

Determination of Molecular Structure by MOLECULAR SPECTROSCOPY

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Much of what we know about molecular structure has been learned by observing and analyzing how electromagnetic radiation interacts with matter. Spectroscopy is the observation and analysis of this interaction. Electromagnetic radiation is energy, and when electromagnetic radiation is absorbed by molecules, the molecules gain energy. The amount of energy absorbed by a molecule gives information about the structure of the molecule.

The scientific instrument that measures how much radiation is absorbed at various energies is called a spectrometer. There are numerous kinds of spectrometers, using different ranges of radiation energy. Some spectrometers use visible radiation, others infrared radiation, and still others operate with microwave radiation.

When molecules absorb energy from electromagnetic radiation, they undergo changes. The changes depend on the amount of energy absorbed. When a molecule absorbs visible radiation, the energy causes an electron in the molecule to move from a lower-energy orbital to a higher-energy orbital. When infrared radiation is absorbed by a molecule, a bond or group of bonds in the molecule begins to vibrate more vigorously. The energy in microwave radiation can cause small molecules to rotate faster, which is what it does to water molecules in a microwave oven. Microwave radiation can also flip the direction of the magnetic fields of subatomic particles (electrons and nuclei). All of these changes give information about how electrons and atoms are arranged in molecules, and together can be used to determine the structure of molecules.

INFRARED SPECTROSCOPY

When a molecule absorbs infrared radiation, a bond or group of bonds begins to vibrate with greater energy. One type of vibration is the alternate stretching and contracting of a bond between two atoms. Another is the alternate widening and narrowing of a bond angle between three atoms, analogous to scissors opening and closing. The amount of energy involved in these changes is related to the masses of the atoms involved and to the strength of the bonds between them. Therefore, the infrared absorptions of a substance reveal a great deal about the bonding between the atoms in its molecules.

A vibrating bond between two atoms can be visualized as a regularly expanding and contracting spring. A stronger spring oscillates more rapidly than a weaker spring, and a spring loaded with a larger mass vibrates more slowly than one loaded with a lighter mass. Vibrating bonds behave the same way. Multiple bonds are like stronger springs, and they vibrate at higher frequencies. Bonds to lighter atoms, such as hydrogen, vibrate at higher frequencies than bonds to heavier atoms. Table 1 shows typical ranges of frequencies of vibrations of some common bonds.

For historical reasons, frequencies of infrared radiation are often expressed as the inverse of

Table 1. Infrared absorption frequencies.

Bond	Frequency range (cm ⁻¹)
C—C, C—N, C—O	800 – 1300
C=C, C=N, C=O	1500 – 1900
C≡C, C≡N	2000 – 2300
C—H, N—H, O—H	2850 – 3650

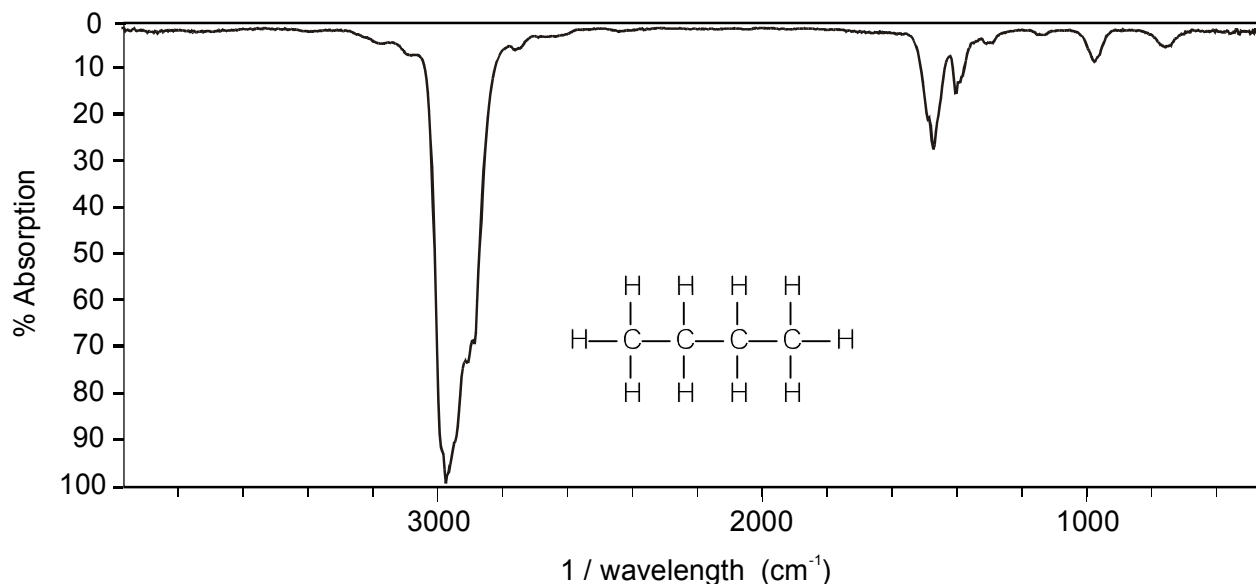


Figure 1. Infrared spectrum of butane.

wavelength, with units of inverse centimeters (cm^{-1}). For electromagnetic radiation, wavelength times frequency is equal to the speed of light, $\lambda \times \nu = c$. Therefore, frequency = speed of light / wavelength, $\nu = c / \lambda$. Because the speed of light is a constant, frequency is proportional to the inverse of the wavelength.

An infrared spectrum of a substance shows which frequencies of infrared radiation are absorbed by the substance. It is a plot of the percent of the radiation absorbed versus the frequency of the radiation. The frequencies of the absorbed radiation reveal which bonds the molecules contain. Figure 1 is an infrared spectrum of butane. The spectrum shows three larger absorptions, a very strong one at 3000 cm^{-1} , a second weaker one at 1460 cm^{-1} , and a third even weaker at 1370 cm^{-1} . These three absorptions are characteristic of a compound containing hydrogen atoms bonded to carbon atoms with sp^3 orbitals. The absorption at 3000 cm^{-1} results from stretching of C—H bonds. The other two absorptions result from bending of H—C—H bonds (the bond angle oscillates

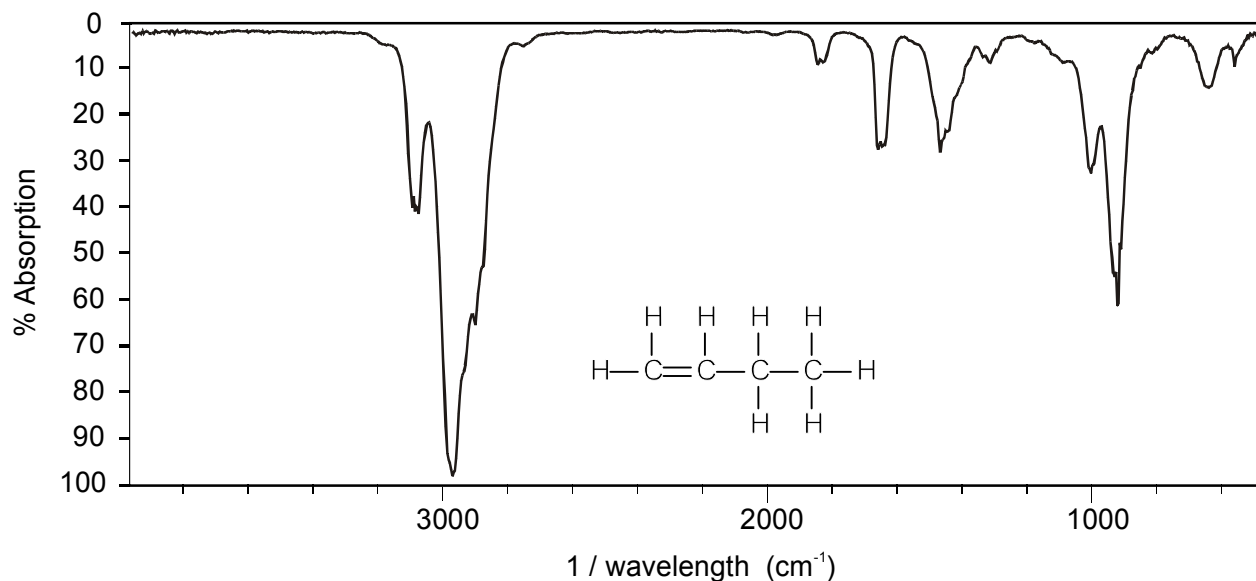


Figure 2. Infrared spectrum of 1-butene.

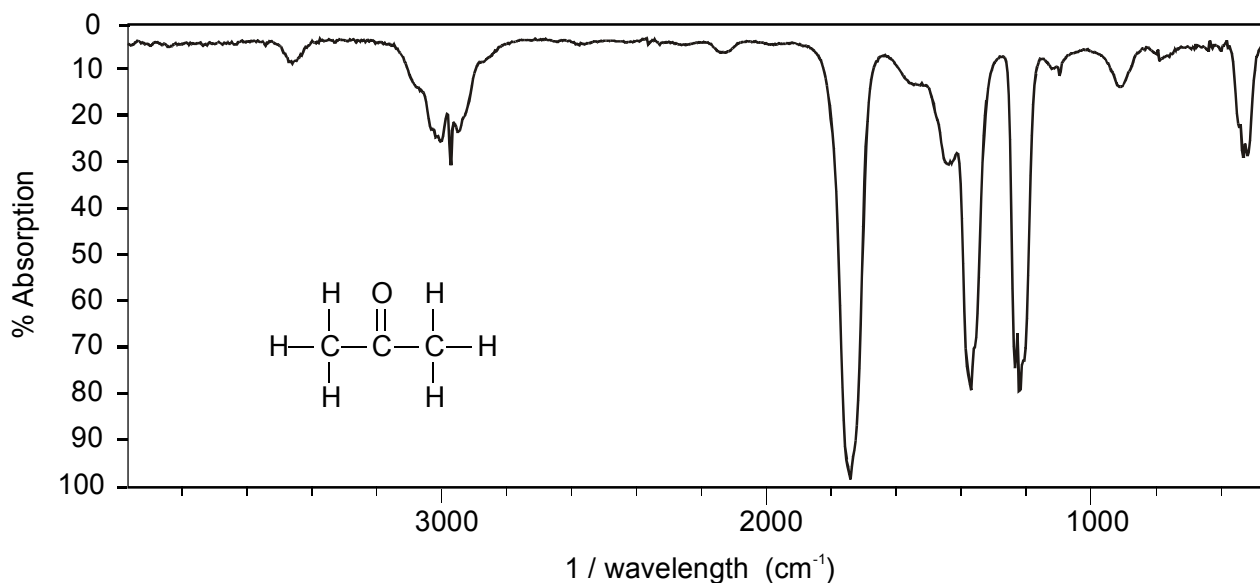
Table 2. Infrared Absorptions

Bond	Frequency (cm ⁻¹)	Bond	Frequency (cm ⁻¹)
(sp ³)C—H	2850 – 3000	C≡C	2100 – 2250
	1450 – 1470	C—O	1070 – 1150
	1370 – 1380	C=O	1700 – 1725
(sp ²)C—H	3080 – 3140	O—H	3400
(sp)C—H	3300	C—F	1000 – 1350
C=C	1640 – 1680	C—Cl	750 – 850

around the 109° tetrahedral angle).

Figure 2 shows the infrared spectrum of a close relative of butane, namely 1-butene. It has the same three absorptions as butane, plus several more. Prominent additions are at 1650 cm⁻¹, 990 cm⁻¹, and 910 cm⁻¹. There is also an additional absorption at high frequency, namely 3100 cm⁻¹. These new absorptions are all characteristic of hydrocarbons containing a double bond between carbon atoms. The absorption at 3100 cm⁻¹ corresponds to the stretching of the bond between hydrogen and sp² hybridized carbon atoms. The absorption at 1650 cm⁻¹ results from vibration of the C=C double bond. The absorptions at 990 and 910 cm⁻¹ result from bending of a C—H bond out of the plane defined by the C=CH₂ atoms.

The infrared frequencies of many different types of bonds have been identified and are tabulated in numerous reference books such as the *CRC Handbook of Chemistry and Physics*. Table 2 contains a small excerpt from this large collection of information. This table can be used to identify some of the absorptions found in the infrared spectrum of acetone, which is shown in Figure 3. In the infrared spectrum, the absorption at 3000 cm⁻¹ results from the —CH₃ groups. The strong absorption at 1720 cm⁻¹ is produced by the C=O group in the center of the molecule. The 30%

**Figure 3.** Infrared spectrum of acetone.

absorption at 1410 cm^{-1} and the 80% absorption at 1370 cm^{-1} are from the $-\text{CH}_3$ groups. The absorption at 1200 cm^{-1} is not listed in Table 2, but from information from Table 1, we can interpret it as a result of stretching of the C—C bonds.

Infrared spectroscopy can provide information about the nature of the bonds in a substance. It can reveal the presence (or absence) of certain types of bonds. However, it can seldom reveal by itself the location of the bonds within the molecule.

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance spectroscopy is extremely useful in determining the arrangement of atoms in a molecule. As its name implies, this form of spectroscopy relies on properties of the nuclei in a molecule. The particles that compose the nucleus, protons and neutrons, have spin, as do electrons. The total spin of the nucleus is determined by the spin of its component particles. Some nuclei have a range of spin states; some, notably those with even numbers of protons and neutrons (e.g., ^{12}C and ^{16}O), have zero spin. Like electrons, several nuclei of some common elements have two spin states, $+\frac{1}{2}$ and $-\frac{1}{2}$. These include ^1H , ^{13}C , ^{19}F , and ^{31}P .

Under usual conditions, ^{13}C nuclei are randomly distributed between the two spin states, because both states have the same energy. As with electron spin, nuclear spin is associated with magnetic effects. Therefore, when a substance containing carbon atoms is placed in a strong external magnetic field, the ^{13}C spin that lines up with the external magnetic field is lower in energy than the spin in the opposite orientation. Therefore, the tiny magnets of the nuclei line up with the external field. It takes a small amount of energy to flip the aligned nuclear magnets to the opposite orientation. This amount of energy occurs in the microwave region of the electromagnetic spectrum. A carbon-containing sample placed in a magnetic field will absorb microwave radiation of an energy equal to the difference between the two spin states. The energy required depends on the strength of the magnetic field – the stronger the field, the more energy it takes to flip the nuclear spin to its opposite state.

What makes this nuclear magnetic absorption so revealing about molecular structure involves the electrons in a molecule. The electrons produce their own small magnetic field. This magnetic field shields the nuclei somewhat from the external magnetic field. The greater the concentration of electrons around a nucleus, the more the nucleus is shielded from the external magnetic field. Thus, a nucleus with a low concentration of electrons around it is more exposed to the external field, and so requires more energy to flip its nuclear spins. Conversely, a nucleus surrounded by a high concentration of electrons will absorb at lower energy. Therefore, the electrons affect to a small

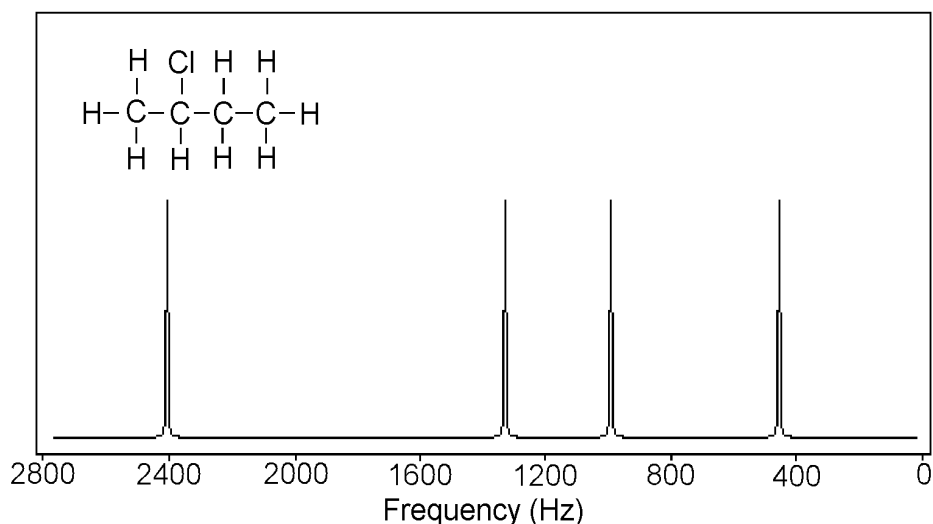


Figure 4. ^{13}C -NMR spectrum of 2-chlorobutane (decoupled).

degree the energy required to change the nuclear spins from one state to another, and the different carbon nuclei in a molecule absorb microwave radiation of slightly different energies.

Figure 4 shows a ^{13}C nuclear magnetic resonance spectrum (^{13}C -NMR) for 2-chlorobutane. The horizontal axis displays the frequency of the microwave energy absorbed and the vertical axis is proportional to the amount of radiation absorbed. The scale on the horizontal axis shows the difference between the frequency of the radiation absorbed by 2-chlorobutane and a base frequency. The reason for doing this is to make the axis easier to read. For this spectrum, the base frequency is 40 MHz ($40,000,000\text{ s}^{-1}$). The frequency of the absorption on the right is 40,000,440 Hz. The absorption on the left occurs at 40,002,400 Hz. If the axis were labeled with the complete frequency, the numbers would be difficult to read.

The four absorptions in Figure 4 show that there are four different carbon atoms in the molecule. These four carbon atoms do not absorb the same energy; the absorption on the left, the high-energy absorption, corresponds to the carbon atom with the lowest concentration of electrons. This would be the carbon atom bonded to chlorine, because chlorine is a very electronegative element, and draws electrons away from the carbon atom to which it is bonded. The absorption on the right occurs at lowest energy, so it corresponds to the carbon atom with the highest concentration of electrons. This would be the one furthest from the chlorine atom. It is harder to determine which of the two central absorptions corresponds to which of the other two carbon atoms in the molecule.

There is an experimental technique that allows the other two absorptions to be assigned. This technique relies on the fact that the nuclei of the hydrogen atoms in the molecule have spins of $+\frac{1}{2}$ and $-\frac{1}{2}$, and so generate tiny magnetic fields of their own. Consider the carbon atom bonded to the chlorine in 2-chlorobutane. It is also bonded to one hydrogen atom. The ^1H nucleus of this hydrogen atom can have a spin of $+\frac{1}{2}$ or $-\frac{1}{2}$. Its spin is either aligned with or opposed to the external field. Therefore, some of the 2-chlorobutane molecules will have a carbon atom bonded to a hydrogen with its spin aligned with the external field, and some will have a carbon atom bonded to a hydrogen with its spin opposed. In these two different cases, the carbon nuclei will be exposed to two slightly different magnetic fields, and they will absorb at two slightly different energies. This generates an effect called coupling; the carbon nuclei are coupled to the hydrogen nuclei.

The spectrum shown in Figure 4 was measured in such a way that coupling was suppressed. This kind of spectrum is called a decoupled spectrum. Figure 5 shows the ^{13}C -NMR spectrum of 2-chlorobutane in which coupling is allowed. Each of the four absorptions observed in Figure 4 is

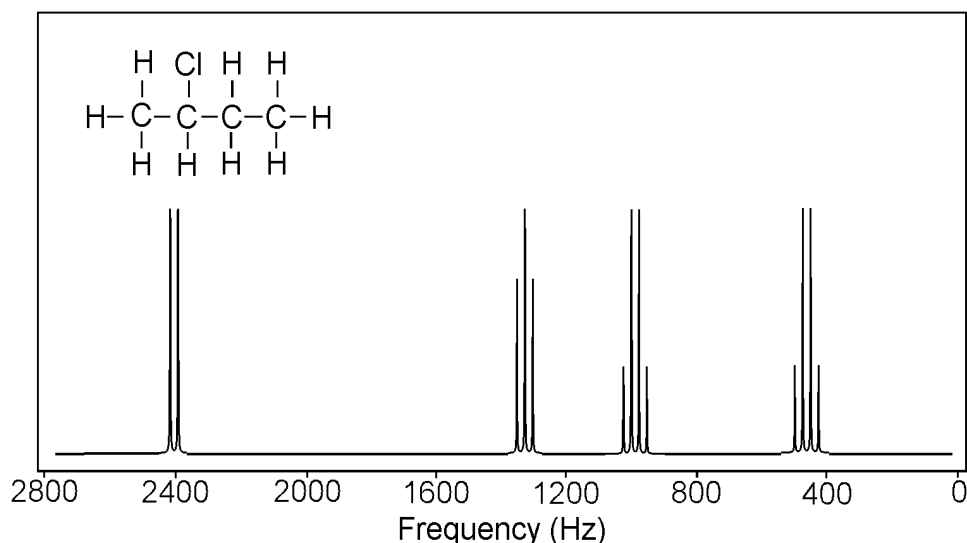


Figure 5. ^1H -coupled ^{13}C -NMR spectrum of 2-chlorobutane.

Table 3. Splitting caused by ^1H coupling.

Number of H bonded to C	^1H spin values			Number of ^{13}C absorptions	
0	0			1	
1	$+\frac{1}{2}$	$-\frac{1}{2}$		2	
2	$(+\frac{1}{2} +\frac{1}{2})$ 1	$(+\frac{1}{2} -\frac{1}{2})$ 0	$(-\frac{1}{2} -\frac{1}{2})$ -1	3	
3	$(+\frac{1}{2} +\frac{1}{2} +\frac{1}{2})$ $+1\frac{1}{2}$	$(+\frac{1}{2} +\frac{1}{2} -\frac{1}{2})$ $+\frac{1}{2}$	$(+\frac{1}{2} -\frac{1}{2} -\frac{1}{2})$ $-\frac{1}{2}$	$(-\frac{1}{2} -\frac{1}{2} -\frac{1}{2})$ $-1\frac{1}{2}$	4

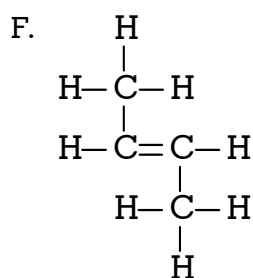
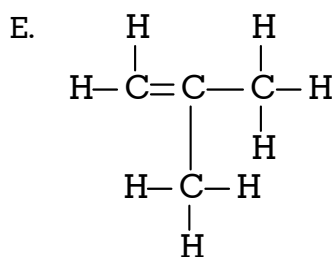
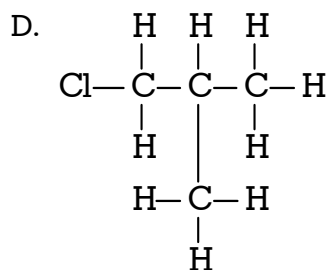
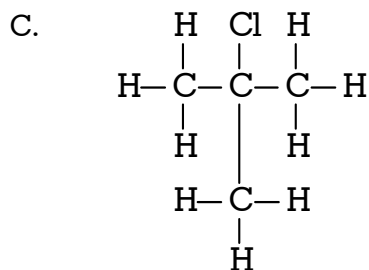
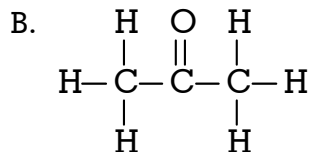
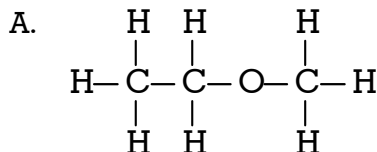
split into two or more absorptions. This splitting is caused by the hydrogen atoms to which the carbon atoms are bonded. When a carbon atom is bonded to one hydrogen, its adsorption is split into two corresponding to the $+\frac{1}{2}$ and $-\frac{1}{2}$ spins of the hydrogen atoms. When a carbon atom is bonded to two hydrogen atoms, the spins of the two hydrogen atoms add together to give three values: $+1$, 0 , and -1 . When a carbon atom is bonded to three hydrogen atoms, the spins of the ^1H nuclei add to four different values: $+1\frac{1}{2}$, $+\frac{1}{2}$, $-\frac{1}{2}$, $-1\frac{1}{2}$. The four cases are summarized in Table 3. As a general rule, the NMR absorption for a ^{13}C nucleus is split into a pattern with one more peak than the total number of hydrogen atoms bonded to it.

In the ^1H -coupled spectrum in Figure 5, the absorption at 2400 Hz is split into two. This means that the corresponding carbon is bonded to one hydrogen atom. This agrees with the assignment of this absorption to the carbon bonded to chlorine. That carbon is bonded to one hydrogen atom. The absorption at 440 Hz is split into four. This indicates that the corresponding carbon is bonded to three hydrogen atoms. This confirms the earlier assignment of this absorption to the carbon furthest from the chlorine atom, because that carbon atom is bonded to three hydrogen atoms. The remaining two absorptions can now be easily assigned, as well. The absorption at 1350 Hz is split into three, which means the corresponding carbon is bonded to two hydrogen atoms. This is the carbon in the middle of the molecule, adjacent to the one bonded to chlorine. The absorption at 1000 Hz is split into four, so its corresponding carbon atom is bonded to three hydrogen atoms. This is the carbon atom at the end of the molecule and adjacent to the one bonded to chlorine.

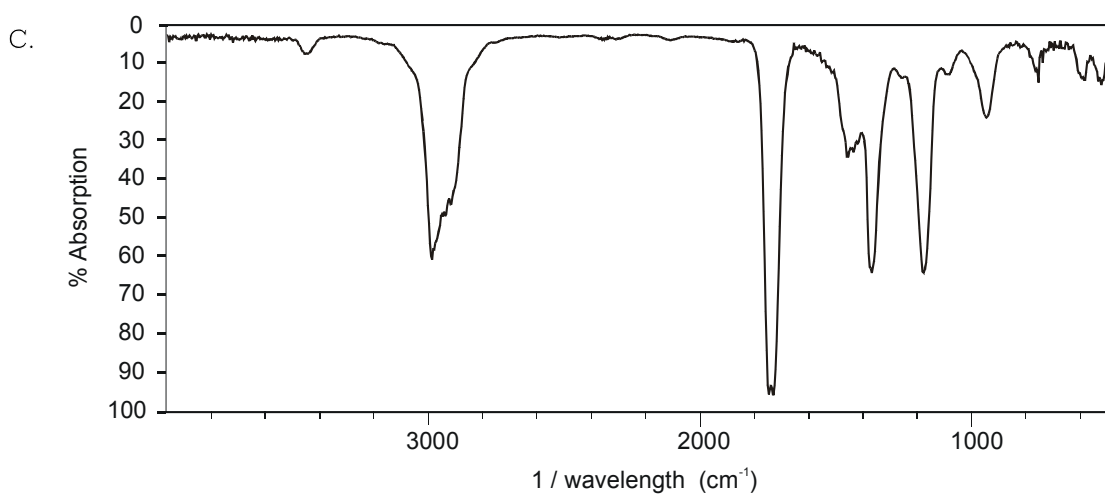
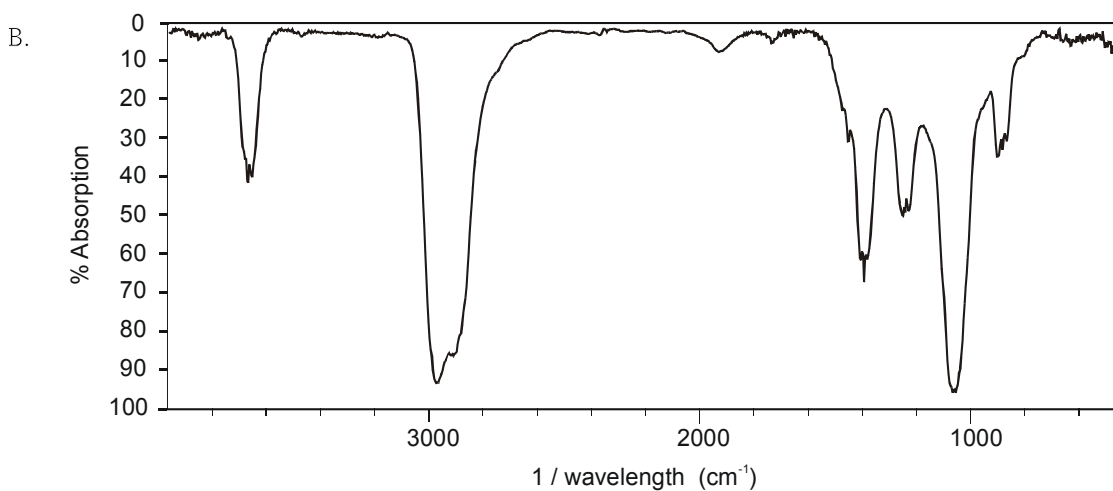
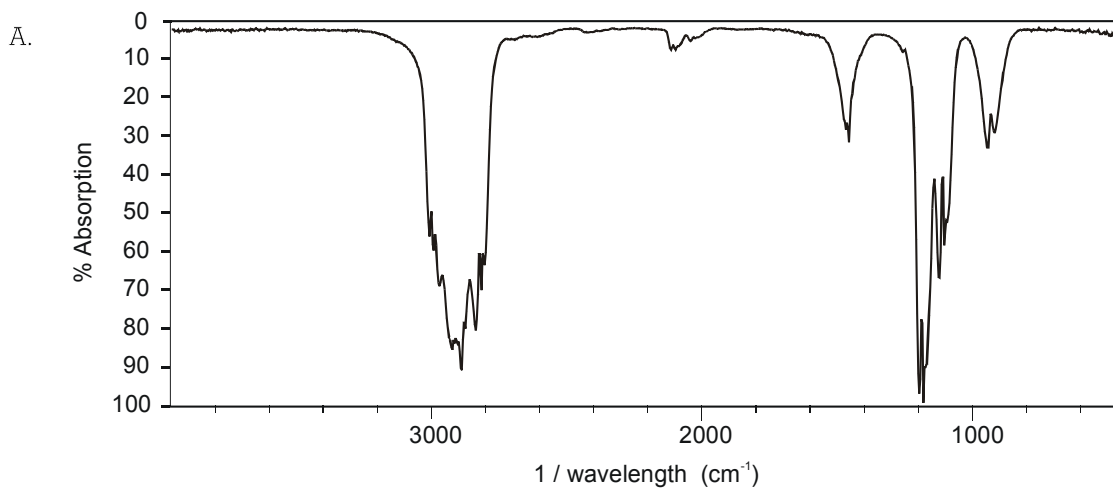
NMR spectroscopy is a very powerful tool for determining the structure of molecules. Because many nuclei have spin, the arrangements of these nuclei in molecules can be investigated by NMR spectroscopy. Combined with infrared spectroscopy, NMR spectroscopy can reveal both the arrangements atoms in molecules and how they are bonded together.

STUDY QUESTIONS

- What is the frequency of vibration in Hz (sec^{-1}) of the O—H bond? (See Table 2.)
What is the wavelength of the light in nm that is absorbed by this bond? What is the energy, in Joules, of one photon of this light?
- In each of the following pairs of bonds, select the one that stretches at the highest frequency.
 - C—O or C=O
 - C—O or C—Cl
 - C=C or C≡C
 - C—C or C—O
 - C—H or O—H
- For each of the following compounds, indicate how many absorptions will occur in the decoupled ^{13}C -NMR spectrum, and indicate into how these will split in the coupled NMR spectrum.



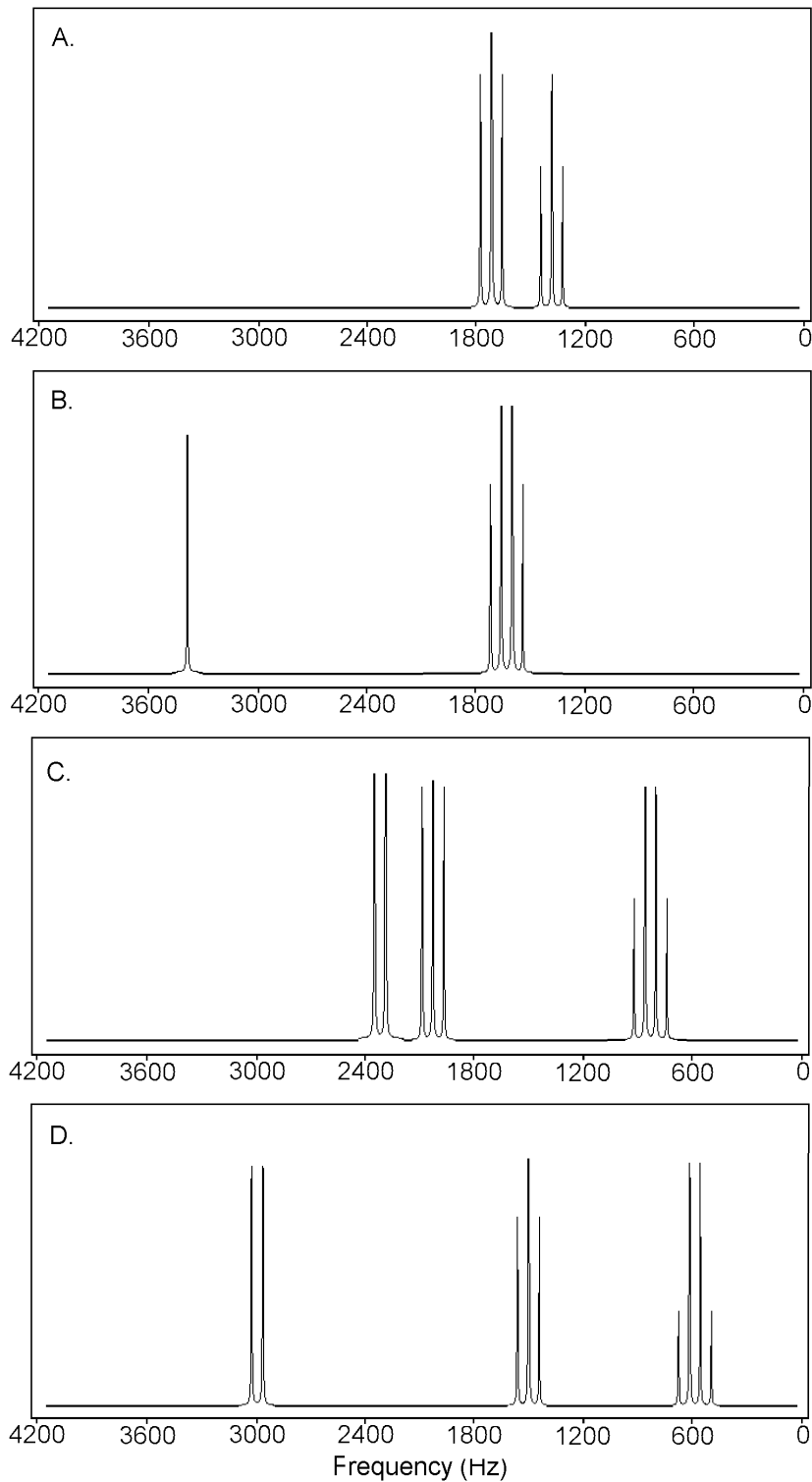
4. Below are the infrared spectra for three compounds, ethanol, dimethyl ether, and butanone. Identify which spectrum is which. The structures of the molecules can be found in the *Chemistry & Chemical Reactivity* textbook, on pages 423 and 447.



5. There are four different molecules (isomers) with molecular formula $C_3H_6Cl_2$.

A. Draw Lewis structures for all four isomers.

B. Below are the ^{13}C NMR spectra for the four isomers. Identify each spectrum with its structural isomer.



6. To identify a certain compound, several tests were performed with it. An elemental analysis revealed its empirical formula to be $C_5H_{10}O$. Its molar mass was determined to be 86 grams per mole. Below are its infrared spectrum and its 1H -coupled ^{13}C -nmr spectrum. Draw a structural formula for the compound.

