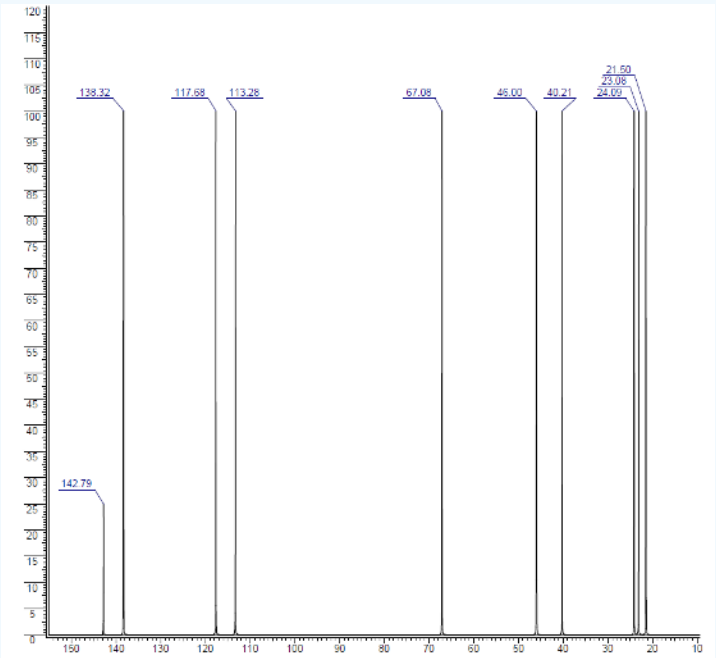
2) With just 2 signals in the spectrum, the product is 2-butene.

Example 6.6.2

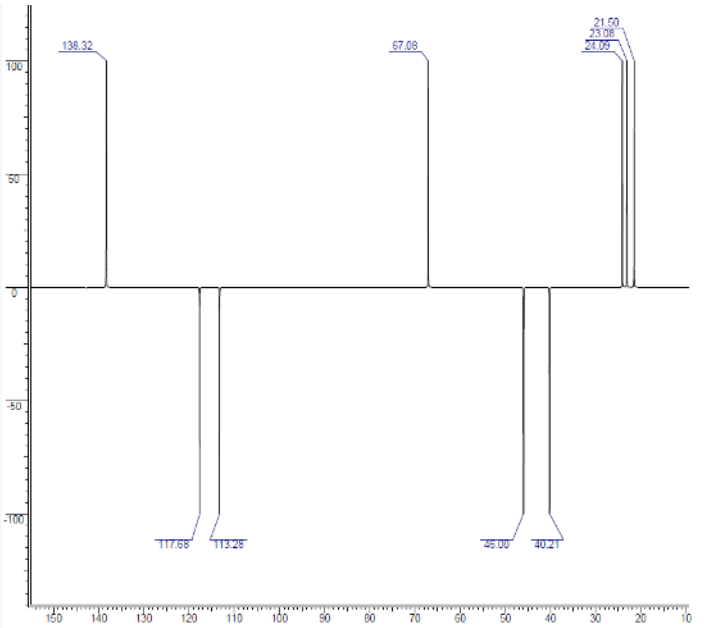
The ^{1}H NMR spectrum had overlapping peaks, which lead to inconclusive results on if the product, ipsenol, was isolated. The structure of ipsenol is below. A ^{13}C NMR spectrum along with a DEPT-135 and DEPT-90 to identify the product.



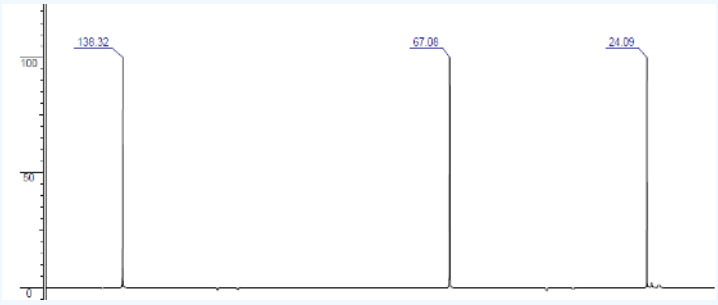
^{13}C NMR spectrum:



DEPT-135 spectrum:



DEPT-90 spectrum:



Solution

Carbon NMR along with DEPT can be a great tool in structure determination. The range for carbon NMR is wider than for 1H NMR, so it can help spread the spectrum out and remove overlapping peaks. In the ^{13}C NMR spectrum, there are 10 distinct peaks, so all of the carbons have been accounted for. If we consider the structure for a moment, then it can be seen that there is 1 quaternary carbon, 3 methines (CH), 4 methylenes (CH_2), and 2 methyl groups (CH_3). In the DEPT-135, the peak at 142.79 ppm has gone away. This is the quaternary carbon, since it is not attached to any hydrogens directly, it is not observed. The negative peaks are methylene groups and there are four - just as expected. There are 5 peaks that are either a methine or methyl group. Finally, the DEPT-90 informs that there are 3 methine groups, which means the peaks at 23.08 ppm and 21.50 ppm would be methyl groups. These 1D-carbon spectra do correlate with the structure.

Contributors and Attributions

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

6.6: Uses of C-13 NMR Spectroscopy is shared under a not declared license and was authored, remixed, and/or curated by Lauren Reutenauer.

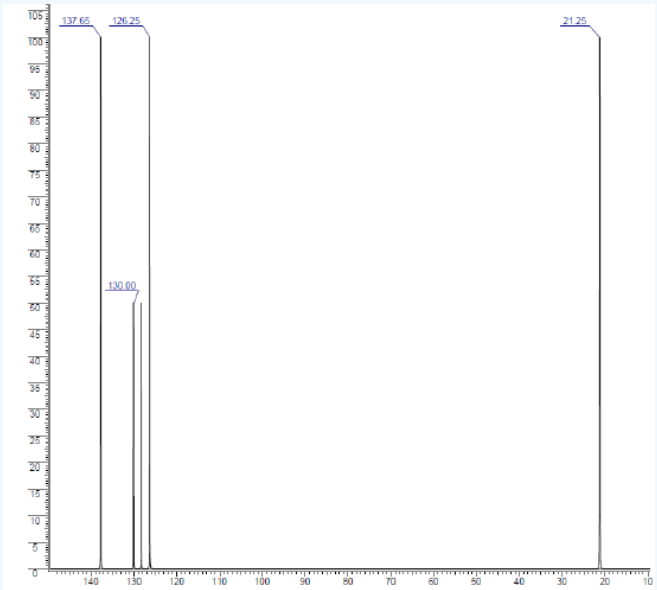
6.7: Structure Determination Problems with C-13 NMR and 1-H NMR

Learning Objectives

- Solve unknown problems using ^{13}C and ^{1}H NMR spectra and molecular formula.

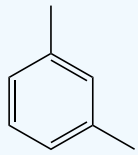
Exercise 6.7.1

Which isomer of ortho, meta, or para xylene do you have based on the ^{13}C NMR spectrum?



Answer

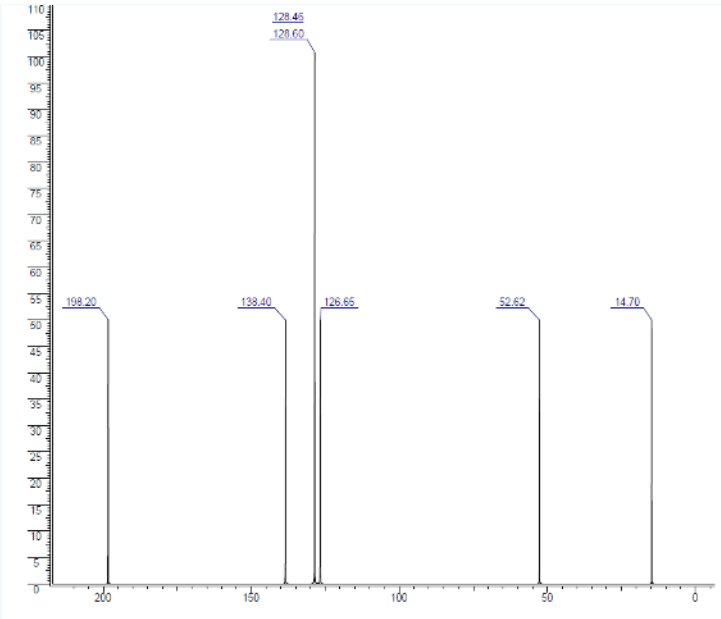
There are 5 different carbons in the spectrum with four different aromatic carbons. *p*-Xylene would have 2 types of aromatic carbons and *o*-xylene would have 3 types. *m*-Xylene is the only one with 4 different types of aromatic carbons, which fits this spectrum. The methyl groups would all be similary, so not a point of difference.



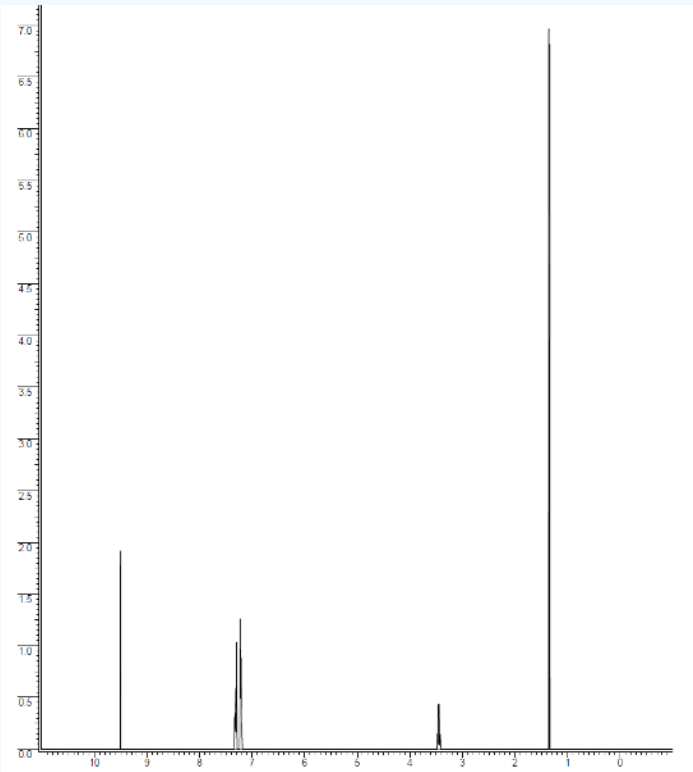
Exercise 6.7.2

Propose a structure using the spectral data below for $C_9H_{10}O$.

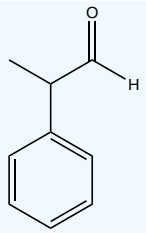
^{13}C broadband decoupled spectrum:



^{1}H NMR spectrum: Integration: 1 (doublet; J = 1 Hz):5 (multiplet):1 (quartet of doublets;J = 7 Hz and 1 Hz):3 (doublet; J = 7 Hz)



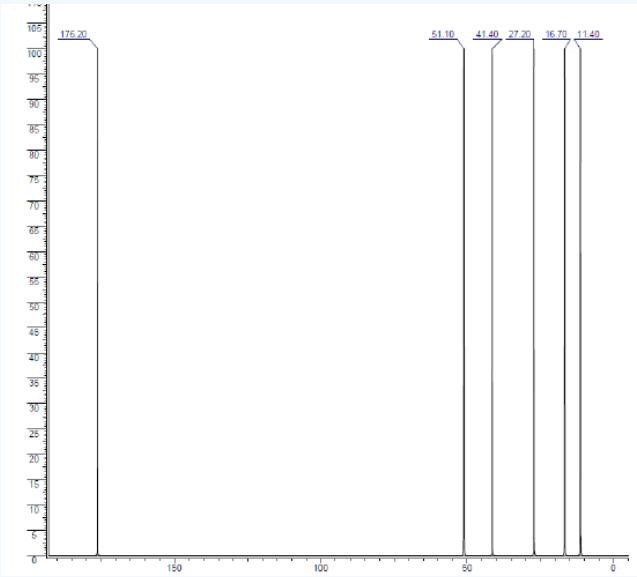
Answer



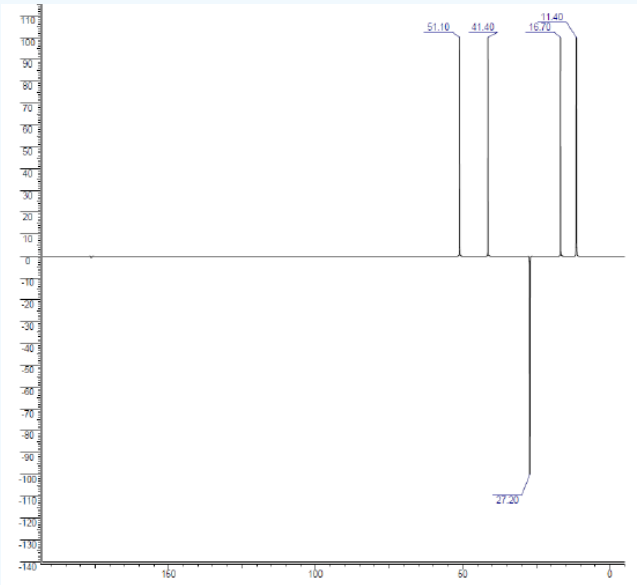
Exercise 6.7.3

Propose a structure using the spectral data below for $C_6H_{12}O_2$.

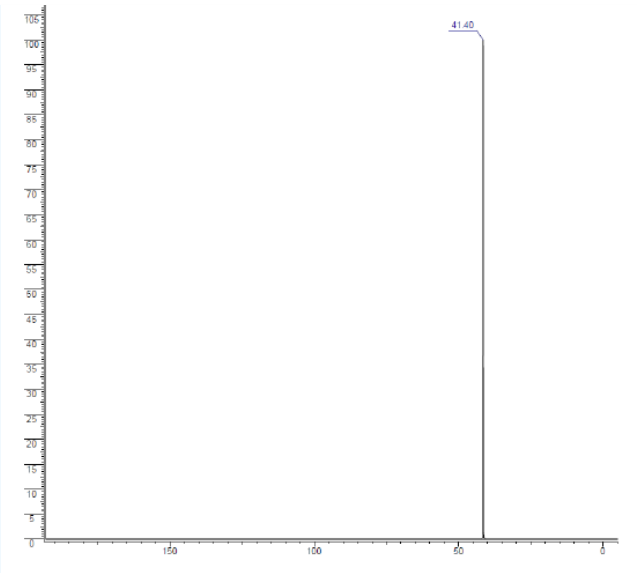
^{13}C broadband decoupled spectrum:



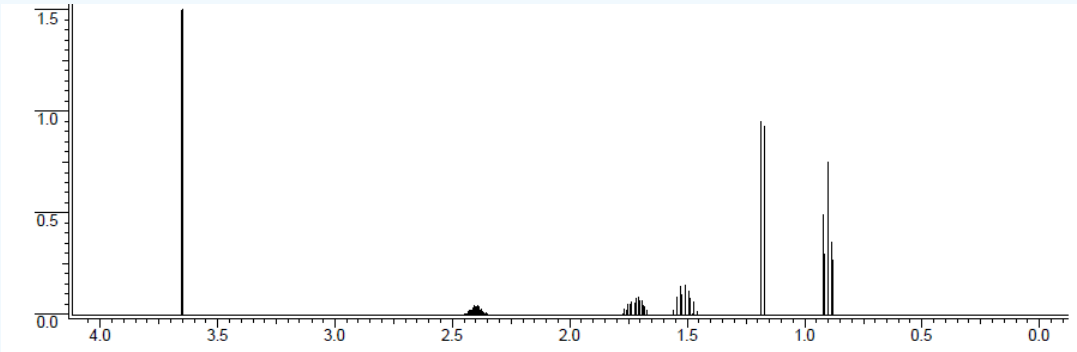
DEPT-135:



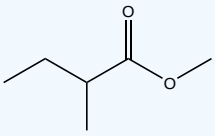
DEPT-90:



^{1}H NMR spectrum: Integration: 3 (singlet):1 (sextet; J = 8 Hz):1 (multiplet;J = 25 Hz and 8 Hz):1(multiplet; J = 25 Hz and 8 Hz):3 (doublet; J = 8 Hz):3 (triplet; J = 8 Hz)



Answer

Structure: 

6.7: Structure Determination Problems with C-13 NMR and 1-H NMR is shared under a not declared license and was authored, remixed, and/or curated by Lauren Reutenauer.

6.S: Summary

Concepts & Vocabulary

6.2 C-13 NMR Spectroscopy- Signal Averaging and FT-NMR

- The magnetic moment of a ^{13}C nucleus is much weaker than that of a proton. This means that NMR signals from ^{13}C nuclei are inherently much weaker than proton signals, which makes ^{13}C NMR harder to acquire good data.
- Chemical shift is similar to ^{1}H, where the environment around the carbon changes for each carbon in the molecule.
- Integration is not done in ^{13}C NMR spectroscopy because the signals for some types of carbons are inherently weaker than for other types.
- Because of the low natural abundance of ^{13}C nuclei, it is very unlikely to find two ^{13}C atoms near each other in the same molecule, which means that spin-spin coupling is not observed between neighboring carbons in a ^{13}C NMR spectrum.
- There is heteronuclear coupling between ^{13}C carbons and the hydrogens to which they are bound, proton-coupled ^{13}C spectra show complex overlapping multiplets, which makes for a very difficult interpretation. For clarity, broadband decoupling is used, which essentially 'turns off' C-H coupling, resulting in a spectrum where all carbon signals are singlets.

6.3 Characteristics of C-13 NMR Spectroscopy

- Carbons resonate from 0-220 ppm relative to the TMS standard, as opposed to only 0-12 ppm for protons. Because of this, ^{13}C signals rarely overlap, meaning we can almost always distinguish separate peaks for each carbon.
- The ^{13}C NMR is used for determining functional groups based on characteristic shift values.
- ^{13}C chemical shifts are greatly affected by electronegative effects and magnetic anisotropy.

6.4 DEPT C-13 NMR Spectroscopy

- Distortionless enhancement by polarization transfer, DEPT, is one of these techniques and making it possible to distinguish between methyl (CH_3), methylene (CH_2), methine (CH), and quaternary carbons.
- In DEPT, it takes advantage of the ^{13}C to ^{1}H coupling that is removed in broadband-decoupled ^{13}C spectra.

6.5 Interpreting C-13 NMR Spectra

- Chemical shift is a big indicator into what type of carbon is at that resonance.
- Different carbons are carbons in distinct chemical environments and each different carbon will appear at a different resonance.
- Tables of chemical shift data can be used to distinguish different types of carbons.

6.6 Uses of ^{13}C NMR Spectroscopy

- ^{13}C NMR spectroscopy derives information that is helpful for structure determination.
- Scientists use ^{13}C as a way to determine how many non-equivalent carbons are in a molecule of interest.

Skills to Master

- Skill 6.1 Distinguish between different types of carbons in a molecule.
- Skill 6.2 Estimate the chemical shift of carbons.
- Skill 6.3 Know which carbons will be more downfield.
- Skill 6.4 Determine which carbons are attached to hydrogens using DEPT
- Skill 6.5 Solve unknown structure determination problems with ^{1}H and ^{13}C NMR spectroscopy.

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CHAPTER OVERVIEW

7: Two-Dimensional NMR Spectroscopy

7.1: Chapter Objectives and Preview of Correlation NMR Spectroscopy
7.2: Theory
7.3: Two Dimensional Homonuclear NMR Spectroscopy
7.4: Two Dimensional Heteronuclear NMR Spectroscopy
7.5: Uses for 2-D NMR Spectroscopy
7.6: Interpreting 2-D NMR Spectra
7.7: 2-D NMR Problems
7.S: Summary

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7.1: Chapter Objectives and Preview of Correlation NMR Spectroscopy

Chapter Objectives and Preview Correlation NMR Spectroscopy; 2-D NMR

Learning Objectives

After completing this chapter, you should be able to

- fulfill all of the detailed objectives listed under each individual section.
- solve road-map problems which may require the interpretation of 2D NMR spectra in addition to other spectral data.
- define, and use in context, the key terms introduced in this chapter.

In Section 5 and Section 6, the focus was on one-dimensional (1D) techniques to elucidate structures of organic molecules. Complex molecules like polymers or biomolecules can be hard to elucidate solely with proton and carbon NMR, which while powerful techniques don't quite solve the entire picture. This is where correlation NMR spectroscopy can be used and many of these experiments are two-dimensional (2D) techniques. While there are many correlation NMR spectroscopy experiments that can be run, this chapter will focus on the more common ones to be used.

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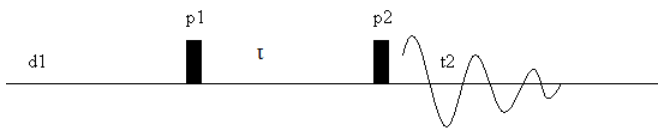
7.2: Theory

Learning Objectives

- Learn the difference between 1-D and 2-D NMR spectroscopy

In 1971, Jean Jeener introduced the two dimensional variation of NMR spectroscopy. Since then, scientists have applied the concept to develop the many techniques of two-dimensional (2-D) NMR. Correlation itself is not a new concept in NMR. In ^{1}H NMR spectroscopy, the splitting of resonances indicates that groups were "correlated" to each other due to the spins within each group. Spin-spin splitting gives information about the neighboring nuclei and in the case of ^{1}H NMR, it was how many neighboring hydrogens there were in the molecule. This coupling of hydrogens will be one type of coupling 2-D NMR will consider. The use of 2-D NMR allows for better resolution in signals that normally overlap in 1-D NMR.

All the basic NMR theory for 1-D NMR still applies. In 1-D Fourier transform NMR, a magnetic field is applied to a sample, which is then hit with a series of pulsed radiofrequency (rf), as seen in the pulse sequence below. The Fourier transform of the outgoing signal results in a 1-D spectra as a function chemical shift.



Two-dimensional NMR adds additional experimental variables and thus introducing a second dimension to the resulting spectrum. A simple 2-D experiment pulse sequence consists of a relaxation delay, a pulse, a variable time interval (t_1), a second pulse, and acquisition (t_2). The pulse sequence is repeated many times while varying the length of time (t_1) the system is allowed to evolve during the first pulse. In 2-D experiments, the signal detected during acquisition is a function of acquisition time (t_2), which has been modulated as a function of the time interval (t_1). This means that magnetization evolves around one frequency during t_1 and a different frequency during t_2. The output once Fourier transformed is a 2-D spectrum with two axes. One axis (v_2) represents the nucleus detected during acquisition (t_2), while the other axis (v1) can represent the same nucleus or a different nucleus. With two axes, it leads to cross peaks along a diagonal connecting coupled nuclei. Due to the nature of how the experiment is run, magnetization is redistributed equally in both directions (just like spin-spin coupling), the cross peaks will be symmetrically disposed about the diagonal.

References

Silverstein, R.M, Webster, F.X, and Kiemle D.J. Spectrometric Identification of Organic Compounds. 7th ed. John Wiley & Sons, Inc. 2005.

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7.3: Two Dimensional Homonuclear NMR Spectroscopy

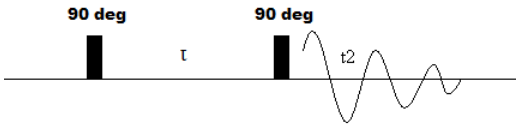
Learning Objectives

- Understand what correlation spectroscopy is and why it is used
- Learn about different types of homonuclear 2-D NMR spectroscopy

The previous sections have discussed one-dimensional NMR techniques, but for particularly complicated molecules it is hard to get the full picture of what is happening. Two-dimensional NMR spectra provide more information about a molecule than one-dimensional NMR spectra in these situations. In this section, homonuclear 2-D NMR spectroscopy is going to be considered and what is meant by homonuclear is looking at the correlation of the same nuclei in a molecule.

Correlation Spectroscopy (COSY)

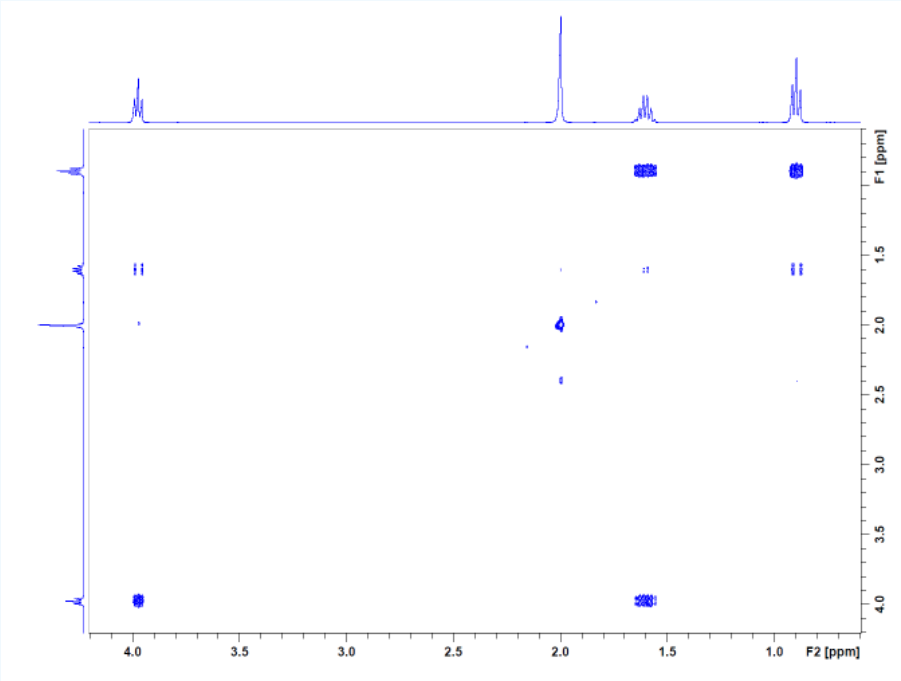
The most basic form of 2-D NMR is the COSY (COrrelation SpectroscopY) experiment. This experiment looks at ^{1}H coupling to ^{1}H through bonds typically 3 bonds away. It relies on the J-coupling to provide spin-spin correlation to indicate which protons are close to each other on the cross peak. In a ^{1}H-^{1}H COSY experiment, the pulse sequence consists of proton pulses separated by the required evolution period (t_1), and the acquisition period (t_2). The evolution period is systematically incremented during the repeated pulse sequences. Specifically, it consists of a 90° RF pulse followed by an evolution time and an additional 90° pulse (shown below). The resulting oscillating magnetization (symbolized by decaying the sinusoidal curve) is then acquired during t_2.



A COSY takes a 1-D ^{1}H NMR and spreads it across two dimensions, which means the peaks are spread out into an array. The spectra of COSY give rise to cross peaks (off diagonal) for all protons that have spin-spin coupling. This means that the peaks off the diagonal are coupled protons. The purpose of a COSY is to determine which protons are coupled to what other protons in the molecule through bonds. In the example below, you will use a simpler molecule, propyl acetate, to understand how to read a COSY and what information you can glean from it.

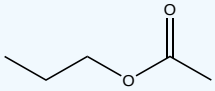
Example 7.3.1

The COSY spectrum for propyl acetate is below:



Assign all of the correlations for propyl acetate and indicate the coupling as geminal, vicinal, or long range.

Solution

The structure of propyl acetate 

From the chapter on 1-D ^{1}H NMR spectroscopy, the methyl group attached to the carbonyl will be a singlet. It does not have any neighboring carbons to couple with. The other hydrogens will have coupling neighbors, so while you may only need 1-D ^{1}H NMR to correlate the coupling hydrogens, this knowledge will help flesh out how to read a COSY.

First, the COSY is set out in an array and spread across two dimensions. The peaks are displayed on the axis. In the above spectrum, it is the same proton spectrum for propyl acetate on each of the axis because it is a homonuclear experiment where you look at the same nuclei. The peaks are then plotted against each other. There peak at 3.9 ppm on both axis, so there is a data point at (3.9, 3.9). This is repeated with all the peaks, which ends up being a diagonal. This information along the diagonal is the same information from the 1-D ^{1}H NMR.

The points of interest are those not along the diagonal or the cross peaks. These peaks inform about which hydrogens are coupled to what other hydrogens. There is a cross peak at (0.9, 1.6). There is also a cross peak at (1.6, 0.9) because these protons are coupled to each other and if you recall coupling is reciprocal. The peak at 0.9 ppm corresponds to the methyl group with a neighboring -CH_2- and the 1.6 ppm peak is the -CH_2- with the neighboring methyl group. However, the peak at 1.6 ppm has another cross peak (1.6, 3.9), which indicates that it is also coupled to the -CH_2- on the other side. And of course, there is a cross peak at (3.9, 1.6) since the coupling goes both ways.

All the cross peaks have now been identified and the bonding between these hydrogens is all vicinal coupling.

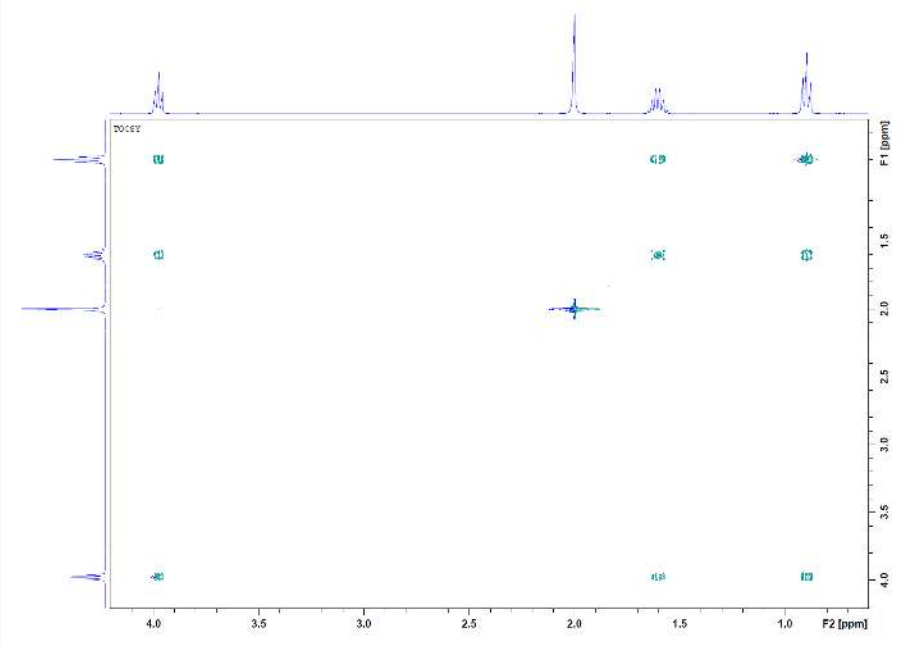
Total Correlation Spectroscopy (TOCSY)

The next type of ^{1}H to ^{1}H correlation spectroscopy is TOtal Correlation SpectroscopY (TOCSY). In this type of coupling, the information obtained creates correlations between all protons within a given spin system. A molecule can have just one spin system or hundreds in more complex systems. The goal in TOCSY is to transfer the magnetization beyond directly coupled spins. This is not just looking at geminal and vicinal correlations as in COSY, but the entire spin system. The pulse sequence is similar to COSY, but in TOCSY, a mixing period is added to the pulse sequence. This allows the magnetization to be relayed from one spin to its

neighbor to its neighbor throughout the entire spin system. The longer this mixing period, the further out the transfer of magnetization can travel with the goal being the entire spin system. The spectra of TOCSY give rise to cross peaks for all protons that are part of a coupled spin network. TOCSY spectra display the entire chain of protons, each coupled to the next.

Example 7.3.2

Below is the TOCSY of propyl acetate:



Does what you know of the structure of propyl acetate match what the TOCSY is indicating?

Solution

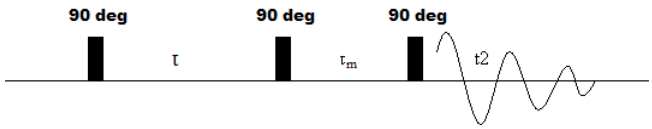
YES! Remember that TOCSY tells information about the entire spin system. As a reminder, a spin system includes nuclei where spin-spin interaction exists between them. In propyl acetate, this is the chain where the hydrogens are coupled. Just like in COSY, the peaks that show up along the diagonal in a TOCSY is the same information as a ^{1}H NMR spectrum and it is the cross peaks that inform about the chain of connection. The peak at 2.0 ppm has no cross peaks since it is a methyl group with no neighboring hydrogens. The other peaks are much more interesting. There is a cross peak at (0.9, 1.6) just like in COSY. This is because those protons are coupled to each other. There is also a cross peak at (1.6, 0.9) again because the reciprocality of how coupling works. However, there is a new cross (0.9, 3.9) because the methylene at 3.9 ppm is coupled to the methylene at 1.6 ppm. For the 1.6 ppm methylene, there are two cross peaks (1.6, 0.9) and (1.6, 3.9) like in COSY because it is coupled to those protons. Then in the 3.9 ppm methylene, there is again two cross peaks (3.9, 0.9), which is new from COSY and (3.9, 1.6), which was the same as COSY. The cross peak (3.9, 0.9) appears for the same reason the cross peak (0.9, 3.9) appeared when looking at the 0.9 ppm peak because the methylene at 1.6 ppm is coupled to the 0.9 ppm methyl group. The TOCSY does corroborate what we know about the connectivity of propyl acetate.

Nuclear Overhauser Effect (NOE) Correlation Spectroscopy

Thus far, only the coupling of nuclei through bonds has been considered. In this type of coupling, the magnetization of nuclei affect those closely bound to them through the electrons that make up those bonds. This is not the only type of coupling that occurs. Coupling directly between nuclei that are in close spatial proximity to each other also occurs. This is called the Nuclear Overhauser Effect (NOE), and it arises when the spin relaxation of nuclei A is felt by nearby nuclei B, stimulating a corresponding change in magnetization in B. In a typical NMR spectrum, the interference of electrons makes this coupling undetectable. However, a sample can be decoupled to “neutralize” the bond coupling through electrons, allowing the space coupling of the NOE to be detected. This is called NOESY (Nuclear Overhouser Effect SpectroscopY) and is another type of homonuclear NMR. The purpose of NOESY is

to determine which signals arise from protons athar are close to each other in space, even if they are not bonded. NOESY can be very useful for looking at stereochemistry and 3-D structure.

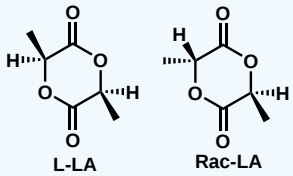
Like COSY, the first step is a 90° pulse followed by a variable evolution time. Unlike COSY, however, pulse two actually consists of two 90 degree pulses separated by a short delay. The first pulse converts the bulk magnetization from the transverse plane to the z-plane, eliminating the effect of electron-aided bond coupling. Then, during the $\tau\tau_m$, there is cross relaxation between spatially adjacent nuclei. Finally, the last 90 degree pulse converts the space coupling of nuclei into an observable transverse magnetization, which can be detected during t_2.The pulse sequence for a NOESY NMR experiment is depicted below.



Just like in COSY, the peaks that show up along the diagonal in a NOESY is the same information as a ^{1}H NMR spectrum and it is the cross peaks that inform about the through space relationships. The cross peaks correlate the spin of one nuclei to that illuminated by the source spin (other nuclei) if nearby. In the example below, you will use a simpler molecule, propyl acetate, to understand how to read a NOESY and what information you can glean from it.

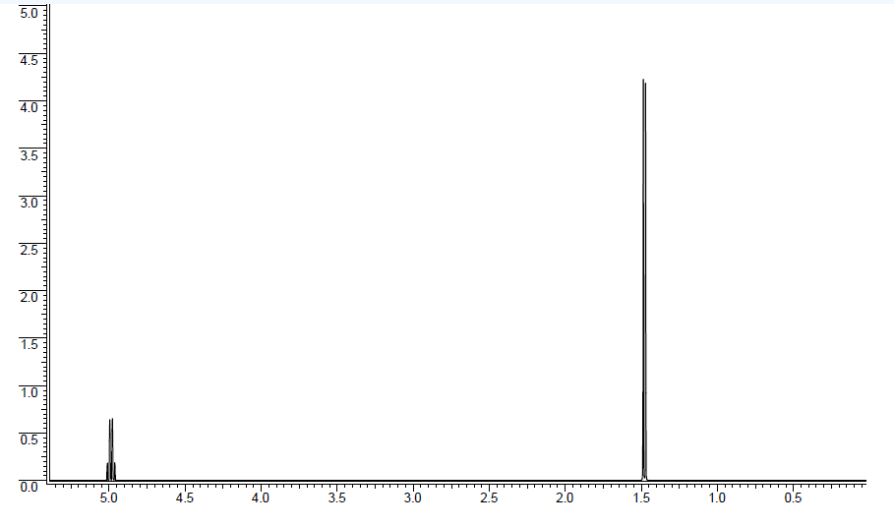
Example 7.3.3

Lactide is a product of the fermentation of corn and soybeans; it can be polymerized to make a sort of brittle plastic, PLA. PLA is used for food packaging because it can be composted in industrial and municipal waste management sites. However, there are three isomers of lactide (D-lactide, L-lactide, and Rac-lactide). L-lactide and Rac-lactide are depicted below:

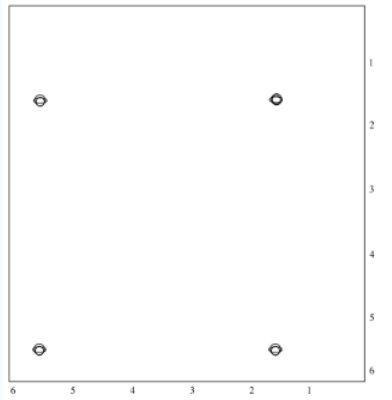


Using the spectral data, do you have L-lactide, or rac-lactide?

^{1}H NMR:



NOESY:



Solution

rac-Lactide is the diastereomer L-lactide (or D-lactide). It has different physical properties, including different NMR spectra. We could carefully compare the spectrum below to reported spectra for rac-LA and L-LA (or D-LA) to see which isomer we have. On the other hand, we could just look at the NOESY spectrum. In rac-LA, the methyl on one end of the molecule is on the same face of the ring as the hydrogen on the other end. NOESY would allow us to see that through-space relationship. We wouldn't see it in L-LA or D-LA, since the two methyl groups are on the same face. Just like in a COSY spectrum, all of the peaks that show up along the diagonal of a NOESY spectrum are simply the ones we would see in a regular ^{1}H spectrum. The peaks that show up off the diagonal tell us about through-space relationships. In this case, the relationship between the methyl hydrogen and the alpha hydrogen suggest we have a sample of rac-LA.

Exercise 7.3.1

The magnetic effect of which type of particle must be removed from an NMR experiment in order to observe an NOE?

Answer

Electrons.

Exercise 7.3.2

What type of information do you get from:

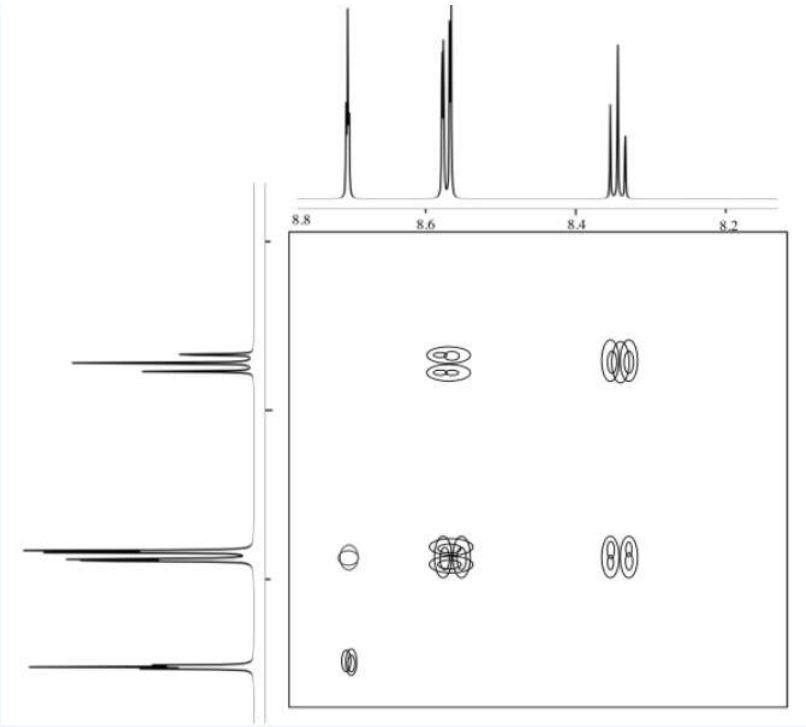
1. COSY?
2. NOESY?
3. TOCSY?

Answer

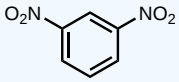
1. COSY gives information on which spins are coupled to each other through bonds.
2. NOESY determines which signals arise from protons that are close to each other in space, even if not bonded.
3. TOCSY creates correlations between all the protons within a spin system (not just geminal and vicinal coupling as in COSY).

Exercise 7.3.3

The following COSY spectrum is for an isomer of dinitrobenzene. Which isomer is it?



Answer



: meta isomer

References

Silverstein, R.M, Webster, F.X, and Kiemle D.J. Spectrometric Identification of Organic Compounds. 7th ed. John Wiley & Sons, Inc. 2005.

https://chem.libretexts.org/Bookshel...R_Introduction

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7.4: Two Dimensional Heteronuclear NMR Spectroscopy

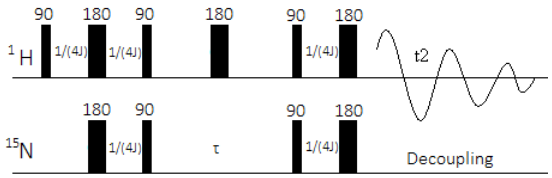
Learning Objectives

- Understand what HSQC is and when to use it
- Understand what HMBC is and when to use it

The previous section discussed the correlation of ^{1}H to ^{1}H, but those are not the only NMR active nuclei in a molecule. Heteronculear 2-D NMR is the correlation between different nuclei, such as a ^{1}H to ^{13}C and heteronuclear 2-D NMR is especially important in biological chemistry, especially in the elucidation of the three-dimensional structure of proteins.

Heteronuclear Single Quantum Coherence

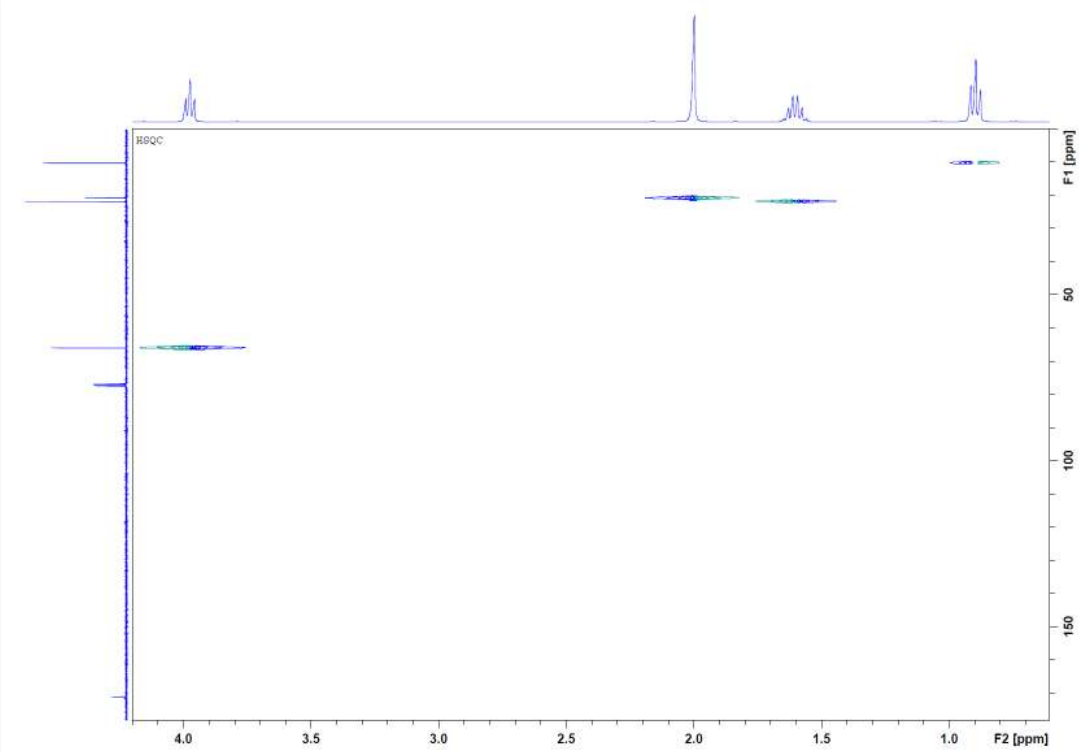
Hetereonuclear Single Quantum Coherence (HSQC) is used to determine the proton to carbon or heteroatom (often nitrogen) single bond correlations. It is also known as heteronuclear multiple quantum coherence (HMQC). While the DEPT may give the same information for ^{13}C to ^{1}H correlations, HSQC is more sensitive, therefore, it may be more adventageous to use this type of experiment in complex situations. In an HSQC experiment, polarization is transferred from a ^{1}H nuclei to a neighboring heteroatom (^{13}C or ^{15}N). This polaraization is then transferred back to the ^{1}H nuclei. The signal from the ^{1}H nuclei is recorded. The pulse sequence for a typical HSQC experiment is detailed below involving ^{1}H and ^{15}N nuclei.



In an HSQC spectrum, a ^{13}C or heteroatom spectrum is displayed on one axis and a ^{1}H spectrum is displayed on the other axis. Cross-peaks show which proton is attached to which carbon or heteroatom. The purpose of a HSQC is to determine which protons are coupled to what other specific carbon or heteroatom in the molecule through bonds.

Example 7.4.1

The HSQC of propyl acetate is below:

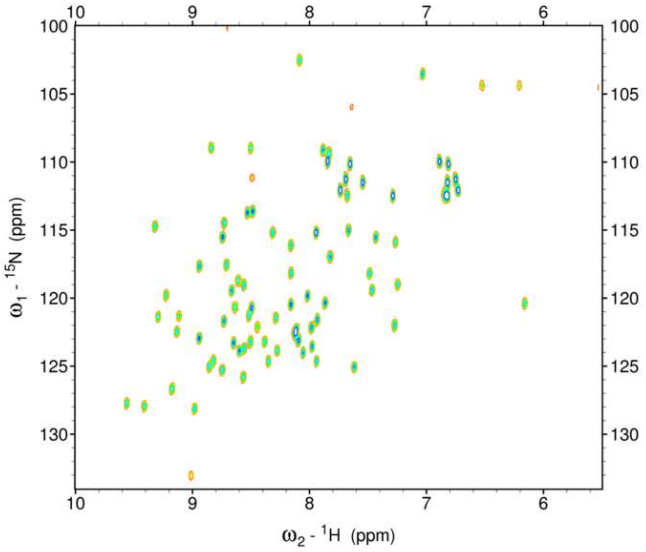


Assign which hydrogens are attached to which carbons.

Solution

An HSQC experiment spreads things out into two dimensions just like the homonuclear experiments did in the previous section. Looking along the x axis, we the ^{1}H NMR spectrum and along the y axis we see the ^{13}C NMR spectrum displayed. The peak at 171 ppm in the ^{13}C has no cross peak. This means that this carbon does not have any hydrogens attached, therefore, this is our carbonyl carbon. The peak at 77 ppm is residual solvent, in this case $CDCl_3$. The cross peak at (3.9, 66) is a methylene attached to a carbon that is attached to an electron-withdrawing group. If you look at a ^{13}C data table, then you can see where different carbon groups show up. In propyl acetate, oxygen is the most electron withdrawing group, so the piece we have at this cross peak is $-CH_2-O$. The cross peak at (2.0, 21.8) is the methyl group that has no coupling neighboring hydrogens. The next cross peak at (1.6, 20.8) is a methylene group, The final cross peak is (0.9, 10.2) is a methyl group.

Another example HSCQ spectrum from ubiquitin is shown below.



$^{1}H^{15}N$ HSQC spectrum of ubiquitin

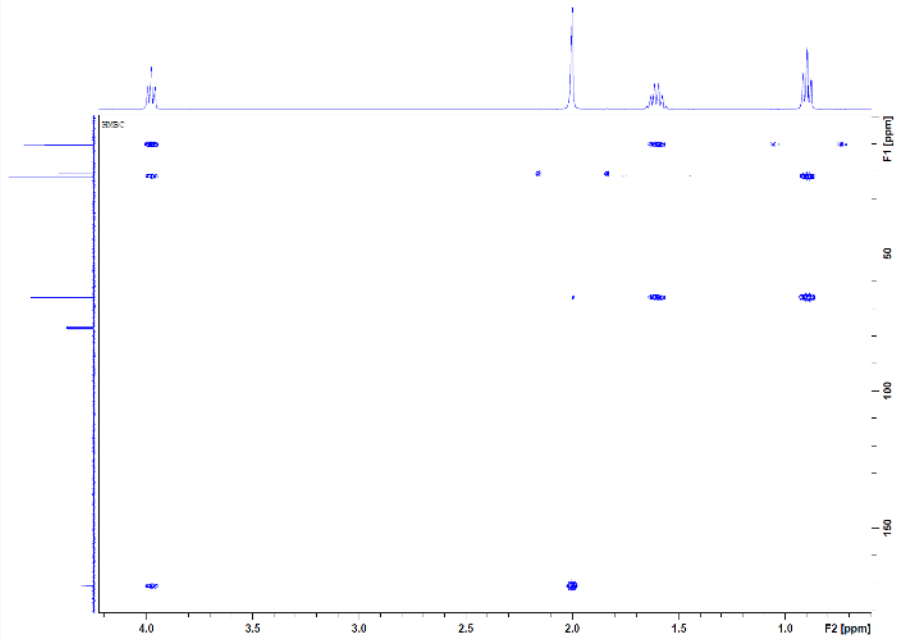
Notice the greater clarity of spectra of the HSQC experiment. This is a strong advantage of heteronuclear NMR. In this diagram, each peak corresponds to a cross peak, showing coupling between sets of ^{1}H and ^{15}N nuclei. Each peak represents the ^{15}N—^{1}H of a unique amino acid along the backbone of the amino acid.

Heteronuclear Multiple Bond Correlation (HMBC)

Hetereonuclear Multiple Bond Correlation (HMBC) is used to determine long range ^{1}H to ^{13}C connectivity. This experiment gives the correlation between ^{1}H and ^{13}C when separated by two, three, and even four (if through a conjugated system) bonds away. In an HSQC experiment, direct one bond correlations are suppressed as part of the sequence and like HSQC is proton detected. The time delay in the pulse sequence can be optimized for different coupling constants, J. The signal from the ^{1}H nuclei is recorded. The spectra of HSQC give rise to cross peaks that correlate one nuclei to another. These correlations help determine which protons are coupled to what other specific heteroatom more than one bond away.

Example 7.4.2

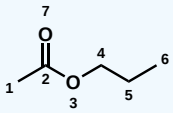
Below is the HMBC of propyl acetate:



Does the HMBC corroborate with the structure of propyl acetate?

Solution

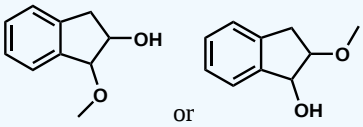
Yes! While propyl acetate is a simpler structure than typically analyzed by 2D NMR spectroscopy, it helps illuminate how to read the spectra and what information to gather from it. By using the HSQC (above), we already know which hydrogen(s) are directly attached to which carbons. The cross peaks here indicate what other carbons are attached beyond one bond away. Below is propyl acetate with the atoms labeled:

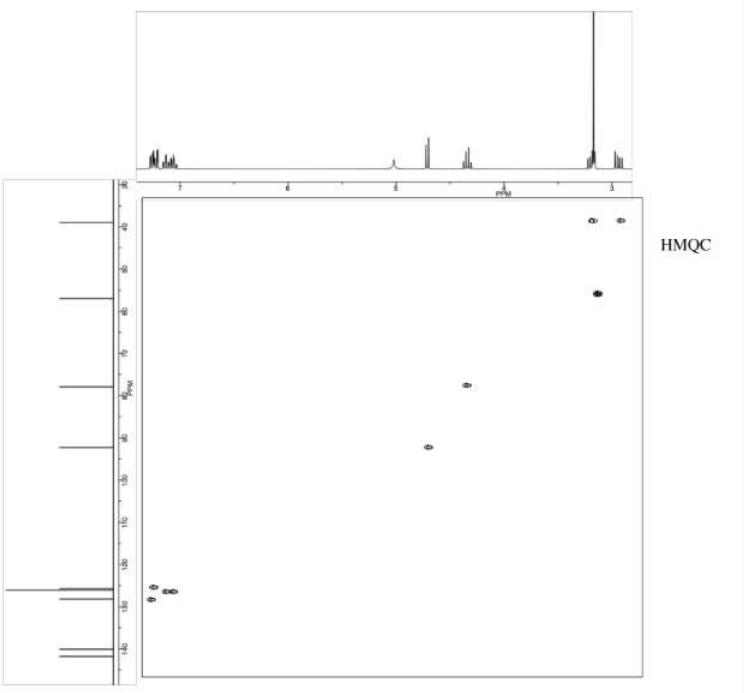


Focus on a column from one hydrogen peak. If we start with the 0.9 ppm methyl group (6), there are two cross peaks in the column (09., 20.8) and (0.9, 65.9). These correspond to a methylene group (5) and the methylene group attached to the oxygen (4). If we move the the methylene (5) at 1.6 ppm, then it has two cross peaks that correspond to C6 and C4. The methyl (1) at 2 ppm has not shown any correlations in previous spectra, but in HMBC there is a cross peak. The methyl (1) is attached to the carbonyl carbon (2). Finally, the methylene at 3.9 ppm has 3 cross peaks. It shows that it is connected through bonds to a methyl (6), a methylene (5), and the carbonyl carbon (2). All of this does match the structure for propyl acetate.

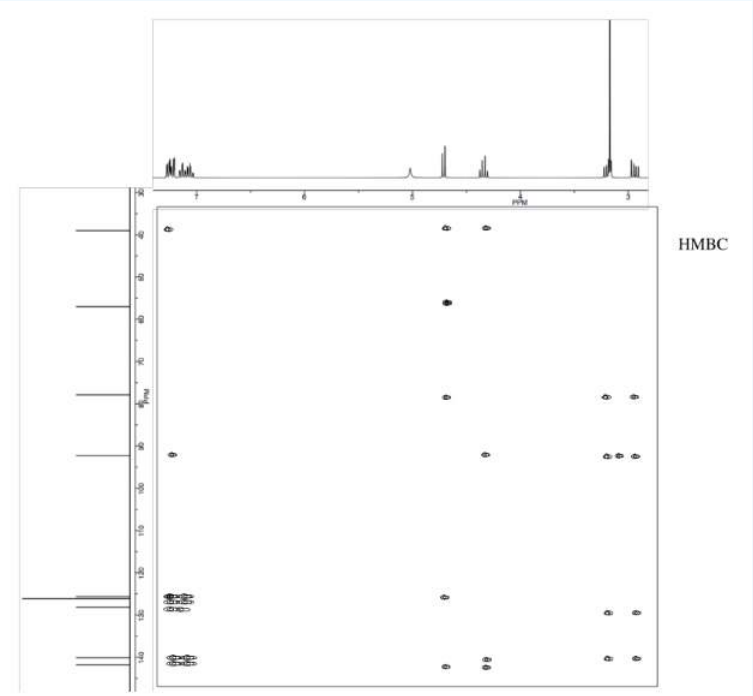
? Exercise 7.4.1

Analyze the data to determine which of the two isomers (below) we are dealing with.



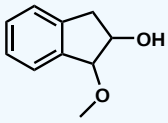


HMQC



HMBC

Answer



Exercise 7.4.2

What type of information do you get from:

1. HSQC?
2. HMBC?

Answer

1. HSQC determines the proton-carbon single bond correlations. It could also be other heteroatoms to hydrogen single bonds.

2. HMBC gives the correlations between carbon and hydrogen separated by 2 to 4 bonds away. This gives more information about connectivity within the molecule.

References

Silverstein, R.M, Webster, F.X, and Kiemle D.J. Spectrometric Identification of Organic Compounds. 7th ed. John Wiley & Sons, Inc. 2005.

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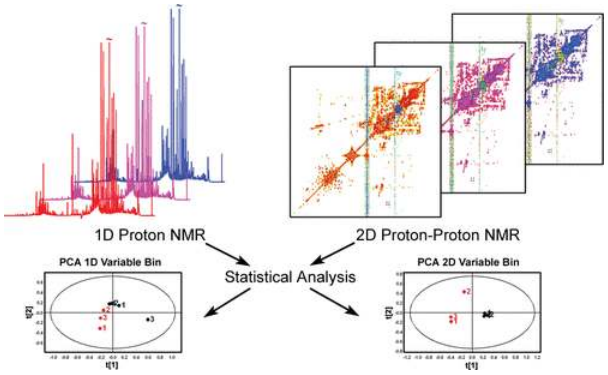
7.5: Uses for 2-D NMR Spectroscopy

Learning Objectives

- Learn in what instances scientists use 2-D NMR
- Understand practical applications of 2-D NMR

It has been previously mentioned in this chapter that the major advantage for using 2-D NMR over 1-D NMR is the ability to distinguish between overlapping signals that exist in larger molecules. 2-D NMR is incredibly important in biological and polymer chemistry to elucidate te three-dimensional structure of these large macromolecules. In these cases, HSQC can be used to determine the profile of metabolites in low concentrations (microMolar) accurately. TOCSY has been utilized to show changes in tumor cells and identify biomarkers associated with these cells. Molecular dynamics can be studied using 2-D NMR spectroscopy to map the molecule's internal mobility patterns. With molecular dynamics the loose ends of proteins can be studied and elucidated to learn more about the flexible surface areas often lost in other methods. 2D NMR has many more applications beyond protein NMR, including characterization of pharmaceuticals, temperature dependence of carbohydrate conformations, and metabolomics, to just name a few.

2-D NMR is often used in metabolic profiling like in the example below. This is due to the fact that NMR is not a destructive analysis, quantitative, reproducible and gives a lot of information about the sample.



Using TOCSY, this particular study compared the global metabolic profiles of urine obtained from two types of mice, specifically of wild-type and a knockout. Both 1-D and 2-D NMR experiments were run to determine if statistical differences between the techniques, especially when looking at low abundance metabolites. Both 1-D and 2-D NMR data could differentiate between the two types of mice, but only the 2-D data could be used to show statistically relevant changes in the low abundance metabolites. The con of 2-D NMR data is that it takes longer to obtain the data compared to 1-D NMR data collection, however, the data obtained resulted in a more meaningful and comprehensive metabolic profile, aided in metabolite identifications, and minimized ambiguities in peak assignments.[2] This is just one example of how 2-D NMR has been applied.

References

1. https://www.news-medical.net/life-sc...lications.aspx; Accessed July 29, 2022.

2. J. Proteome Res. 2008, 7, 2, 630–639 Publication Date:December 15, 2007 https://doi.org/10.1021/pr700594s

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7.6: Interpreting 2-D NMR Spectra

Learning Objectives

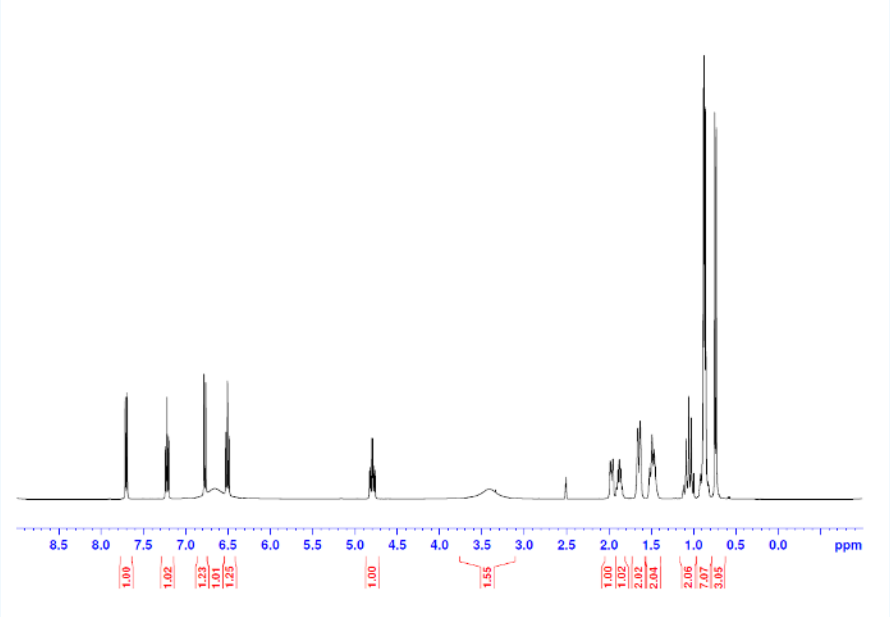
- understand how to analyze the different 2-D spectra and what information you can gather from each.
- determine the structure of an unknown molecule using different types of NMR spectroscopy.

This page is devoted to explaining solved structure elucidation problems using different types of 1-D and 2-D NMR spectra to help guide you through different scenarios. The first scenario involves analyzing different types of NMR spectra to determine if you made the desired product.

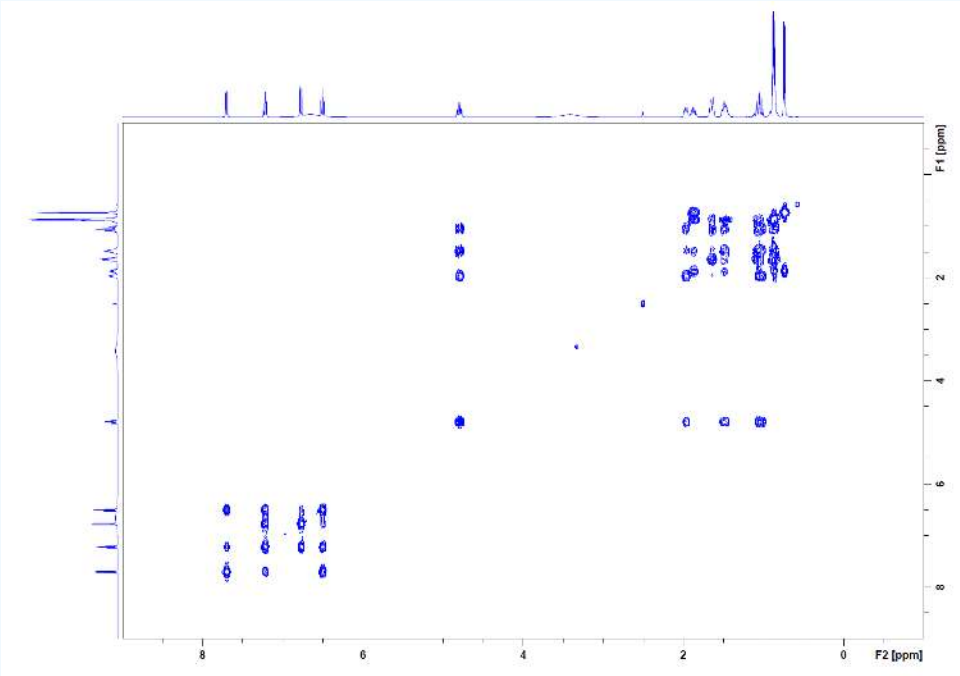
Example 7.6.1

Did you synthesize menthyl anthranilate? The spectra were taken in DMSO-d6. Use the spectra to determine whether the product desired was made.

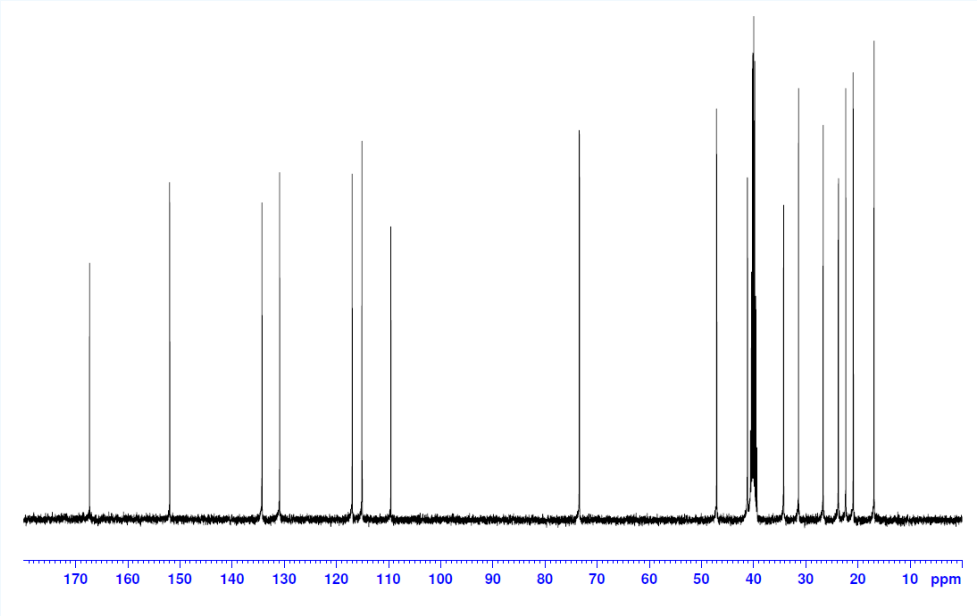
^{1}H:



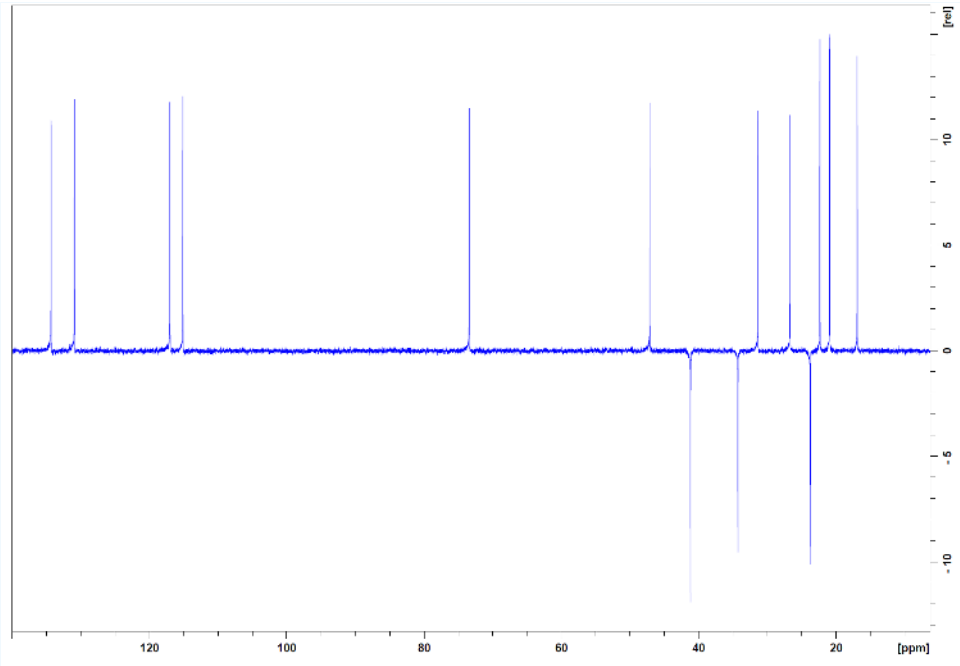
COSY:


F1 [ppm]
F2 [ppm]

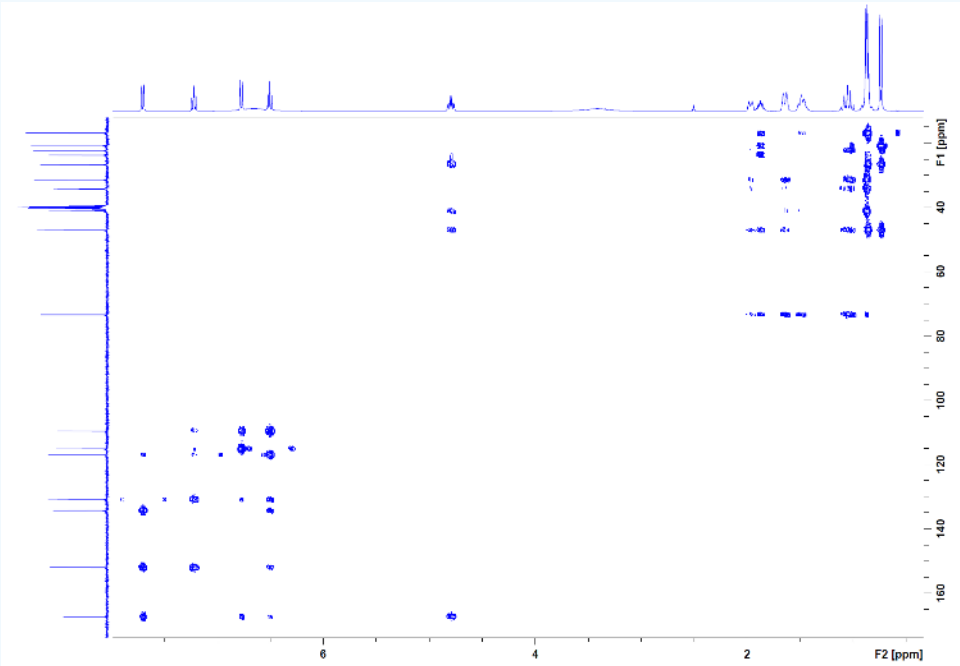
^{13}C:


170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

DEPT-135:

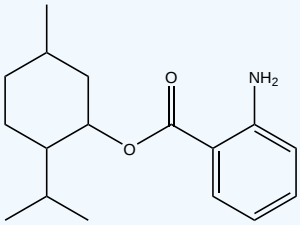


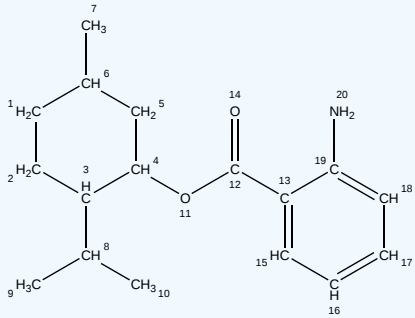
HMBC:



Solution

With this example, we have the advantage to knowing what our structure is. It would be helpful to look up what menthyl anthranilate's structure is to start before moving on.

Menthyl Anthranilate: 

Atoms Numbered in Menthyl Anthranilate: 

Step 1: Characterization of the peaks in ^{1}H NMR spectrum by considering chemical shift, integration, spin-spin splitting, and coupling constants. Remember if protons are coupled to each other, they will have the same coupling constant, J.

The deuterated solvent is DMSO and the peak for residual solvent appears at 2.50 ppm, which is why this peak is missing integration. The peak at 0.7 ppm is the methyl group at position 7 on the numbered structure. The integration is 3 and there is no other peak that will have that integration. The next peak at 0.9 ppm are the other methyl groups labeled 9 and 10. Both of these peaks are doublets, which correlates to them having one neighboring hydrogen (positions 6 and 8) and this is the case for both. The next three peaks to come all integrate to 2 protons, which will correspond to positions 1, 2, and 5. The hydrogens at position 5 will be the furthest downfield since it is closest to an electron-withdrawing group. Remember, the closer the hydrogen is to an electron-withdrawing group, the more the magnetic field surrounding the hydrogen is influenced. The peak at 4.8 ppm is H4. It is directly attached to an electron-withdrawing group and it integrates to 1H. The broad peak at 3.4 ppm corresponds to the NH_2. Broad peaks in NMR often correspond to an averaging and do not show spin-spin splitting. In this case, the hydrogens attached to nitrogen are exchangeable leading to an averaging of "seeing" a different H spin state depending on if an H is attached or not. The peaks in the 6.5 to 8.0 ppm range are the aromatic protons. COSY will help identify the peaks that were not labeled specifically in the ^{1}H spectrum.

Step 2: Even with the COSY, it is difficult to completely elucidate the structure. The cross peaks in the 6.5-8.0 ppm range are all protons that are part of an aromatic ring. The correlations are indicating that the two groups coming off the ring will be ortho to each other. The correlations indicate that the peak at 7.7 ppm has two other neighbors, which leads to the doublet of doublets. This is the same for the peak at 6.6 ppm, which is also a doublet of doublets. The 7.2 ppm peak is a triplet of doublets, so a total of 3 neighbors and there are 3 cross peaks to confirm this. The peak at 6.5 ppm is also a triplet of doublets and has 3 cross peaks. The only way this pattern can occur is to have ortho groups coming off the aromatic ring. The next protons that can be used to help elucidate the structure come from the peak at 4.8 ppm. This is the methine group attached to the oxygen at C4. The cross peak at (4.8, 1.1) is a methylene group (C5) attached to C4. The cross peak at (4.8, 1.5) indicates a correlation to another methylene group (possibly C2). The cross peak at (4.8, 1.9) is a correlation to another methine group (C3). The peak at 0.9 ppm is a methyl group. The cross peaks of this methyl group indicate that it is attached to a methine group (C6). The remaining correlations are difficult to decipher since it is squished into a small region with overlapping cross peaks.

Step 3: ^{13}C NMR analysis is a necessary step in full structural characterization. However, ^{13}C NMR alone does not provide enough information to assign the carbons in the molecule. It can be used to confirm the number of carbons in the molecule and this is where DEPT or 2-D NMR will assist. The ^{13}C spectrum above does indeed show all seventeen carbons. The group of peaks around 40 ppm is DMSO-d6, so will not be counted towards the seventeen. However, the peak at 41 ppm is one of the seventeen total carbons.

Step 4: DEPT will tell what kinds of carbons do we have in the molecule. There are three quaternary carbons (absent from the DEPT spectrum compared to the ^{13}C spectrum), three methylene groups (negative peaks), and eleven methine and methyl groups.

Step 5: In the HMBC, there are cross peaks that extend to our carbonyl at 167 ppm. These cross peaks indicate that the carbonyl is attached to the aromatic ring just as we can see in the structure. It also shows that there is a correlation between the carbonyl carbon and the methine attached to the oxygen, this confirms the ester functionality. The two other quaternary carbons (152 ppm and 110 ppm) also have cross peaks indicating connection as part of the aromatic ring. Because the carbon spectrum is a wider range, it spreads out the cross peaks and there is less overlap and it is easier to analyze each cross peak. As this is done, each one confirms that the structure is indeed menthyl anthranilate.

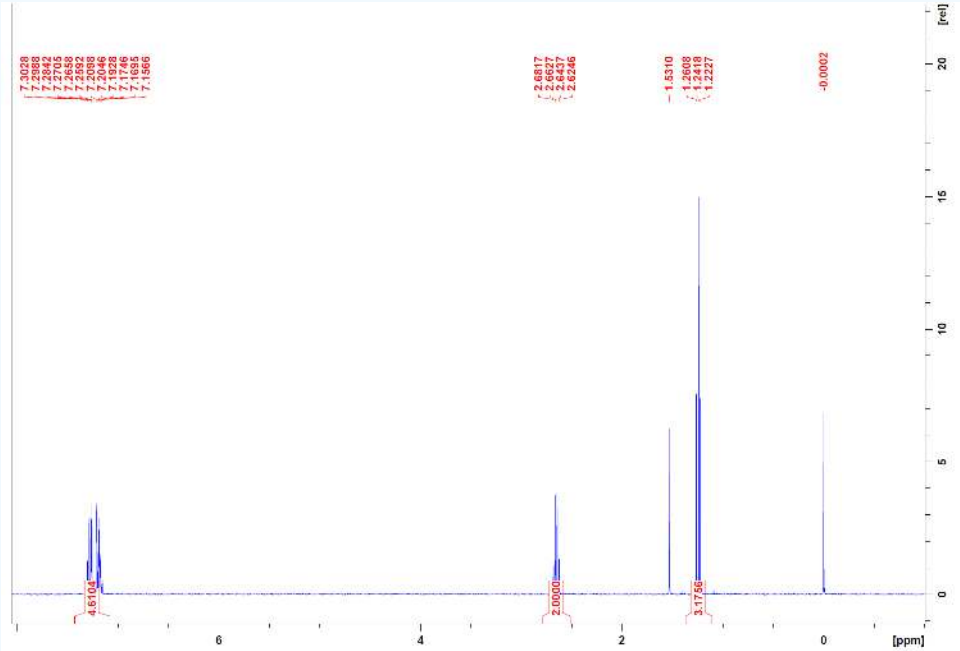
This process can be used for known and unknown structure elucidation. You can also see that in more complicated molecules, multiple spectra help shine light on all parts of the molecule.

This next example show how you attempt to determine an unknown structure from molecular formula and different types of 1-D and 2-D NMR spectra.

Example 7.6.2

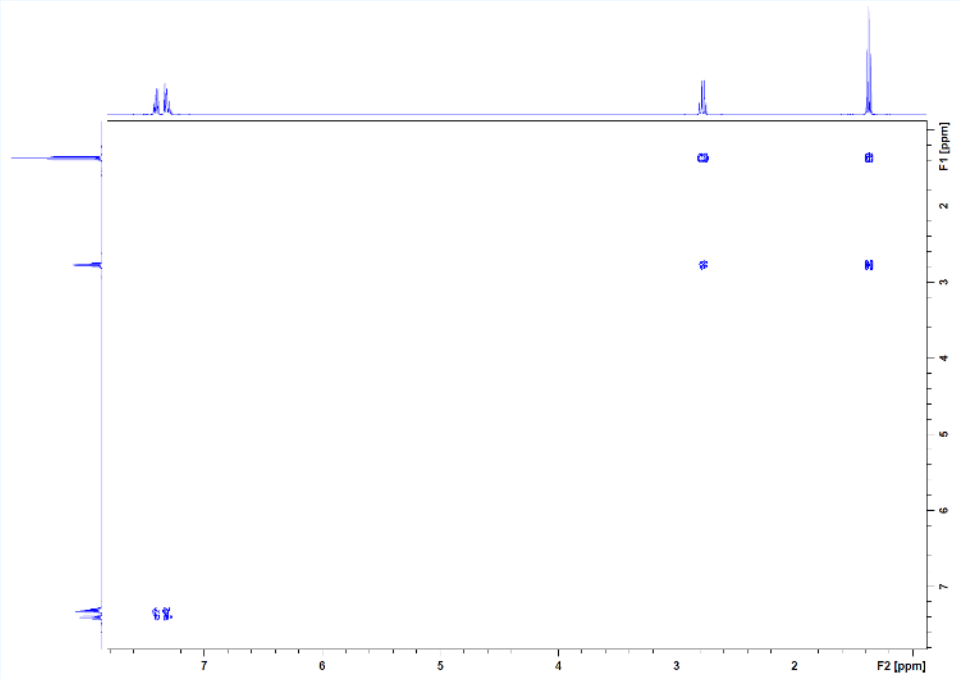
Identify the compound C8H10 from the spectra below. The sample was dissolved in $CDCl_3$.

^1H:

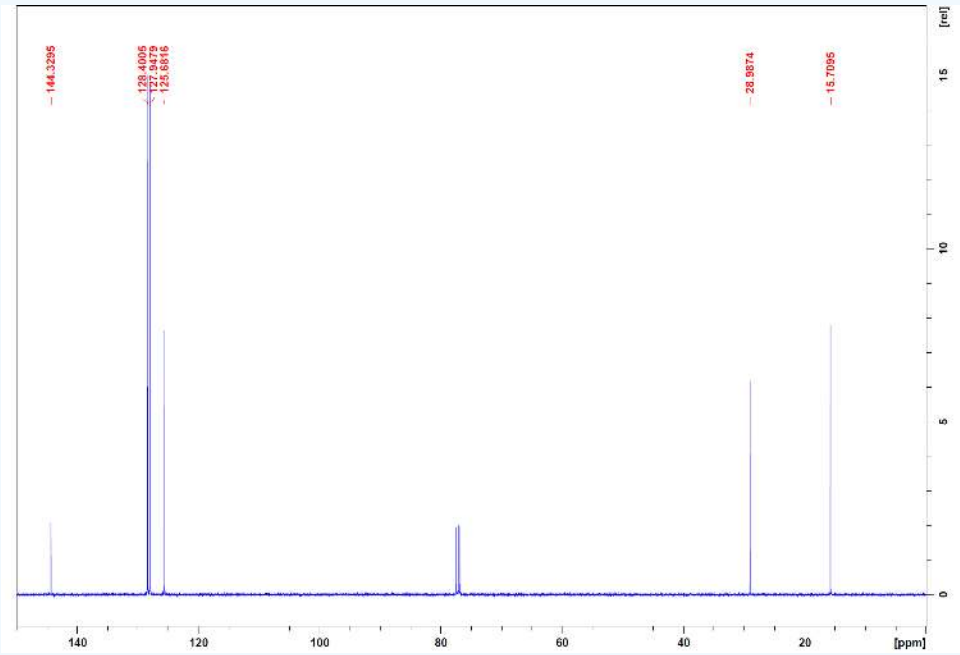


Note: The peak at 0 ppm is TMS and the peak at 1.5 ppm is water. These can be disregarded in analysis.

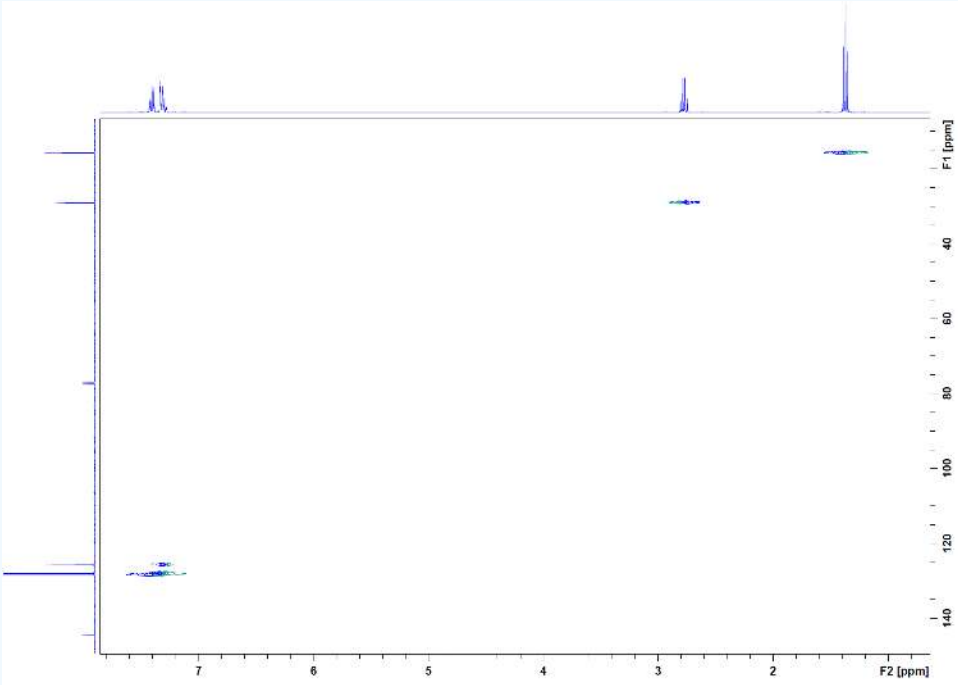
COSY:


F1 [ppm]
F2 [ppm]

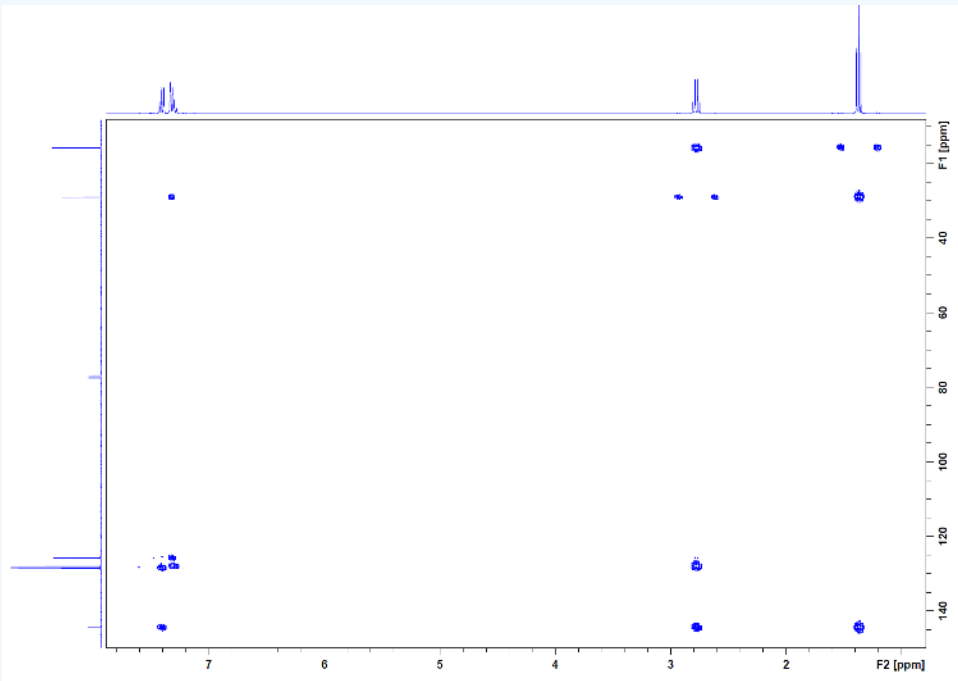
^{13}C:


144.3295
128.4006
127.9479
125.6816
28.9874
15.7095
[rel]
[ppm]

HSQC:



HMBC:



Solution

Degrees of unsaturation = 4.

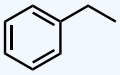
^{1}H NMR spectrum: At 1.2 ppm there is a triplet that integrates to 3H. This means the fragment must be -CH_2-CH_3. The peak at 2.67 ppm is a quartet that integrates to 2H, so this is also a -CH_2-CH_3. The multiplet at 7.2 ppm that integrates to 4.6 is in the aromatic region and with a degree of unsaturation of 4, these are most likely 5 aromatic protons.

COSY: The COSY corroborates with the fragment of a methylene coupling to a methyl group. This information was determined from the two cross peaks: (1.2, 2.67) and (2.67, 1.2). Coupling is reciprocal, so it makes sense that there is symmetry with the coupling. The aromatic region protons do not couple beyond that system itself.

^{13}C: The ^{13}C indicates that there are 6 different types of carbon nuclei. This means there must be some symmetry within the carbons since there should be a total of 8. The peak at 76 ppm is $CDCl_3$.

HSQC: The first cross peak (1.2, 15) corresponds to the methyl group. The next cross peak (2.4, 29) corresponds to the methylene group. The final cross peaks (7.27, 125), (7.27, 128), and (7.27, 128.4) all correspond to the aromatic protons. These carbons are also in the double bond region. There is no cross peak for the carbon at 144 ppm, so this carbon must not have any hydrogens attached to it.

HMBC: Cross peak (1.2, 29) indicates that the methyl group is attached to the methylene group carbon. The cross peak at (2.4, 15) is the reciprocity of this correlation. The methyl hydrogens also have a cross peak at (1.2, 144), so the methylene must be attached to that carbon. When looking down the column for the methylene, there is a cross peak to corroborate this as well as a cross peak at (2.4, 128). This indicates that beyond its attachment to the quarternary carbon is the aromatic system. The cross peaks under the 7.2 ppm peak confirm this.

Final structure: 

7.6: Interpreting 2-D NMR Spectra is shared under a not declared license and was authored, remixed, and/or curated by Lauren Reutenauer.

7.7: 2-D NMR Problems

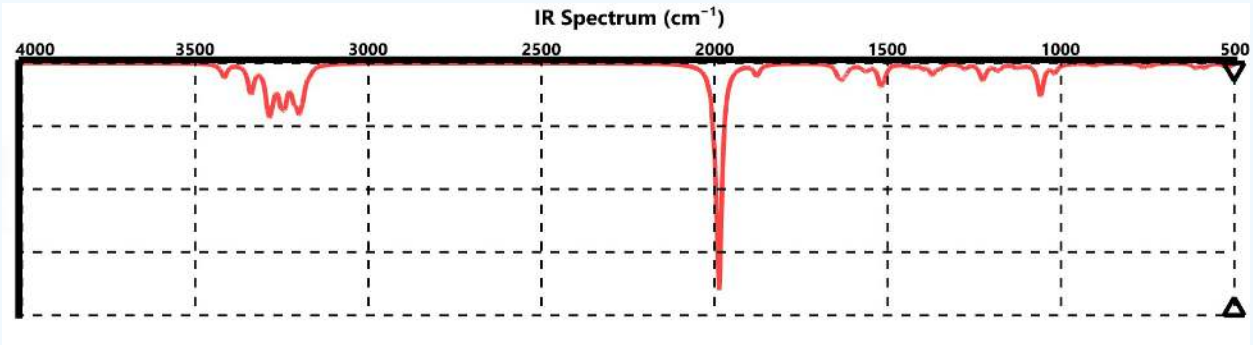
Learning Objectives

- Solve unknown problems using a variety of spectra and the molecular formula.

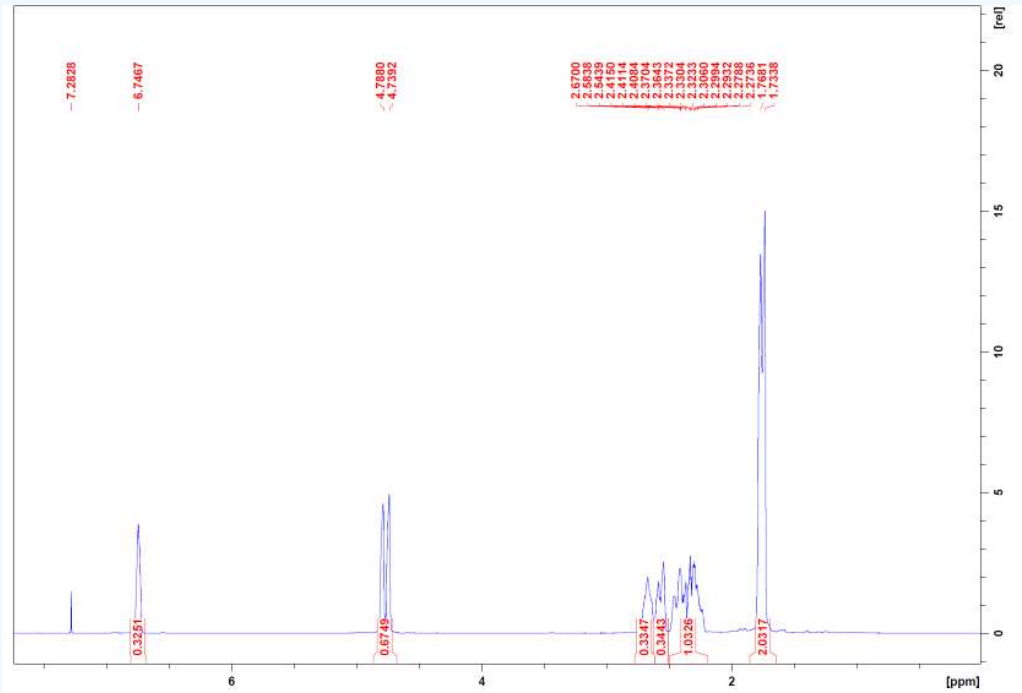
Exercise 7.7.1

Propose a structure using the spectral data below for $C_{10}H_{14}O$. Note: You may need to check for solvent peaks. This sample was dissolved in $CDCl_3$.

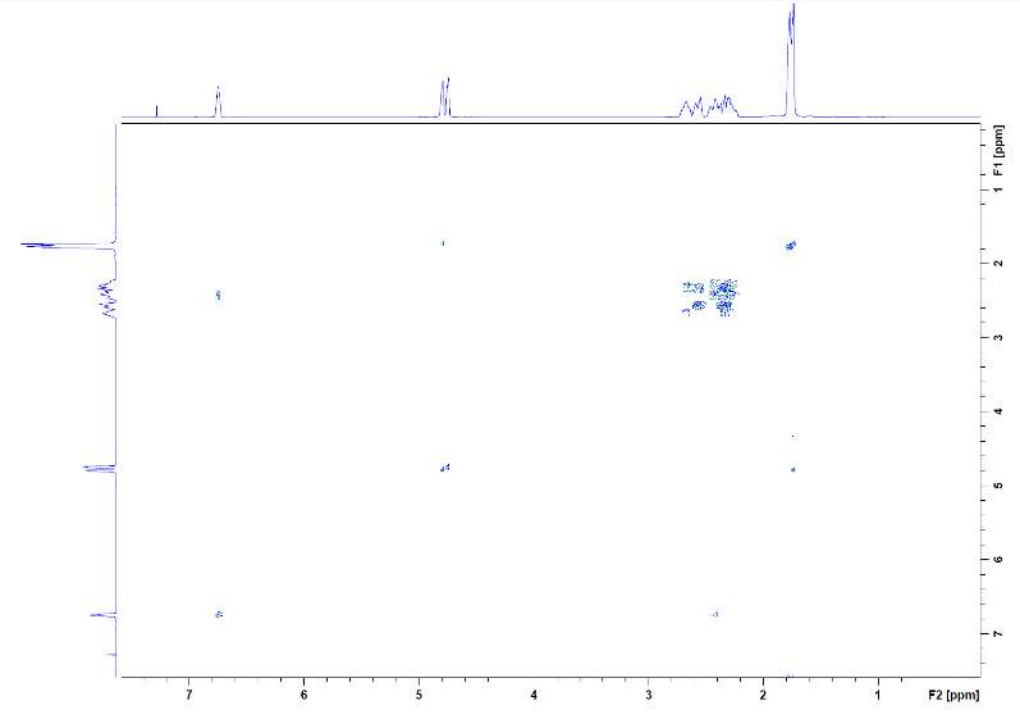
IR:



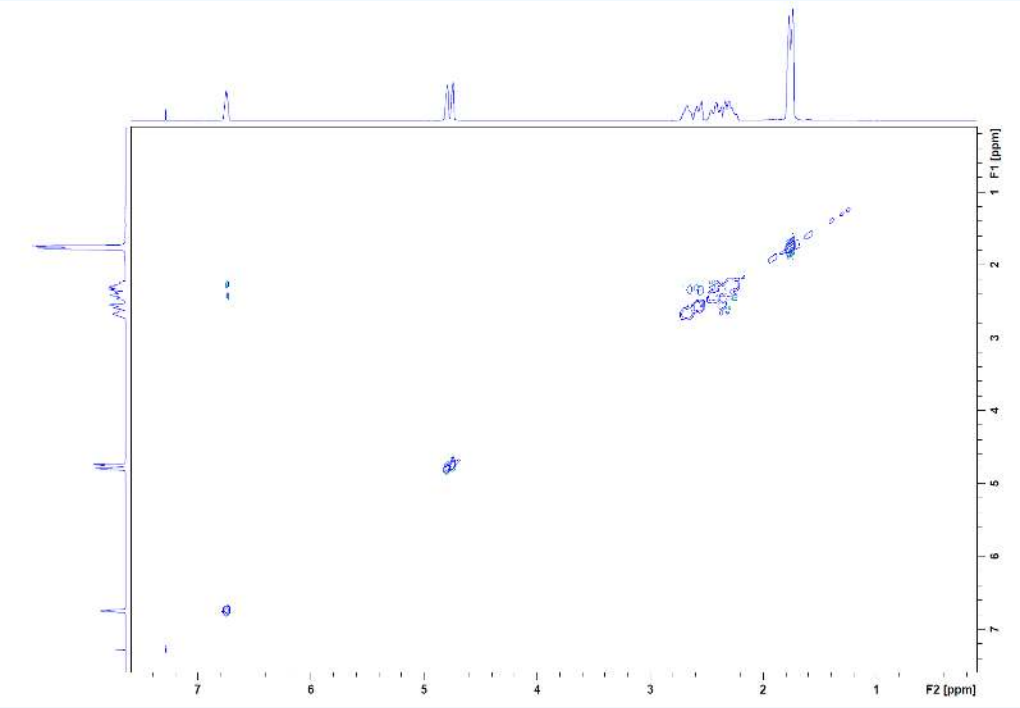
^1H:



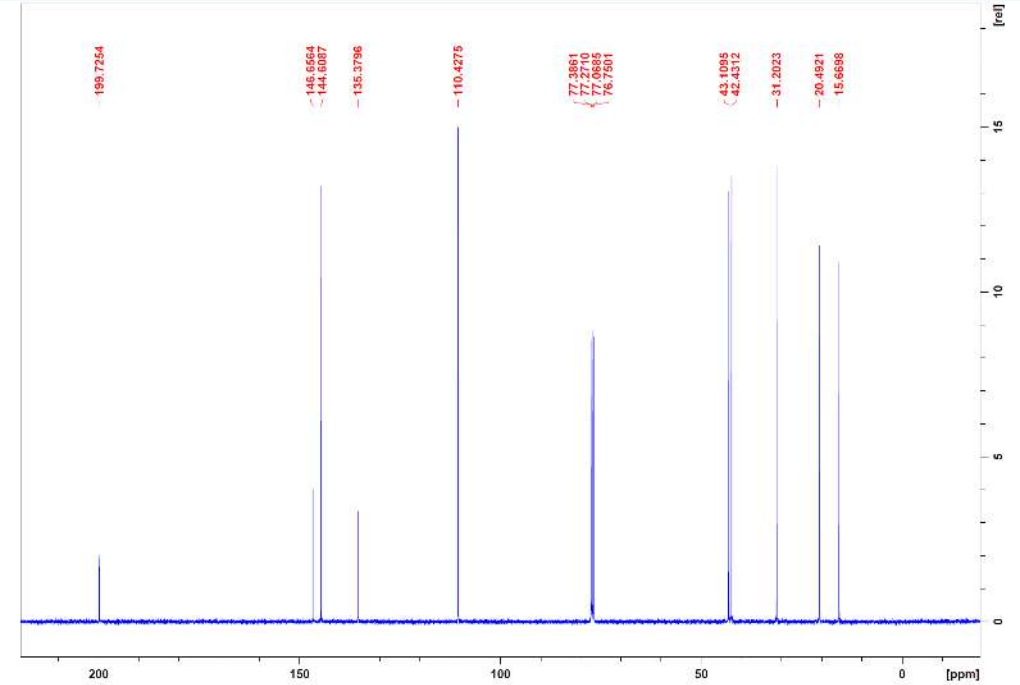
COSY:



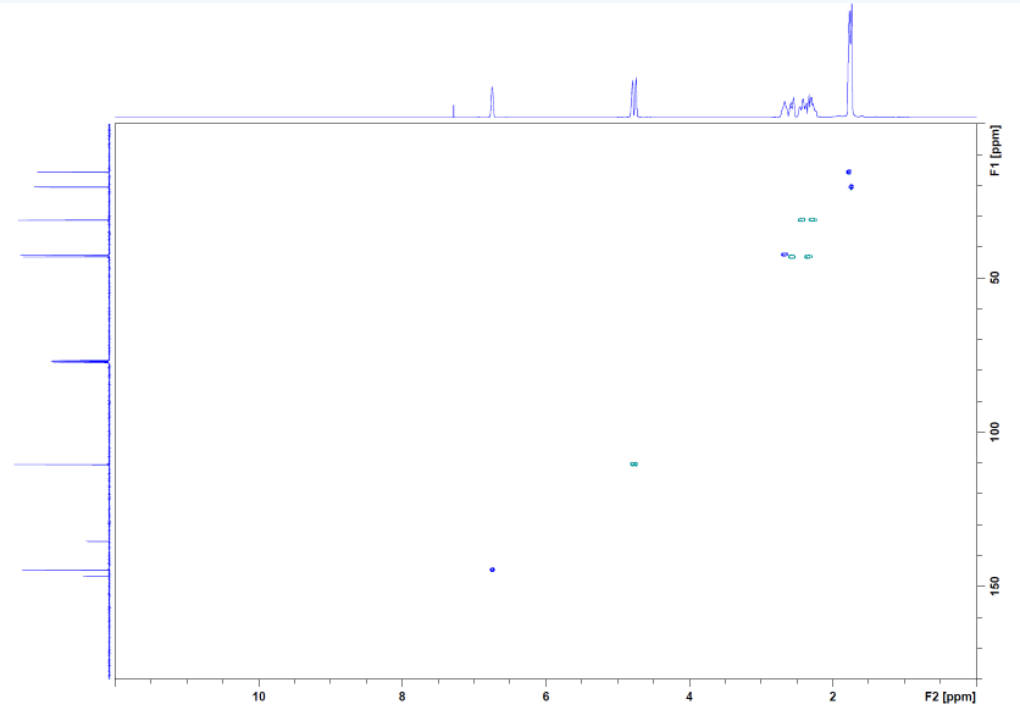
NOESY:



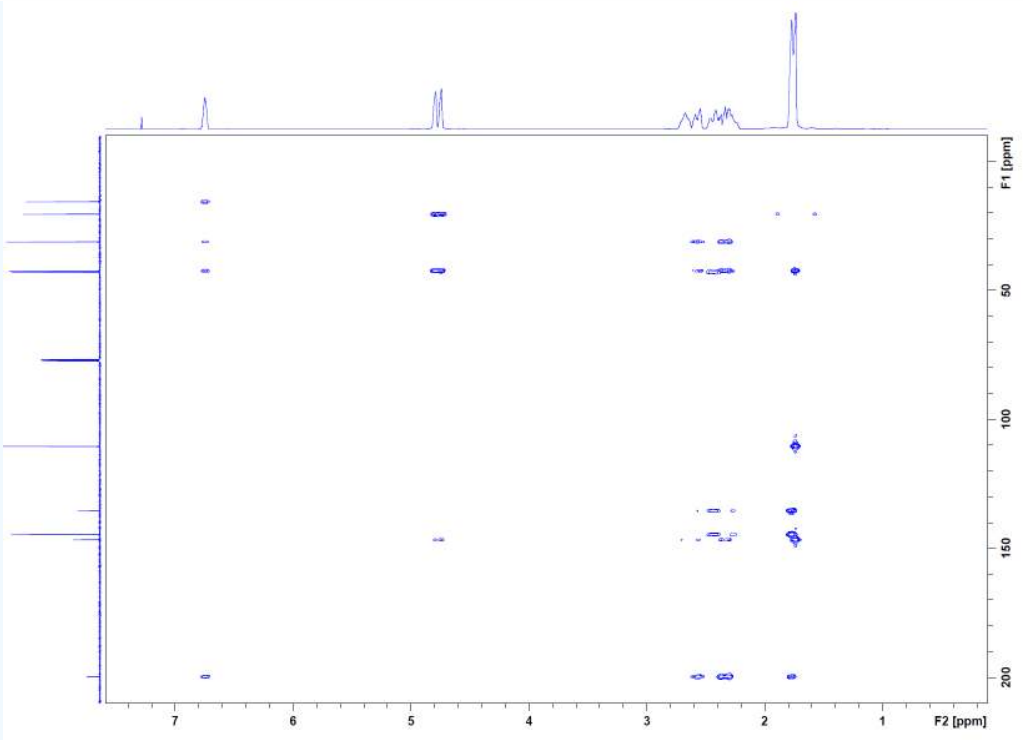
^{13}C:


199.7254
146.6564
144.6087
135.3796
110.4275
77.3861
77.2710
77.0685
76.7501
43.1095
42.4312
31.2023
20.4921
15.6698
[rel]
[ppm]

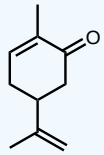
HSQC:


F1 [ppm]
F2 [ppm]

HMBC:



Answer

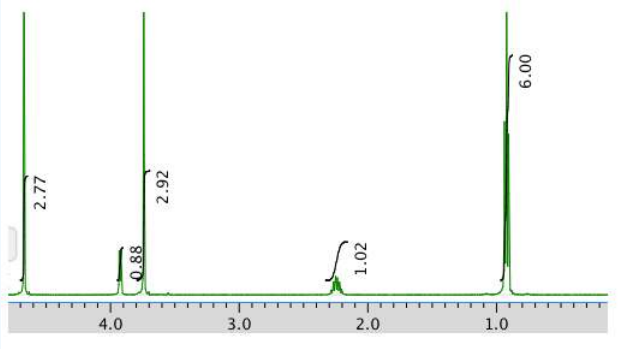


Exercise 7.7.2

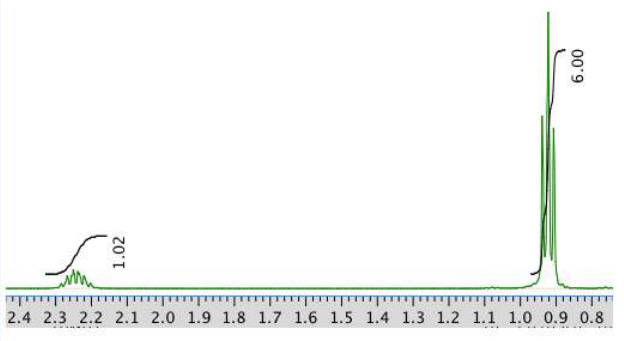
Present an analysis of the following data and propose a structure.

MW: 131 amu

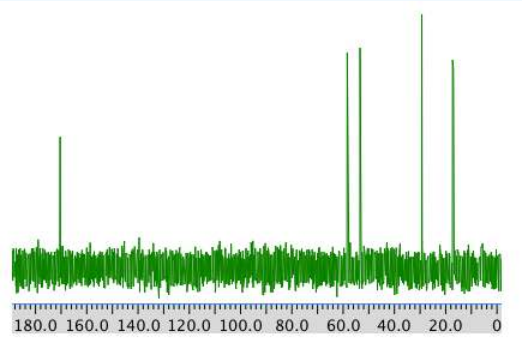
The full ^{1}H NMR spectrum in D_2O:



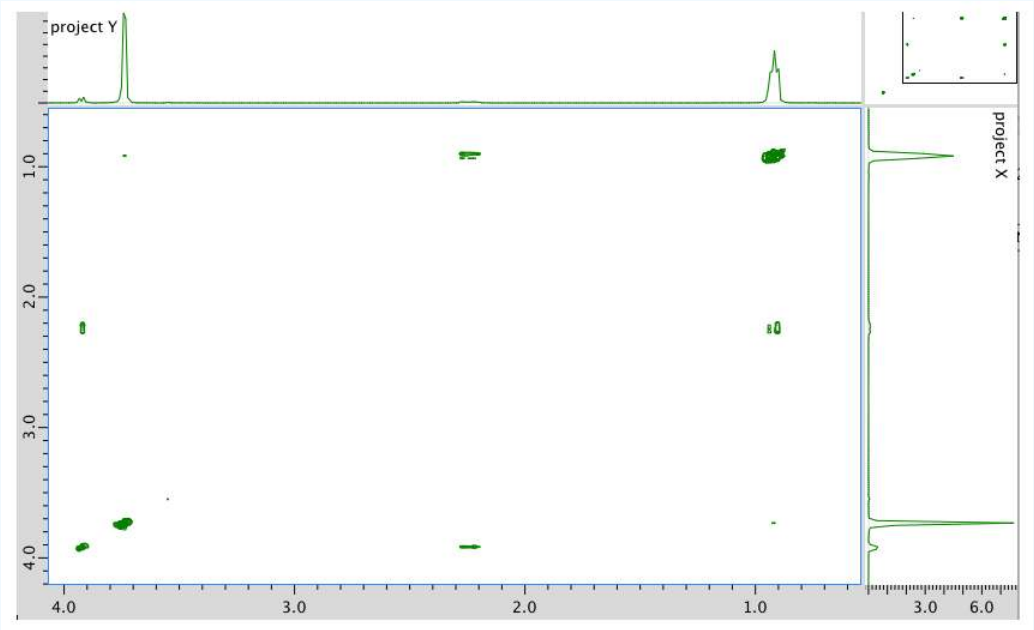
An expansion:



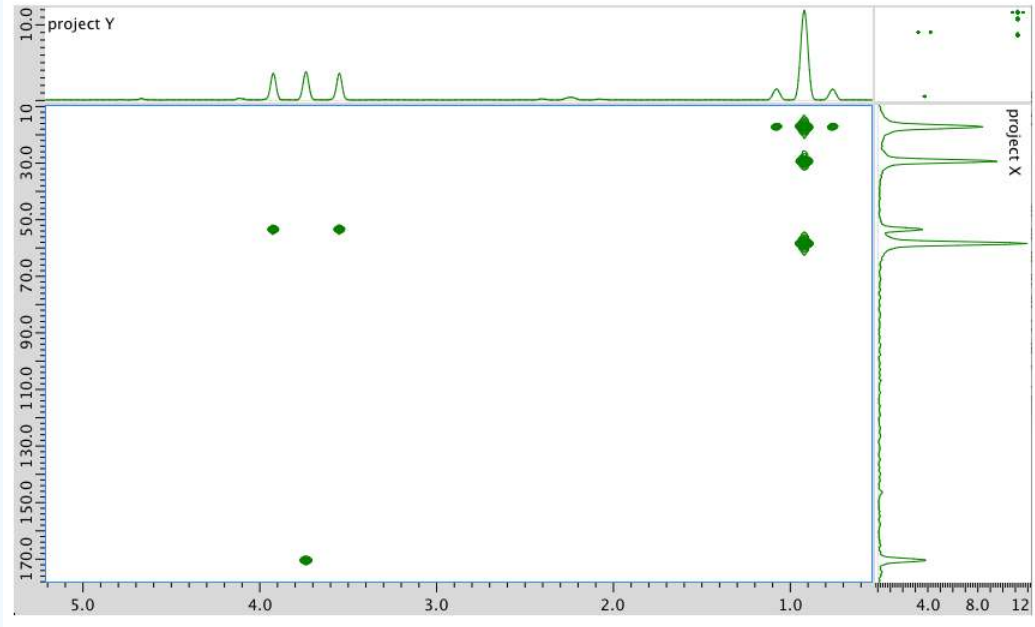
^{13}C NMR:



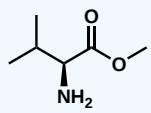
COSY:



HMBC:



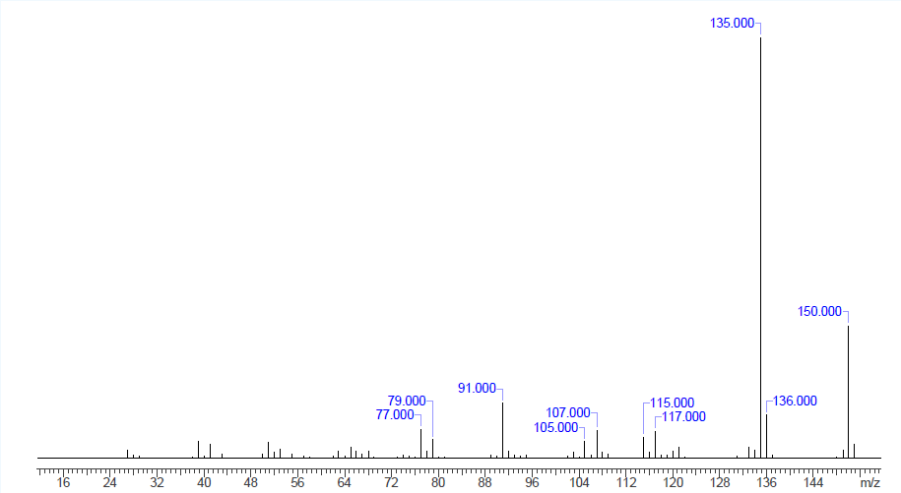
Answer



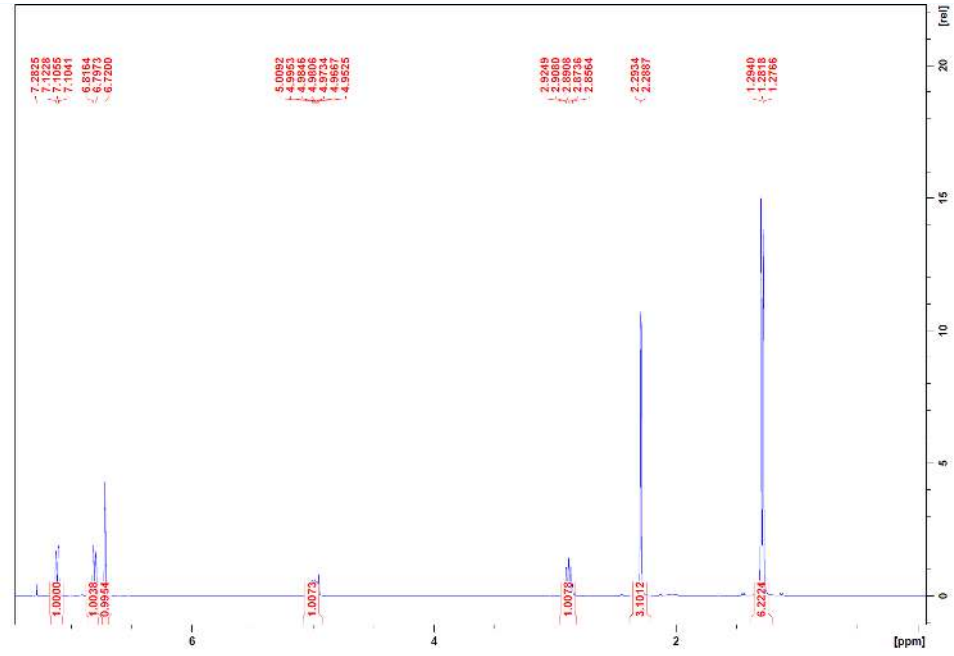
Example 7.7.3

Propose a structure using the spectral data below for $C_{10}H_{14}O$. Note: You may need to check for solvent peaks. This sample was dissolved in $CDCl_3$.

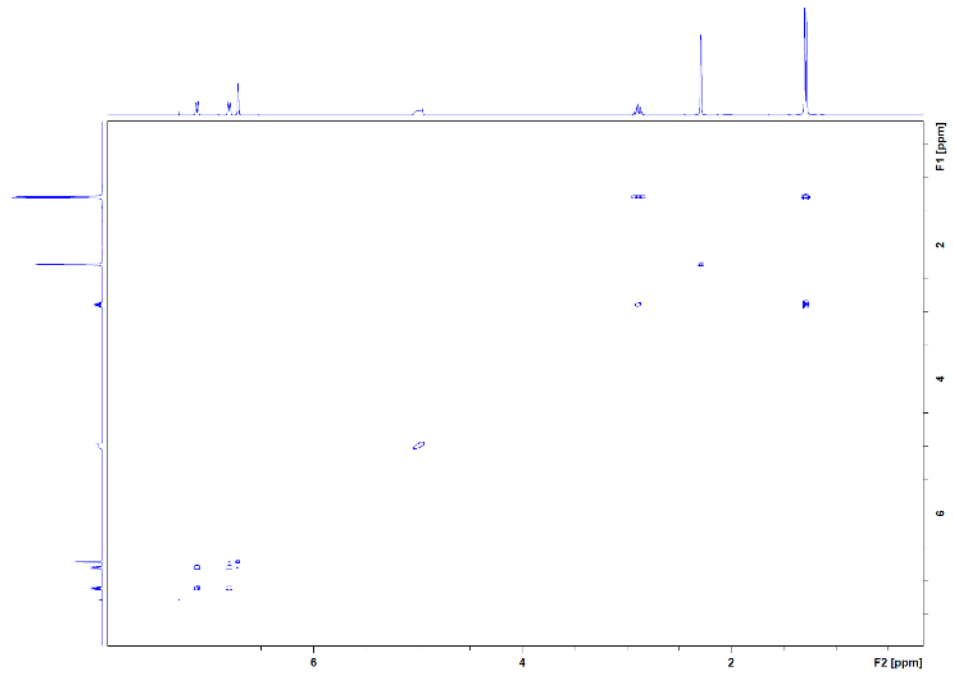
Mass Spectrum:



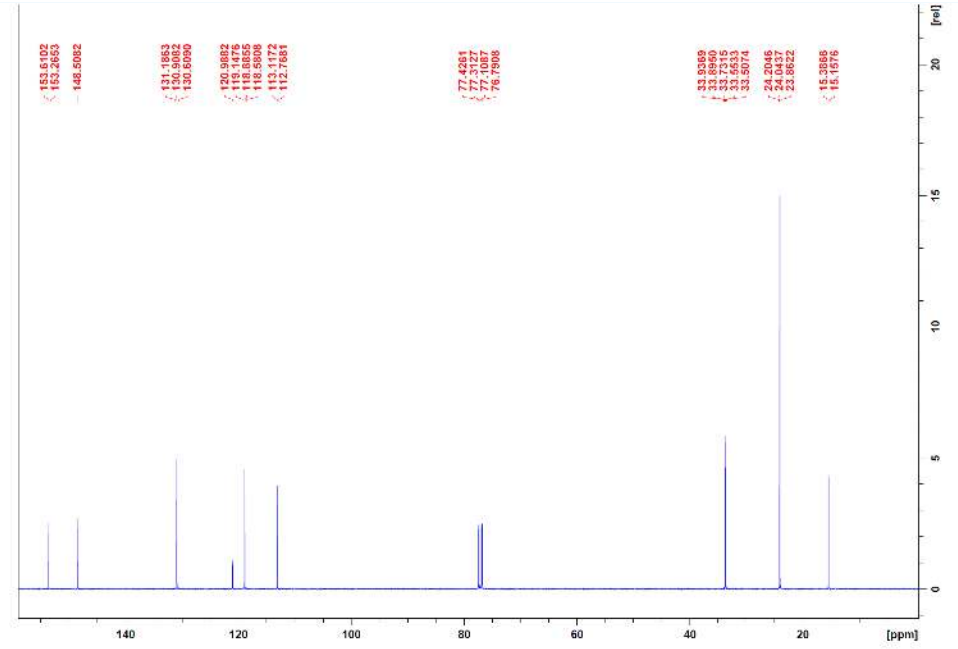
^1H:


7.2825
7.1228
7.1055
7.1041
6.8154
6.7973
6.7200
5.0052
4.9953
4.9846
4.9806
4.9734
4.9657
4.9525
2.9249
2.9080
2.8908
2.8736
2.8564
2.2534
2.2887
1.2940
1.2818
1.2766
1.0000
1.0038
0.9954
1.0073
1.0078
3.1012
6.2224
[ppm]
[rel]

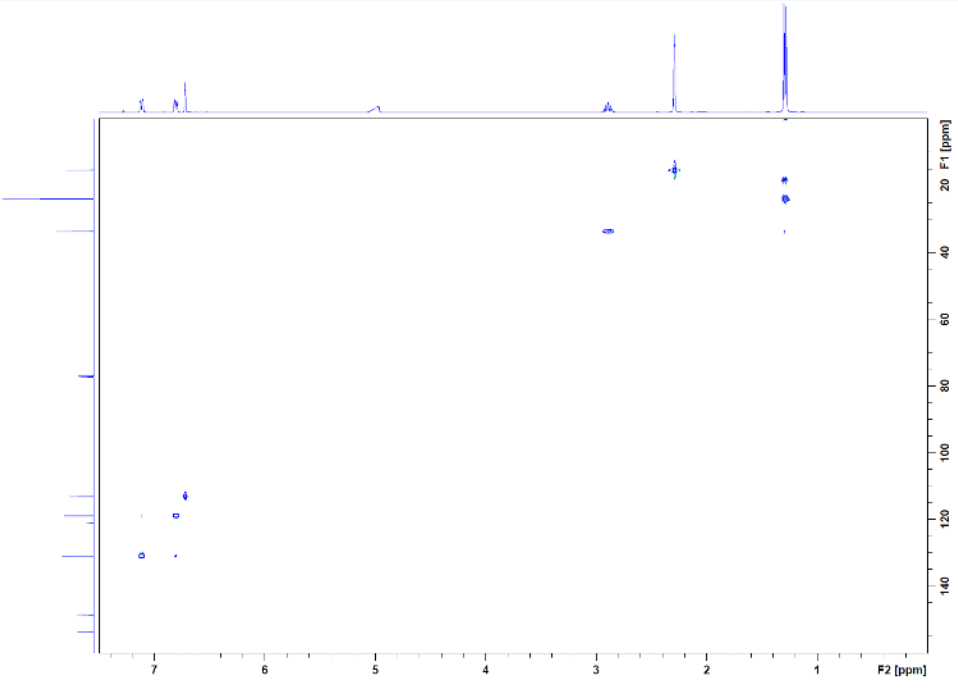
COSY:


F1 [ppm]
F2 [ppm]

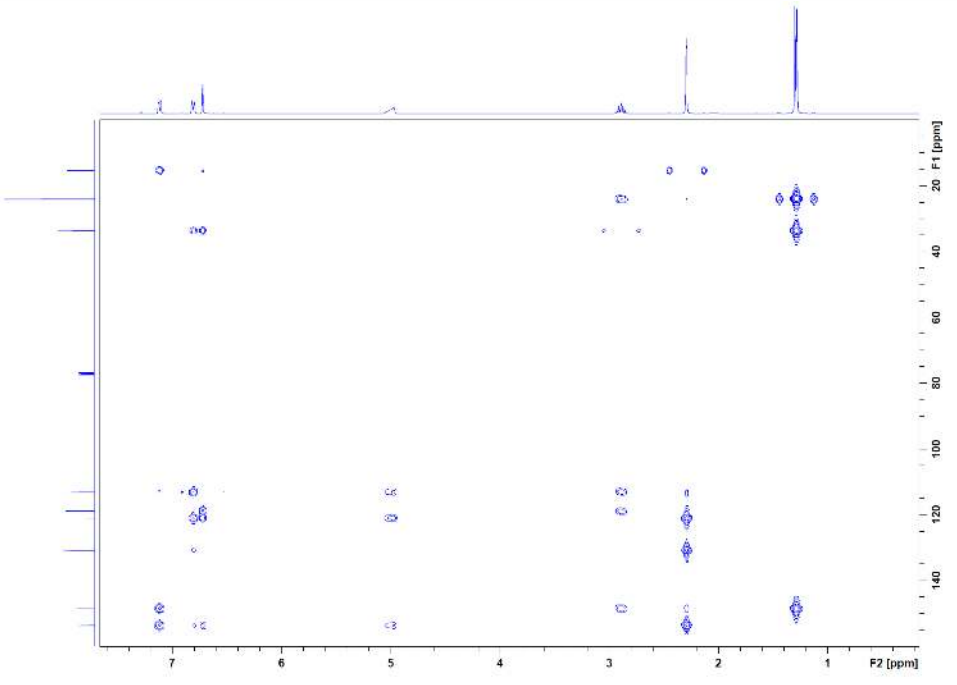
^{13}C:


153.6102
153.2653
148.5082
131.1863
130.9082
130.6090
120.9882
119.1476
118.6855
118.5808
113.1172
112.7681
77.4261
77.3127
77.1087
76.7908
33.9369
33.8950
33.7315
33.5533
33.5074
24.2046
24.0437
23.8622
15.3868
15.1576
[rel]
[ppm]

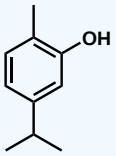
HSQC:


F1 [ppm]
F2 [ppm]

HMBC:



Solution



7.7: 2-D NMR Problems is shared under a not declared license and was authored, remixed, and/or curated by Lauren Reutenauer.

7.S: Summary

7.1: Chapter Objectives and Preview of Correlation NMR Spectroscopy

- Complex molecules can be hard to elucidate solely with 1-D NMR because it doesn't quite solve the entire picture. This is where correlation NMR spectroscopy can be used.

7.2 Theory

- The splitting of resonances indicates that groups were "correlated" to each other due to the spins within each group.
- A simple 2-D experiment pulse sequence consists of a relaxation delay, a pulse, a variable time interval (t_1), a second pulse, and acquisition (t_2).
- In 2-D experiments, the signal detected during acquisition is a function of acquisition time (t_2), which has been modulated as a function of the time interval (t_1). This means that magnetization evolves around one frequency during t_1 and a different frequency during t_2.
- The output once Fourier transformed is a 2-D spectrum with two axes.
- One axis (v_2) represents the nucleus detected during acquisition (t_2), while the other axis (v1) can represent the same nucleus or a different nucleus.
- With two axes, it leads to cross peaks along a diagonal connecting coupled nuclei.

7.3 Two Dimensional Homonuclear NMR Spectroscopy

- Homonuclear 2-D NMR spectroscopy is looking at the correlation of the same nuclei in a molecule.
- COSY looks at ^{1}H coupling to ^{1}H through bonds typically 3 bonds away and relies on the J-coupling to provide spin-spin correlation to indicate which protons are close to each other.
- TOCSY obtains correlations between all protons within a given spin system and begin to chain together fragments of a molecule.
- A molecule can have just one spin system or hundreds in more complex systems.
- The goal in TOCSY is to transfer the magnetization beyond directly coupled spins.
- NOESY determines which signals arise from protons athar are close to each other in space, even if they are not bonded.

7.4 Two Dimensional Heteronuclear NMR Spectroscopy

- Heteronculear 2-D NMR is the correlation between different nuclei, such as a ^{1}H to ^{13}C.
- HSQC is used to determine the proton to carbon or heteroatom (often nitrogen) single bond correlations.
- The purpose of a HSQC is to determine which protons are coupled to what other specific carbon or heteroatom in the molecule through bonds.
- HMBC is used to determine long range ^{1}H to ^{13}C connectivity.
- HMBC gives the correlation between ^{1}H and ^{13}C when separated by two, three, and even four (if through a conjugated system) bonds away.

7.5 Uses of 2-DNMR Spectroscopy

- Complex structure elucidation often requires 2-D NMR spectroscopy.
- HSQC can be used to determine the profile of metabolites in low concentrations (microMolar) accurately.
- TOCSY has been utilized to show changes in tumor cells and identify biomarkers associated with these cells.
- Molecular dynamics can be studied using 2-D NMR spectroscopy to map the molecule's internal mobility patterns.

Skills to Master

- Skill 7.1 Distinguish between 1-D and 2-D techniques.
- Skill 7.2 Learn to read COSY, TOCSY, NOESY, HSQC, HMBC spectra.
- Skill 7.3 Know what type of experiment to use to gain the information needed.
- Skill 7.4 Understand applications of 2-D NMR spectroscopy.
- Skill 7.5 Solve unknown structure determination problems with 2-D spectroscopy.

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CHAPTER OVERVIEW

8: Structure Elucidation Problems

8.1: 8.1 Chapter Objectives and Preview
8.2: 8.2 Problem 1
8.3: 8.3 Problem 2
8.4: 8.4 Problem 3
8.5: 8.5 Problem 4
8.6: 8.6 Problem 5

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8.1: 8.1 Chapter Objectives and Preview

Learning Objectives

After completing this chapter, you should be able to

- fulfill all of the detailed objectives listed under each individual section.
- solve road-map problems which may require the interpretation of spectral data.

This chapter is devoted to using your skills obtained in the previous sections to practice structure determination. There are five structure elucidation problems in this chapter using a variety of different spectral data to help solve the structures.

8.1: 8.1 Chapter Objectives and Preview is shared under a not declared license and was authored, remixed, and/or curated by Lauren Reutenauer.

8.2: 8.2 Problem 1

Learning Objectives

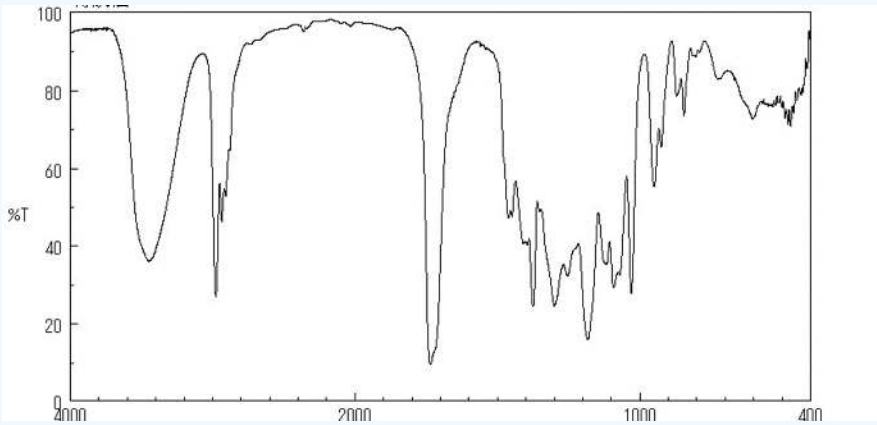
- Determine the structure for the following problem.

Exercise 8.2.1

Solve the structure using the following spectral data.

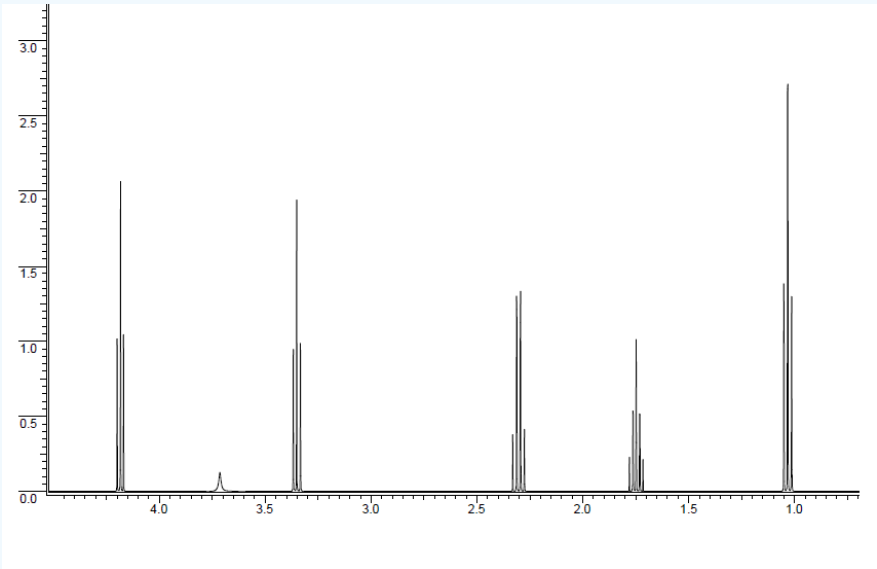
Molecular Formula: $C_6H_{12}O_3$

IR Spectrum:

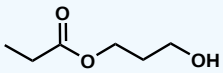


^{1}H NMR Spectrum:

Integration: 2:1:2:2:2:3



Answer



8.2: 8.2 Problem 1 is shared under a not declared license and was authored, remixed, and/or curated by Lauren Reutenauer.

8.3: 8.3 Problem 2

Learning Objectives

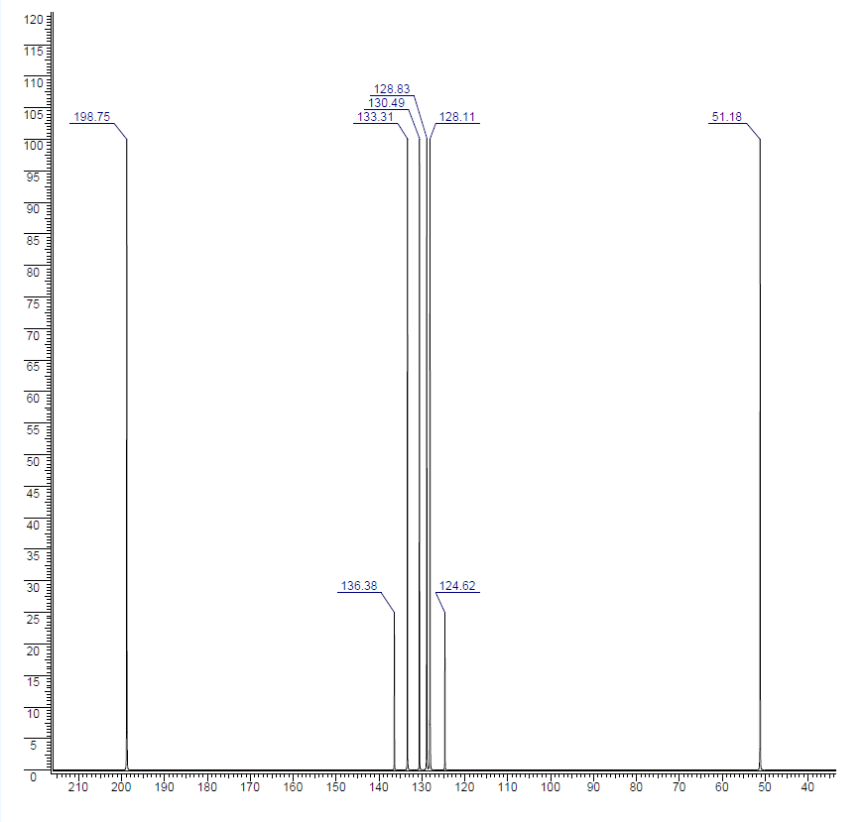
- Determine the structure for the following problem.

Exercise 8.3.1

Solve the structure using the following spectral data.

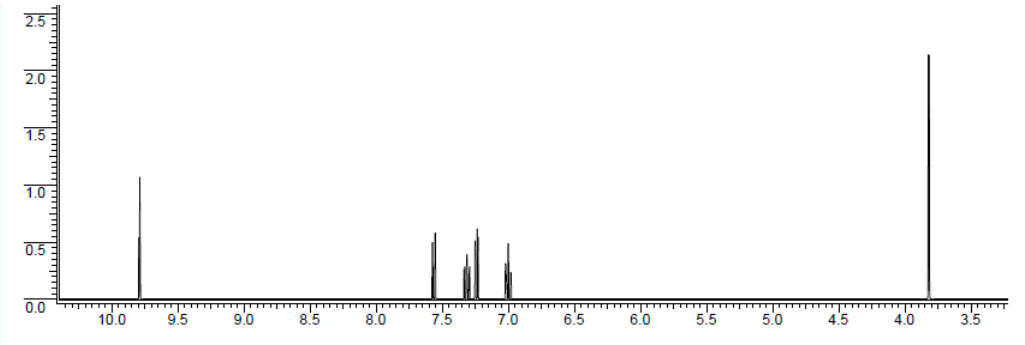
Molecular Formula: C_8H_7BrO

^{13}C Spectrum:



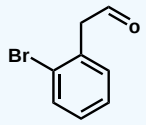
^{1}H NMR Spectrum:

Integration: 1:1:1:1:1:2 (left to right)



Chemical Shift	Splitting	Coupling Constant (Hz)
3.8	doublet	2
7	triplet of doublets	7 and 2
7.2	doublet of doublets	7 and 2
7.3	triplet of doublets	7 and 2
7.5	doublet of doublets	7 and 2
9.8	triplet	2

Answer



8.3: 8.3 Problem 2 is shared under a not declared license and was authored, remixed, and/or curated by Lauren Reutenauer.

8.4: 8.4 Problem 3

Learning Objectives

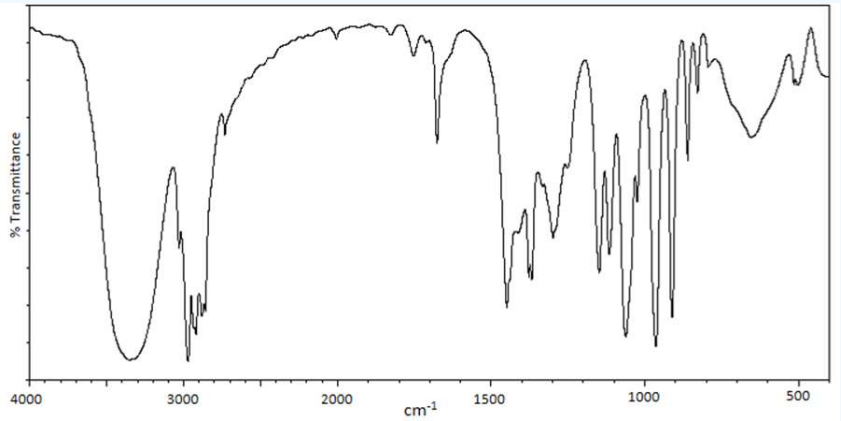
- Determine the structure for the following problem.

Exercise 8.4.1

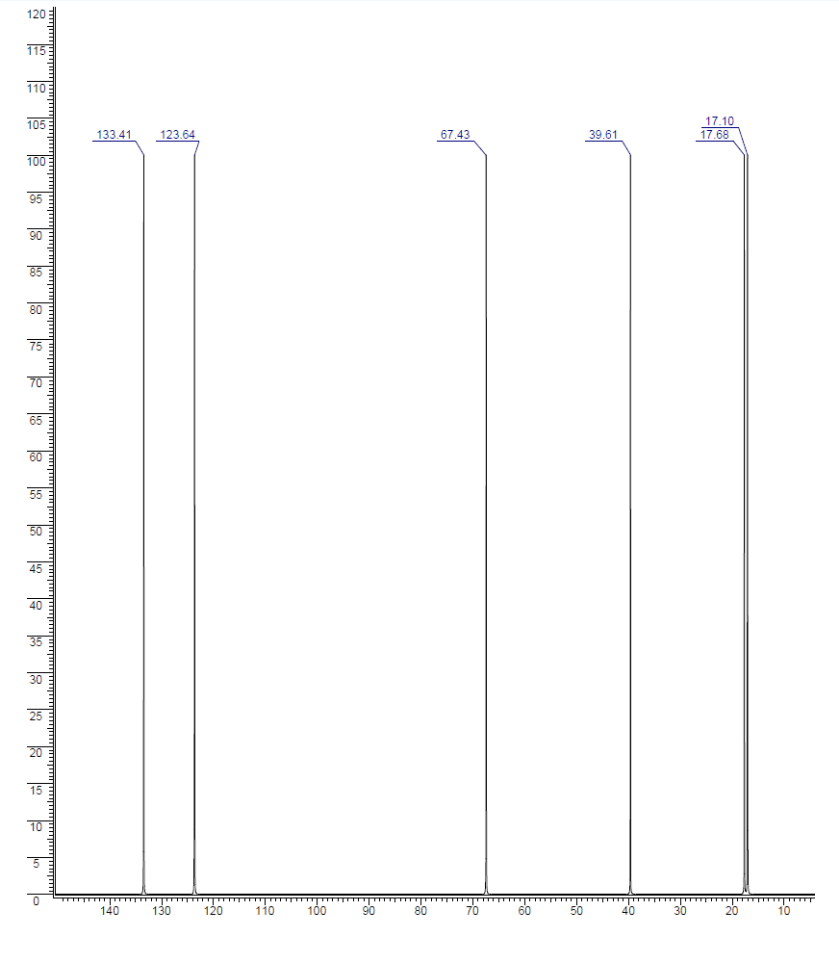
Solve the structure using the following spectral data.

Molecular Formula: $C_6H_{12}O$

IR spectrum:

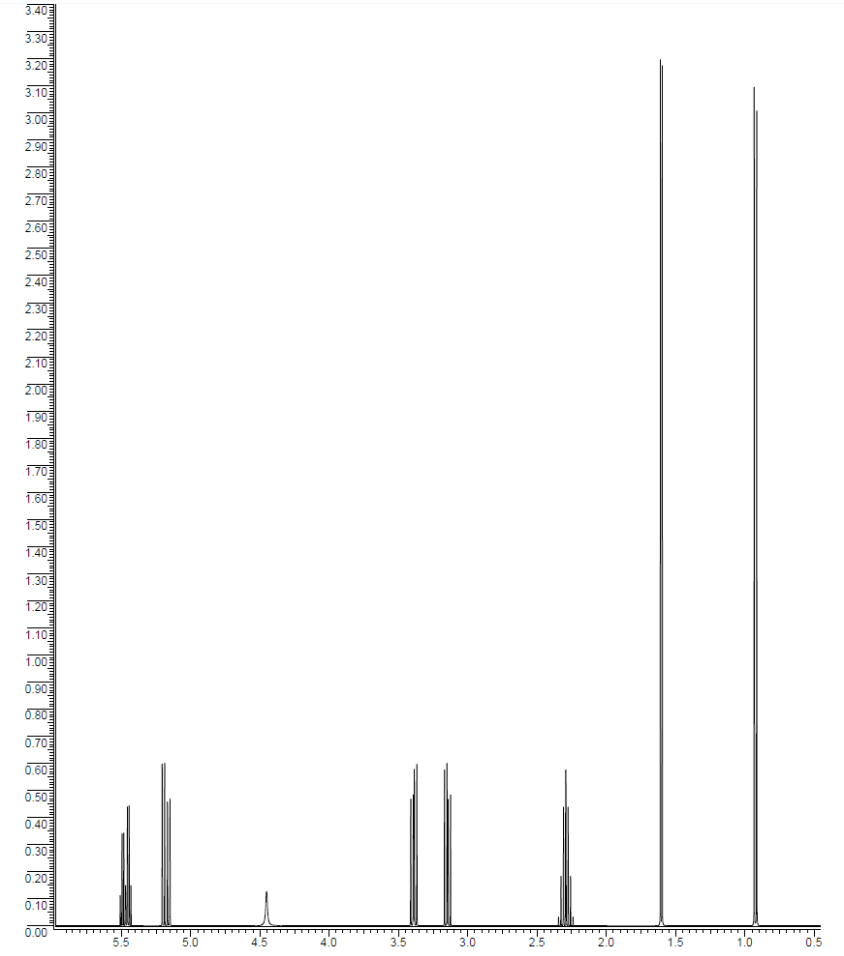


^{13}C Spectrum:

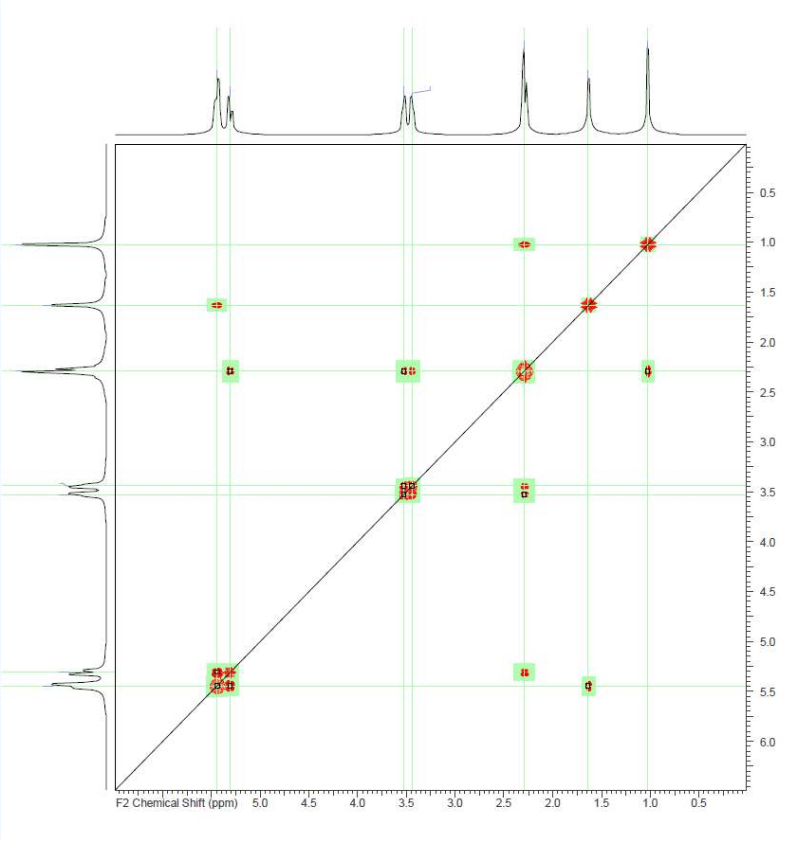


^{1}H Spectrum:

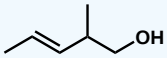
Integration: 1:1:1:1:1:1:3:3


3.40
3.30
3.20
3.10
3.00
2.90
2.80
2.70
2.60
2.50
2.40
2.30
2.20
2.10
2.00
1.90
1.80
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

COSY:



Answer



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8.5: 8.5 Problem 4

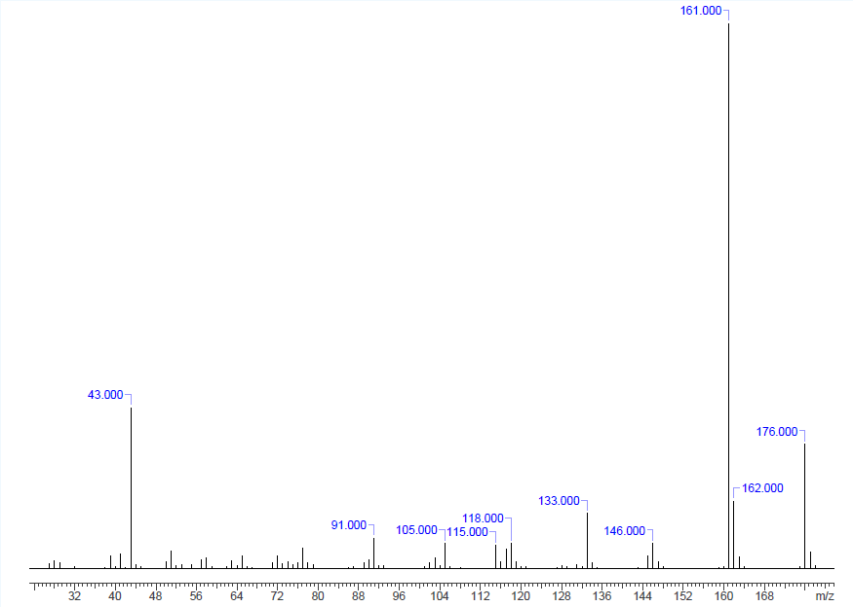
Learning Objectives

- Determine the structure for the following problem.

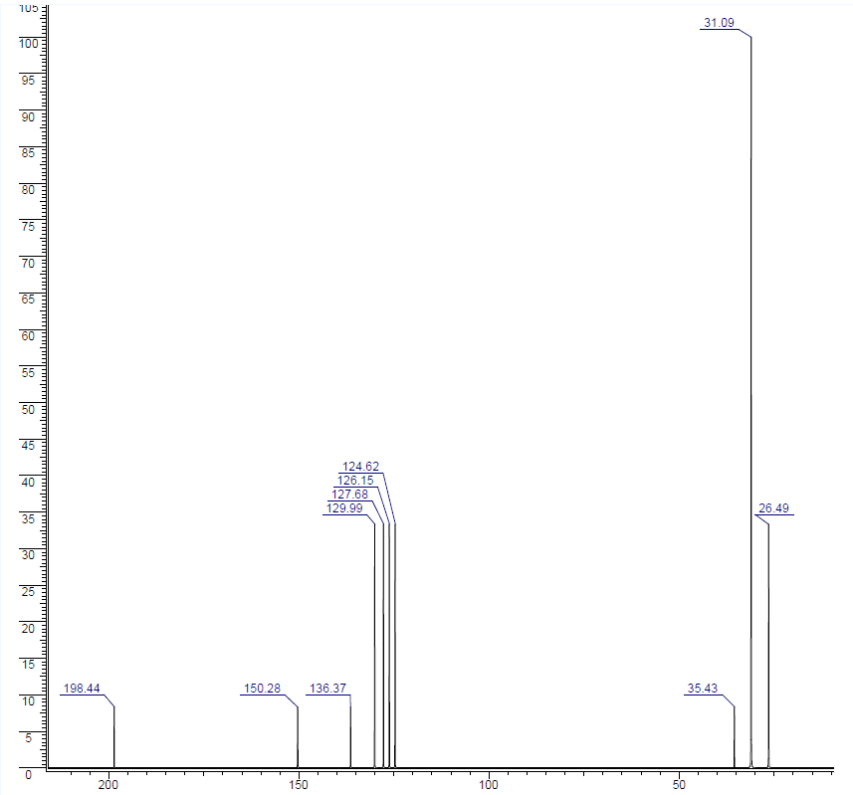
Exercise 8.5.1

Solve the structure using the following spectral data.

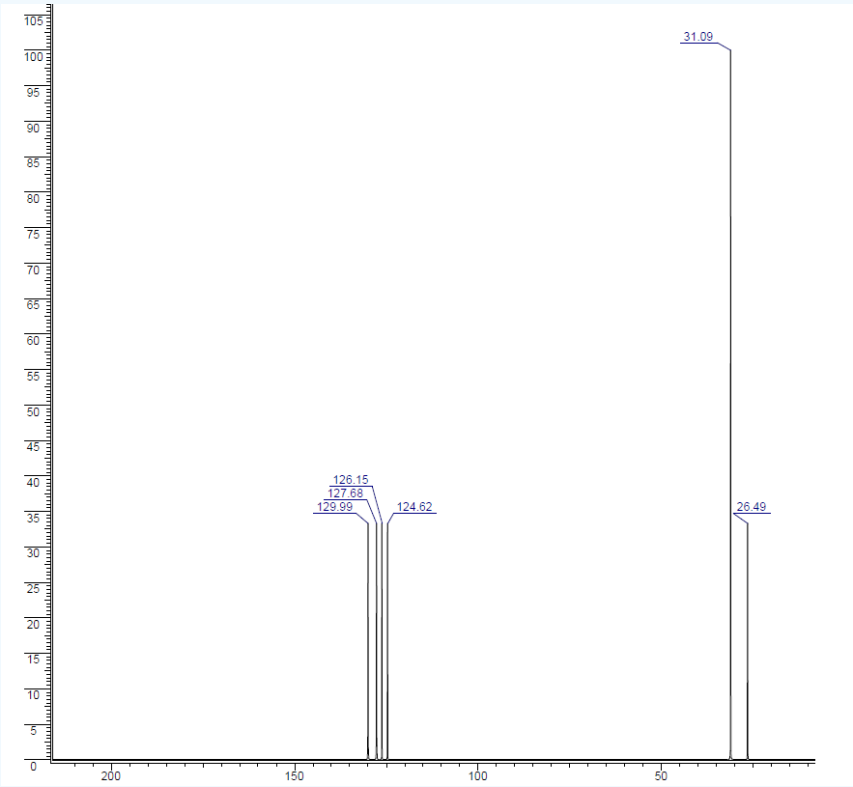
Mass Spectrum:



^{13}C Spectrum:

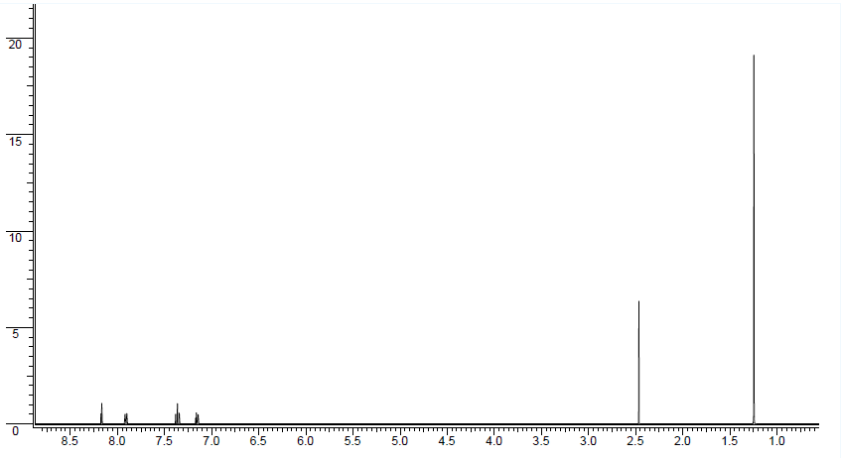


DEPT-135 Spectrum:

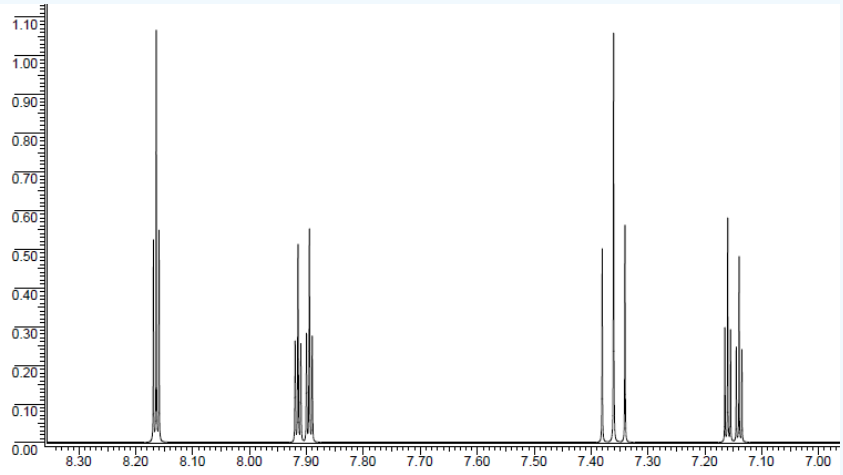


^{1}H NMR Spectrum:

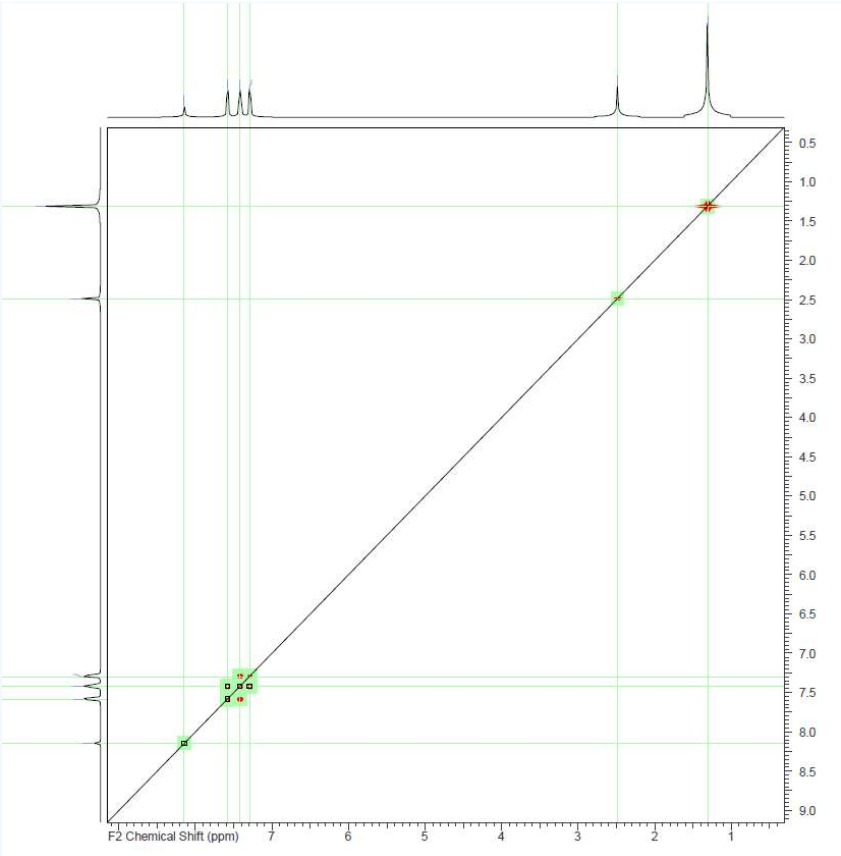
Integration: 1:1:1:1:3:9



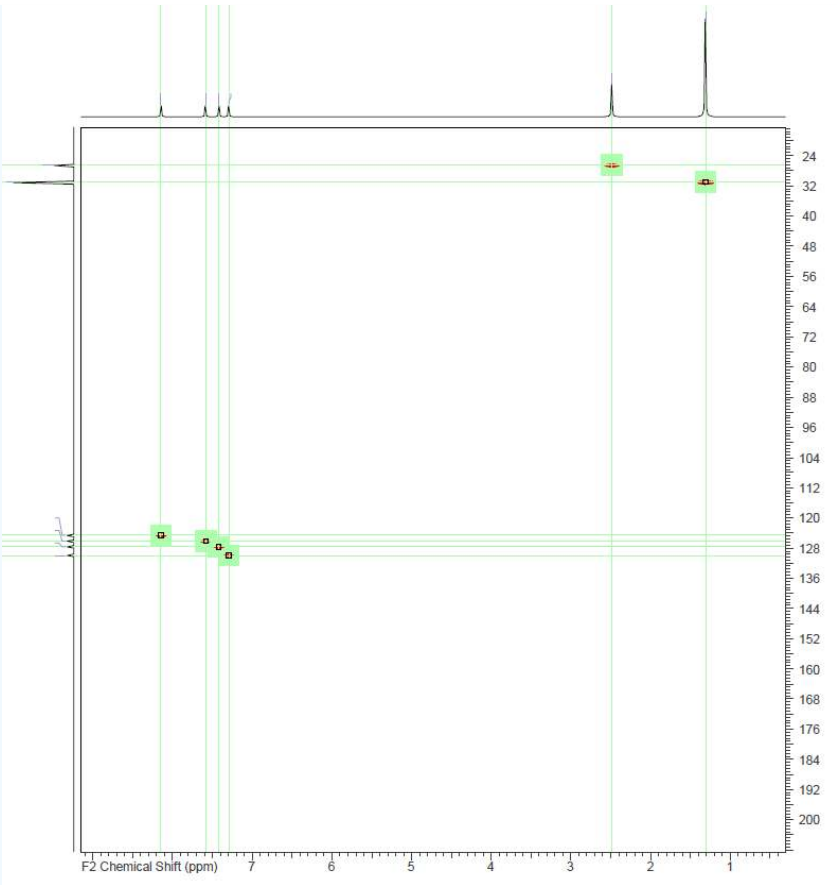
^{1}H NMR Spectrum Zoomed in from 7 ppm to 8.3 ppm:



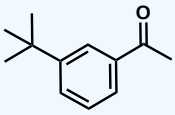
COSY:


F2 Chemical Shift (ppm)
7
6
5
4
3
2
1
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0

HSQC:



Answer



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8.6: 8.6 Problem 5

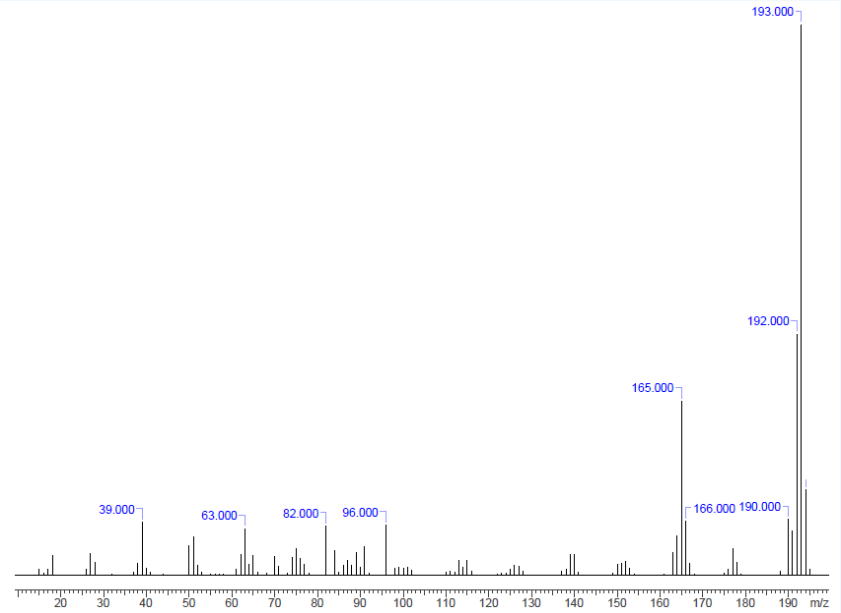
Learning Objectives

- Determine the structure for the following problem.

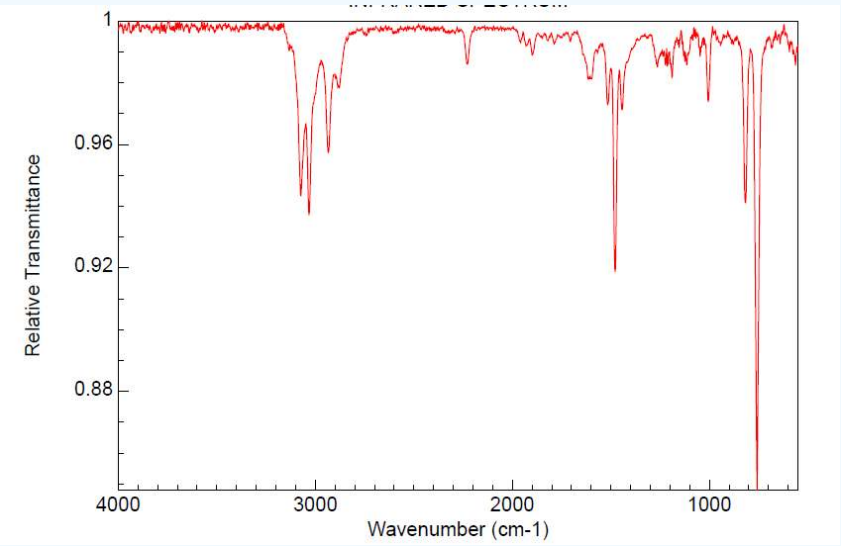
Exercise 8.6.1

Solve the structure using the following spectral data.

Mass Spectrum:

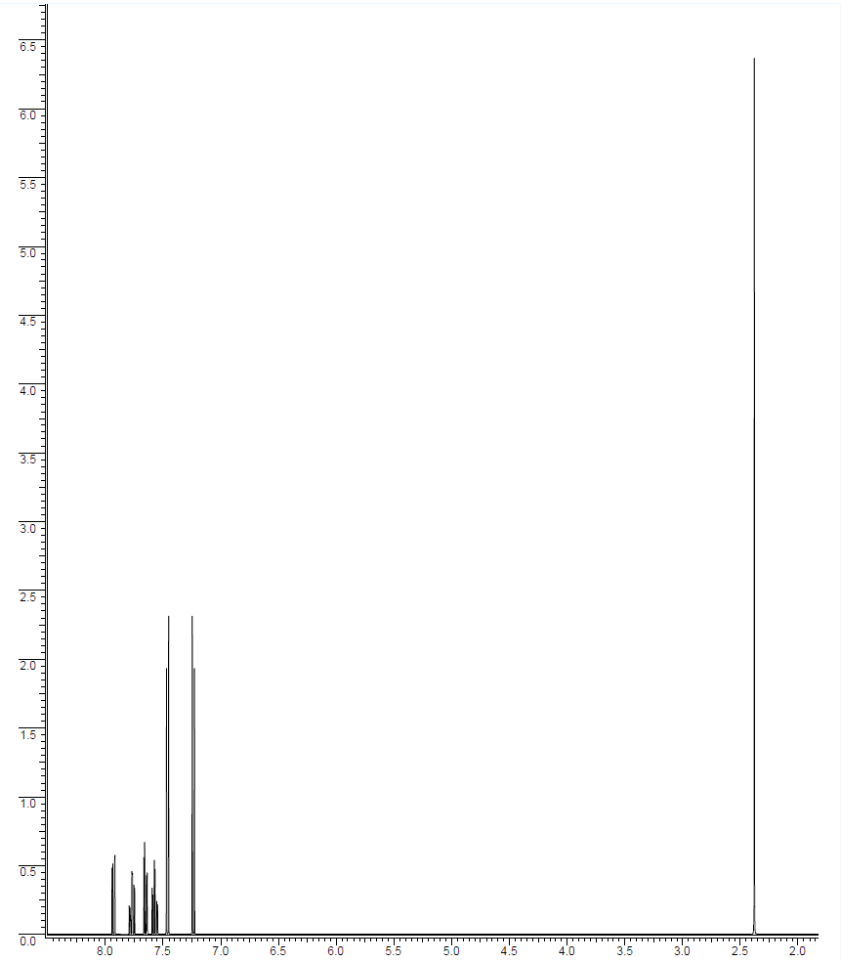


IR Spectrum:

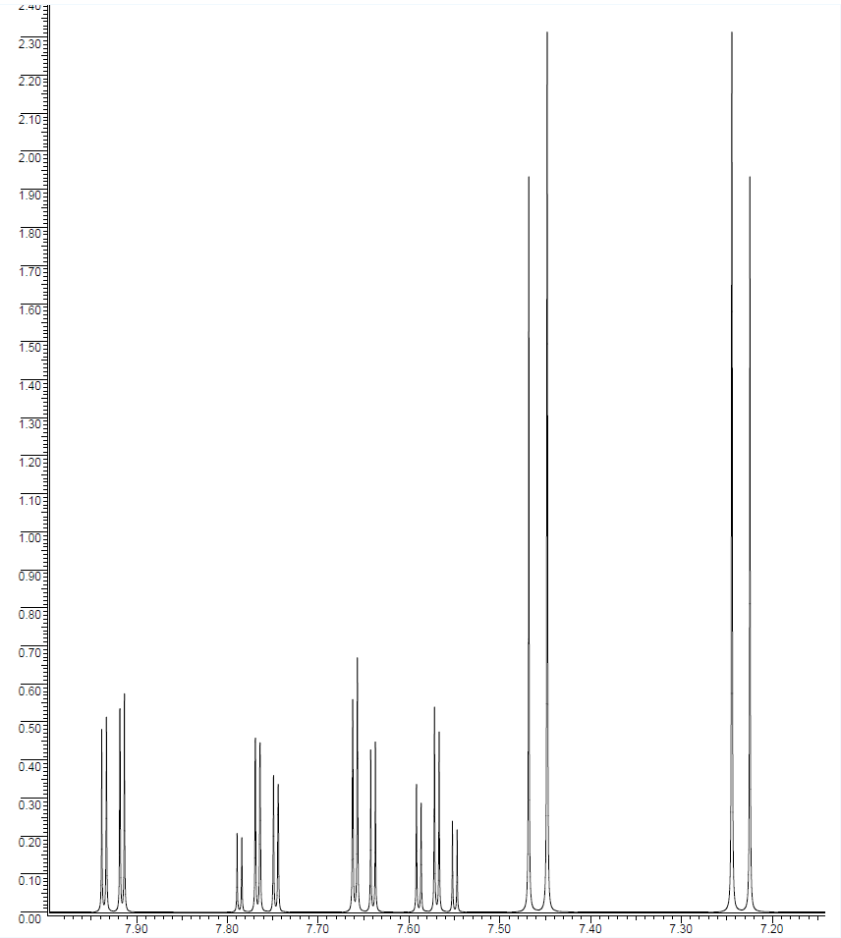


^{1}H NMR Spectrum:

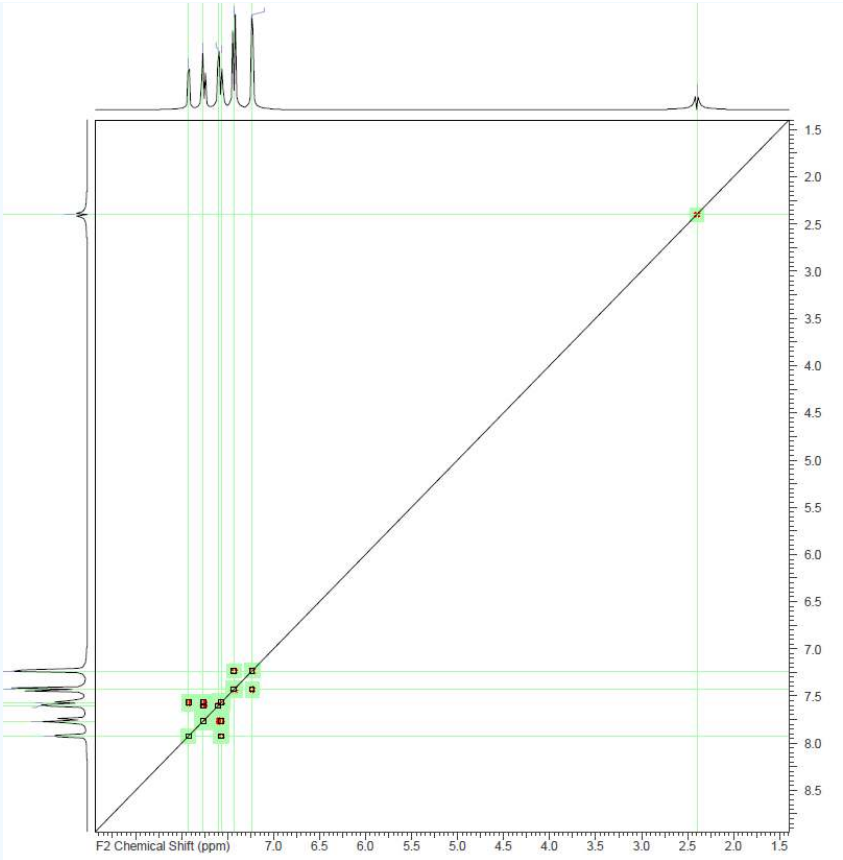
Integration: 1:1:1:1:2:2:3



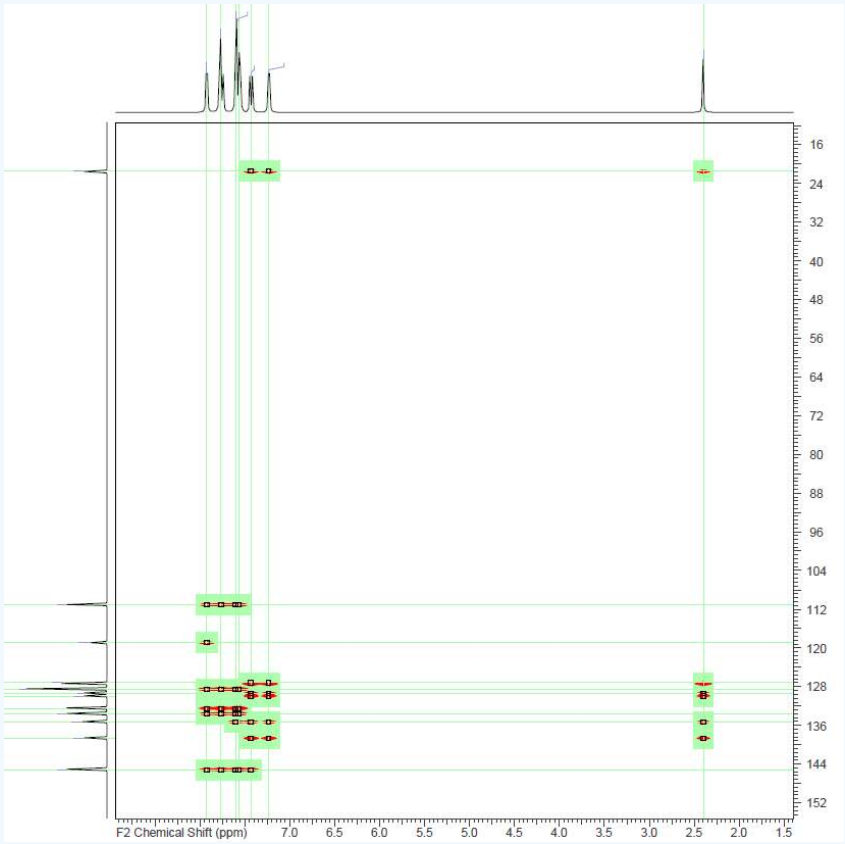
Zoomed in on Aromatic Region:


2.30
2.20
2.10
2.00
1.90
1.80
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
7.90
7.80
7.70
7.60
7.50
7.40
7.30
7.20

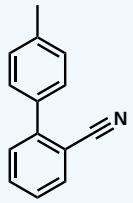
COSY:


F2 Chemical Shift (ppm)
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5

HMBC:


F2 Chemical Shift (ppm)
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
16 24 32 40 48 56 64 72 80 88 96 104 112 120 128 136 144 152

Answer



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clark

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