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Infrared Spectroscopy: A Key to Organic Structure

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Introduction

Molecular structure is a major theme in chemistry, and is especially important in organic chemistry. Have you ever wondered how chemists determine the molecular structures of new reaction products or new materials isolated from natural sources? The instruments most directly concerned with molecular structure are the spectrometers. We are familiar with various kinds of electromagnetic radiation: light (visible, ultraviolet, infrared), microwaves, x-rays, radio and radar waves. When a beam of electromagnetic radiation is passed through a substance, the radiation can be either absorbed or transmitted, depending on its frequency and the structure of the molecules it encounters. The energy gained by a molecule in this way may bring about increased vibration or rotation of the atoms, or may raise electrons to higher energy levels. The particular frequency of radiation that a given molecule can absorb depends upon the changes in vibrations or rotations or electronic states that are permitted to a molecule of that structure. This curriculum unit will focus on infrared spectroscopy as one way of knowing or determining the structure of organic compounds. The unit is designed to be used in a second year high school chemistry class during the study of organic chemistry. The students would have previously studied atomic structure and bonding.

Molecules are made of atoms joined by chemical bonds. The movement of the atoms and bonds can be modeled using balls connected by springs. The movements can be divided into bending and stretching of bonds. The frequency of vibration involved depends on the masses of atoms involved, the nature of the bonds and the geometry of the molecule. Each organic molecule, with the exception of enantiomers, has a unique infrared spectrum. Like fingerprints, IR spectra can be compared with the spectra of known molecules and be used for identification purposes.

Of more importance to the organic chemist is the fact that certain atomic vibrations give rise to absorptions or bands which appear at approximately the same frequency in a large variety of molecules. These bands are characteristic of the presence of certain functional groups. By examining these key regions the chemist can determine which functional groups are present or absent.

The infrared region of the electromagnetic spectrum falls between the visible and microwave portions and corresponds to wavelengths between 0.7 (m and 100 (m (1014 –1012 Hz or14,000-100 cm-1). Infrared radiation in this range is absorbed and converted by an organic molecule into energy of molecular vibration. The frequency of absorption depends on the relative masses of the atoms, the force constants of the bonds, and the geometry of the atoms.

Upon completing this unit the student will be able to:

- Describe the factors affecting the frequency of vibration.
- Understand terms used in infrared (IR) spectroscopy.
- Understand the reasons for compounds exhibiting infrared activity and how light can interact with matter.
- Use a correlation table to determine the presence or absence of functional groups.
- Determine if a given IR spectrum is consistent with a structural formula.
- Determine the identity of certain unknown organic compounds given their IR spectra, molecular mass, and other physical and/or chemical properties.

Vibrations and Waves

Molecular spectroscopy involves the interaction of electromagnetic radiation with the molecules of the material in question. Before considering the spectroscopy itself, we will look at the electromagnetic spectrum and briefly explain the nature of light.

Many things in nature wiggle back and forth. We call a wiggle in time a vibration. We call a wiggle in time and space a wave. Some examples are the vibrations of a guitar string, a mass attached to a spring, the swinging of a pendulum, and atoms in molecules.

The to-and-fro motion of a pendulum bob along a single plane in a small arc is called simple harmonic motion. If a pendulum bob leaks sand while undergoing simple harmonic motion, it will trace and retrace a short straight line. If we were to swing a pendulum above a conveyor belt that moves in a perpendicular direction to the plane of the swinging pendulum, the trace it now makes is called a sine curve. This curve is a pictorial representation of a wave.

The points of maximum displacement above the equilibrium position are called crests and the points of maximum displacement below the equilibrium position are called troughs. The amplitude is equal to the maximum displacement of the pendulum from its position of rest. The distance from the top of one crest to the top of the next one is equal to the wavelength. How often a vibration occurs is described by its frequency. The frequency of a vibrating object specifies the number of to-and-fro vibrations it makes in a given time (usually seconds). The source of all periodic waves is something that vibrates. The frequency of the vibrating source and the frequency of the wave it produces are the same.

If the end of a stick is moved back and forth in still water waves are produced on the water surface. Similarly if an electrically charged rod is shaken to and fro in empty space electromagnetic waves are produced. This is because the moving charge is actually an electric current, and a magnetic field surrounds an electric current. In accordance with Faraday’s law a changing magnetic field induces a changing electric field. The changing electric field, in accordance with Maxwell’s counterpart to Faraday’s law, will induce a changing magnetic field. The vibrating electric and magnetic fields regenerate each other to make up the electromagnetic wave which moves outward from the vibrating charge. For most purposes, light can be thought of as a traveling electrical field alternating from positive to negative values. An electric field is measured by the force it exerts on a charge.

In a vacuum, all electromagnetic waves move at the same speed and differ from one another in their frequency (() and wavelength ((). The frequency of the electromagnetic wave as it vibrates through space is identical to the frequency of the oscillating electric charge generating it. The classification of electromagnetic waves according to frequency is the electromagnetic spectrum. The spectrum is broken into arbitrary regions for classification. Visible light makes up a very small portion of electromagnetic spectrum. The highest frequency visible light appears violet. Higher frequencies cannot be detected by the human eyes and are referred to as the ultraviolet. Frequencies higher than the ultraviolet extend into the x-ray and gamma ray region. Below the lowest frequency of visible light is the infrared radiation, often called heat waves. Still lower are microwaves and radiowaves.

Some useful relationships between the speed of electromagnetic radiation (c), wavelength ((), frequency ((), and the energy per photon (E) are given below. Planck’s constant (h= 6.63 x 10 -34 joule·seconds) allows us to calculate the energy if the frequency or wavelength is known. Notice that energy is directly proportional to frequency and inversely proportional to wavelength.

E=h(E=hc/(c=((

Molecular spectroscopy involves the absorption of electromagnetic radiation by the material whose molecular structure we are attempting to determine. The relationship that describes the amount of radiation absorbed is Beer’s law. The absorption (A) is proportional to the inherent absorbing ability of the substance ((; molar absorptivity or extinction coefficient), the concentration of the absorbing compound (c) and the distance the radiation is traveling through the sample (l).

A=((c)l

Molecular Vibrations

One of the oldest forms of spectroscopy uses the infrared region of the electromagnetic spectrum. In order to understand IR spectroscopy, we must first consider the motion of atoms in molecules.

Atoms in a molecule do not maintain fixed positions with respect to each other, but actually vibrate back and forth about an average value of interatomic distance with a certain frequency. Think of a child on a swing. The frequency of the back and forth motion can be found by counting the number of swings in a minute. If the child is pushed on the swing when the frequency of pushing matches the frequency of the swinging the child swings higher (greater amplitude) but the frequency remains the same. Organic molecules absorb infrared radiation when the frequency of IR radiation is synchronized with a natural vibration frequency of the molecule. When IR radiation is absorbed, the molecule begins to vibrate with a greater amplitude (but with the same frequency), and thus the molecule has gained energy.

Activity One

Students will investigate the factors affecting the frequency of oscillation of a swing. (See Investigation 1) Teachers should note that the only factor that should affect the frequency of the swing is the length of the swing, therefore, swings of different lengths should be made available. If swings of different lengths are not available the activity can be modified to use pendulums constructed with strings of different lengths.

A molecule can have the following types of motions: (1) translation of the entire molecule, which can be regarded as translation of the center of mass, (2) rotation of the molecule as a framework around its center of mass, (3) vibrations of the individual atoms within the framework, which occur in such a way that the center of mass does not change position and the framework does not rotate. The number of degrees of freedom of a particle equals the number of coordinates required to specify its position in space. A molecule has as many degrees of freedom as the total degrees of freedom of its individual atoms. Each atom has three degrees of freedom corresponding to the Cartesian coordinates (x,y,z) necessary to describe its position relative to other atoms in the molecule. For a molecule composed of n atoms there are 3n degrees of freedom associated with the momentum coordinates. For nonlinear molecules, three degrees of freedom describe rotation and three describe translation; the remaining 3n-6 degrees of freedom are vibrational degrees of freedom or fundamental vibrations. Linear molecules have 3n-5 vibrational degrees of freedom, for only two degrees of freedom are required to describe rotation. Fundamental vibrations involve no change in the center of mass of the molecule.

The ability of a compound to absorb IR energy depends on a net change in the dipole moment occurring when the molecule vibrates. Whether or not such a change occurs depends on the distribution of electrical charges in the molecule. The carbon monoxide molecule can be thought of as a carbon atom joined to an oxygen atom by means of a compressible bond. The carbon has six electrons surrounding its nucleus and oxygen has eight. During a vibration a change in the charge distribution occurs, this appears to the incident IR radiation as an oscillating charge. It is this oscillating charge that the light interacts with. When the frequency of the radiation matches the frequency of the oscillating charge the IR radiation is absorbed. Consequently, carbon monoxide shows an absorption band in the IR region at the frequency corresponding to the vibrational frequency of the nuclei. There is no net change in the dipole moment during the vibration of homonuclear molecules such as O2, N2, and H2, and these molecules do not absorb IR radiation. The ability of a molecule to absorb radiation during a particular vibration depends on its electrical geometry.

The water molecule consists of three atoms and is nonlinear; therefore, it should produce three fundamental vibrations. The three fundamental vibrations of the water molecule can be depicted as symmetrical stretching, asymmetrical stretching, and scissoring. (See Figure 1) The carbon dioxide molecule also consists of three atoms but is linear, therefore, it has four fundamental vibrations: symmetrical stretching, asymmetrical stretching, scissoring in the x-y plane, and scissoring perpendicular to the x-y plane. (See Figure 2) The symmetrical stretching vibration in carbon dioxide is inactive in the infrared since it produces no change in the dipole moment of the molecule. The bending vibrations are equivalent, and are the resolved components of bending motion oriented at any angle to the internuclear axis; they have the same frequency and are said to be doubly degenerate. Some sets of vibrations are degenerate, they are identical in frequency but in perpendicular directions and these multiple vibrations only result in one infrared absorption band being seen in the spectrum. In addition, bands of low intensity may occur as overtones. As a result, the infrared spectrum of an organic compound is usually rather complex. Computer software like MacSpartan or PC Spartan can be used to show the students a model of the vibrations possible for a number of molecules.

The vibrational motion is quantized. At room temperature most of the molecules in a given sample will be in the lowest vibrational state. Absorption of light of the appropriate energy allows the molecule to become excited to a higher vibrational level. In general, such absorption of an infrared light quantum can occur only if the dipole moment of the molecule is different in the two vibrational levels. The variation of the dipole moment with the change in interatomic distance during the vibration corresponds to an oscillating electric field that can interact with the oscillating electric field associated with electromagnetic radiation. The requirement that absorption of a vibrational quantum be accompanied by a change in dipole moment is known as a selection rule. Such a vibrational transition is said to be infrared-active. Vibrational transitions that do not result in a change of dipole moment of the molecule during vibration are not observed directly and are referred to as infrared-inactive transitions. The greater the change in dipole moment the stronger the infrared absorption. This explains why the groups whose components differ considerably in electronegativity show stronger absorption bands.

There are two types of molecular vibrations: stretching and deformations. A stretching vibration is a rhythmical movement along the bond axis such that the interatomic distance is increasing or decreasing. A deformation may consist of a change in bond angle between bonds with a common atom (much like a pair of scissors opening and closing) or the movement of a group of atoms with respect to the remainder of the molecule without movement of the atoms in the group with respect to one another. For example, twisting, rocking, and torsional vibrations involve a change in bond angles with reference to a set of coordinates arbitrarily set up within the molecule.

Each of these vibrational modes has a natural frequency of motion. This natural frequency is determined by the mass of the atoms bonded and for stretching of a single bond the strength of the bond. The larger masses have a lower frequency and the stronger bonds have a higher frequency. If we attach a small mass to a large, loose spring it would bounce with a certain frequency, let’s arbitrarily say 50 per minute. If we put a larger mass on the same spring the natural rate of motion would be less, maybe 30 per minute. If we keep that same large mass but replace the spring with a tighter one the mass will bounce with a higher frequency, maybe 40 per minute.

Activity Two

Students will explore the effects of mass and bond nature on vibration frequency using a mass on a spring as a model. (See Investigation 2)

The frequency of vibration of various masses on the same spring will be measured by displacing the mass from its equilibrium position and counting the number of oscillations in 30 seconds. The number of oscillations multiplied by two will give the number of vibrations per minute or the frequency. Students should conclude that the frequency of vibration is inversely related to the mass of the object. The greater the mass the lower the frequency. The effect of bond nature on vibration frequency will be tested by keeping the mass constant and varying the number of springs or the spring strength and measuring the frequency of vibration in the same way as before. Teachers should note that the frequency is proportional to the square root of the spring constant (k) divided by the mass (m).

Activity Three

For real molecules, or covalent bonds within larger molecules, the natural frequency follows the same trends. The O-H bond has a higher frequency of vibration than the O-C bond has since the average mass, calculated as (m1m2)/(m1+m2), of the atoms is less for OH. The O=C bond has a higher frequency than the O-C bond has since the double bond is stronger than a single bond.

Students will be asked to predict the relative frequencies of vibration for isolated bonds by applying the relationships between mass and frequency and spring strength and frequency that they determined in activity one to organic molecules. (See Worksheet 1 and Worksheet 2)

Infrared Spectroscopy

History

Sir William Herschel was the first to recognize the existence of infrared in 1800. Interest in IR was not explored further for 80 years. During 1882-1900 several investigations were made into the IR region. Abney and Festing photographed absorption spectra for 52 compounds and correlated absorption bands with the presence of certain organic groups in the molecule (Smith).

W. W. Coblentz laid the real groundwork for IR spectroscopy. Starting in 1903 he investigated the spectra of hundreds of substances, both organic and inorganic. His work in the rock salt region, from 0.7 to 18 (m, was so thorough and accurate that many of his spectra are still usable. The experimental difficulties of the early researchers were many. They not only had to design and build their own instruments but all the components too. Obtaining a spectrum was a tedious job requiring 3-4 hours or more since each point in the spectrum had to be measured separately and at least 10 points per micrometer were measured. After World War II advances in electronics made it possible to obtain a spectrum in 1-2 hours (Smith).

The end result of this early work was the recognition that each compound had a unique IR spectra and that certain groups, even when they were in different molecules, gave absorption bands that were found at approximately the same wavelength.

Applicability

The IR absorption spectrum of a compound is its most unique physical property. The samples can be liquids, solids, or gases. They can be organic or inorganic. The only molecules transparent to IR radiation under ordinary conditions are monatomic and homonuclear molecules such as Ne, He, O2, N2, and H2. One limitation of IR spectroscopy is that the solvent water is a very strong absorber and attacks NaCl sample cells.

In terms of a comparison of physical properties, a melting point, refractive index, or specific gravity gives only a single point of comparison with other substances. An IR spectrum, in contrast, gives a multitude of such points. Not only can the position of bands be compared but their intensity as well since the intensity is indicative of the number of a particular group contributing to an absorption. IR is usually preferred when a combination of qualitative and quantitative analysis is required. It is often used to follow the course of organic reactions allowing the researcher to characterize the products as the reaction proceeds.

Definitions

A term often encountered in IR spectroscopy is wavenumber ((), whose relationship to wavelength (is ((cm-1)

= (104/() where (is measured in micrometers. The wavenumber may be visualized as the number of wavelengths per centimeter.

Instrumentation

All IR spectrometers have the following elements in common, the source, optical system, detector, and amplifier. In the region 100-4000 cm-1 the most popular sources are the Globar and the Nernst glower, which are heated electrically to about 1500 C. The purpose of the optical system is to channel the radiation along the proper path. Mirrors are used rather than lenses because lenses are subject to chromatic aberration.

Because infrared radiations are essentially radiant heat, thermal detectors are used to detect changes in the radiations. Thermal detectors are made as small as possible to reduce their heat capacity so that for a given amount of energy there will be a large temperature rise. In order to make the detector rapid in response it must be able to dissipate the heat very rapidly. There are three main types of detector.

The thermocouple uses the principle that the change in temperature of a junction of two dissimilar metals creates an electromotive force (emf) which may be measured. The bolometer uses the principle that the electrical resistance of a pure metal or semi-conductor is temperature-sensitive. If a constant potential is applied to such a detector the variation of the resistance with temperature may be measured by the variations in the current flowing in the circuit. In the Golay cell the detector is a small metal cylinder enclosed by a blackened metal plate at one end and a flexible metallised diaphragm at the other. The cylinder is filled with a gas and sealed. As IR radiation falls on the blackened plate the gas in the cylinder expands deforming the diaphragm. Light from a lamp inside the detector is focused on the diaphragm. The light is reflected from the metallised diaphragm and falls onto a photocell. Movement of the diaphragm moves the light beam across the photocell. The output of the photocell is proportional to the expansion of the gas.

Early IR spectrometers used optical amplification of the detector signal obtained from a galvanometer or radiometer. Current instrumentation uses chopped radiation with electronic amplification.

An infrared spectrometer may use either a single beam or double beam design. In the single beam design light from the radiation is focused and passed through a sample contained in a special cell. After passing through the sample the emergent light beam is dispersed by a monochromator, either a prism or a diffraction grating, into its component wavelengths. The spectrum is scanned by slowly rotating the prism or grating. The main difference in a double beam spectrometer is that the original light is split into two beams, one of which passes through the sample and the other through a reference cell. The instrument records the difference in intensity of these two beams. The double beam spectrometer is especially useful if the spectrum is to be measured in solution. In this case the reference cell would contain pure solvent and any absorption due to the solvent would be canceled out.

The prism and cells used in IR spectrometers cannot be made of glass because glass absorbs strongly in the infrared region of interest. The prism and sample cell walls are usually made from large NaCl or KBr crystals.

If we build an instrument in such a way as to allow a sample of unknown material to be held in position while various wavelengths of the IR region shine on it in turn, we can find which wavelengths are absorbed and which are not. This scan can be plotted on a graph and is called the infrared spectrum of the material. A spectrum is a plot of absorbance (or transmittance) versus wavelength, frequency, or wavenumber. For IR spectra, we usually plot wavenumber (in units of cm-1) which is the reciprocal of wavelength calculated as follows: cm-1= 1/(m x 104 .

Interpretation of Spectra

Certain atomic movements give rise to bands that occur in approximately the same position in a large variety of compounds and are only slightly affected by the rest of the molecule. These vibrations are assigned to groups of atoms termed functional groups. Although absorption bands are characteristic of the molecule as a whole, it is a useful approximation to consider that molecular vibrations are localized in particular functional groups. This allows one to relate absorption band position with a particular functional group and to tabulate these relationships. The tables showing the positions where the functional group absorptions occur are called correlation tables. The intensity of the absorption bands is also shown on good correlation tables.

Most of the spectral features that allow us to readily identify functional groups are found in the left part of the spectrum. The right hand portion of the spectrum is more complex, and each peak is not readily identified with a particular part of the molecule. The entire spectral pattern is unique for a given compound.

The steps used by a chemist to find information about molecular structure from the IR spectrum are as follows:

1. Obtain a spectrum of the material on an IR spectrophotometer.
2. Using information from correlation tables and absorbances from the functional group region of the spectrum, identify the functional groups that are present or sometimes more importantly absent.
3. Compare this spectrum with those of known compounds or obtain a known sample of a suspected material and run its spectrum for comparison.

Many of the group frequencies vary over a wide range because the bands arise from complex interacting vibrations within the molecule. Absorption bands may, however, represent predominantly a single vibrational mode. Certain absorption bands, for example, those arising from C-H, O-H, and C=O stretching modes, remain within fairly narrow regions of the spectrum.

The two important areas for a preliminary examination of a spectrum are the region 4000-1300 cm-1 and the 909-650 cm-1 region. The high frequency portion of the spectrum is called the functional group region. The characteristic stretching frequencies for important functional groups such as OH, NH, and C=O occur in this portion of the spectrum. The absence of absorption in the assigned ranges for the various functional groups can usually be used as evidence for the absence of such groups from the molecule. The absence of absorption in the 1850-1540 cm-1 region excludes a structure containing a carbonyl group. Strong skeletal bands for aromatics and heteroaromatics fall in the 1600-1300 cm-1 region of the spectrum. These skeletal bands arise from the stretching of the carbon-carbon bonds in the ring structure.

The lack of strong absorption bands in the 909-650 cm-1 region generally indicates a nonaromatic structure. Aromatic and heteroaromatic compounds display strong out-of-plane C-H bending and ring bending absorption bands in this region.

The intermediate portion of the spectrum, 1300-909 cm-1 is usually referred to as the fingerprint region. The absorption pattern in this region is complex, with bands originating in interacting vibrational modes. Absorption in this intermediate region is probably unique for every molecular species.

Conclusions reached after examination of a particular band should be confirmed by examination of other portions of the spectrum if possible. For example the assignment of a carbonyl band to the presence of an ester should be confirmed by observation of a strong band in the C-O stretching region, 1300-1100 cm-1.

Characteristic Group Frequencies of Organic Molecules Table 1 Characteristic Infrared Group Frequencies

Class	Group	Wavenumber (cm-1)
Alkane	C-H	2850-3000
	C-C	800-1000
Aromatic	C-H	3000-3100
	C=C	1450-1600
Alkene	C-H	3080-3140
	C=C	1630-1670
Alkyne	C-H	3300-3320
	C(C	2100-2140
Alcohol	O-H	3400-3600
	C-O	1050-1200
Ether	C-O	1070-1150
Aldehyde	C=O	1720-1740
	C-H	2700 &2900
Carboxylic Acids	C=O	1700-1725
	O-H	2500-3000
Ester	C=O	1735-1750
	C-O	1000-1300 (2 bands)
Ketone	C=O	1700-1780

Hydrocarbons

Hydrocarbons are classified as saturated or unsaturated based on the absence or presence of multiple bonds. The presence of multiple bonds decreases the number of hydrogens from the number in a saturated compound of formula CnH2n+2 . The decrease in number of hydrogens alone does not confirm the presence of a multiple bond. For example, 1-octene and cyclooctane have the same molecular formula, C8H16. What are the structural features that are present in 1-octene that are absent in cyclooctane? The carbon-carbon double bond and sp2-hybridized C-H bonds distinguish 1-octene from cyclooctane. It is characteristic group absorbances of these structures that will be present in the spectrum of 1-octene and absent in the spectrum of cyclooctane.

The energy of the infrared light absorbed by a C-H bond depends on the hybridization of the hybrid orbital. The bond strengths of carbon-hydrogen bonds are in the order of sp3>sp2>sp, because the increased s character of the hybrid gives better overlap with the hydrogen s-orbital. The sp3-hybridized C-H bonds in saturated hydrocarbons like octane absorb in the 2850-3000 cm-1 region. The sp2-hybridized C-H bonds in alkenes such as 1-octene absorbs at 3080 cm-1. A sp-hybridized C-H bond in a molecule such as 1-octyne absorbs infrared at 3320 cm-1.

Hydrocarbons can also be classified based on absorptions due to the carbon-carbon bond. Carbon-carbon bond strength increases in the order of singledoubletriple. Therefore, the wavenumber position of the absorption corresponding to the stretching of these bonds increases in the same order. Saturated hydrocarbons all contain carbon-carbon single bonds that absorb in the 800-1000 cm-1 region. Unsaturated hydrocarbons also contain carbon-carbon single bonds that absorb in this same region. This is not a very diagnostic region because we already know that most organic compounds have carbon-carbon single bonds.

Alkenes are identified by the absorption of the carbon-carbon double bond, which occurs in the 1630-1670 cm-1 region. Terminal alkenes have the most intense absorptions as the absorption decreases with increased substitution. Alkyne C(C stretches occur in a region of the IR spectrum where very little else appears. The alkyne carbon-carbon stretch occurs in the range of 2100-2260 cm-1. The intensity can very dramatically since the dipole moment change depends entirely upon what is attached to each carbon. Terminal alkynes, alkynes which have an H attached to one of the alkyne carbons, generally display greater band intensities as well as characteristic signals near 3300 cm-1.

Activity Four

Provide students with unlabelled spectra for octane, 1-octene, and 1-octyne (or any other straight chain hydrocarbons with the same number of carbon atoms). Ask students to assign the hydrocarbon to its spectra and justify their selections.

Oxygen-Containing Compounds

Many functional groups contain oxygen. These functional groups have the characteristic infrared absorptions given in Table 1. The characteristic group frequencies of aldehydes and ketones are from 1700-1780 cm-1. The carbon-oxygen double bond of carbonyl compounds requires more energy to stretch than does the carbon-oxygen single bond of ethers and alcohols. Therefore, aldehydes and ketones absorb infrared at higher wavenumber positions than alcohols and ethers. Since the carbonyl is highly polar, stretching of this bond results in a relatively large change in dipole moment producing an intense band. The carbonyl region is also free of conflicting absorptions making the recognition of the carbonyl band easy. Carefully examining the precise wavenumber of the C=O stretch, as well as the presence or absence of other signals, will usually allow one to distinguish among the many possible C=O containing compounds.

The position of the carbonyl group absorption of acyl derivatives depends on the inductive and resonance effects of atoms bonded to the carbonyl carbon atom. We can represent a carbonyl group by two contributing resonance structures. (See Figure 3) Since less energy is required to stretch a single bond than a double bond, any structural feature that stabilizes the contributing polar resonance form with a carbon-oxygen single bond will cause the infrared absorption to occur at lower wavenumber position. In other words, any group that donates electrons by resonance causes a shift in the absorption to lower wavenumbers. For example, the nitrogen atom of amides is very effective in donation of electrons to the carbonyl carbon atom. (See Figure 4) Therefore, the double bond character of the carbonyl decreases. As a result, in amides the carbonyl group absorbs in the 1650-1690 cm-1 region, which is at a lower wavenumber than for aldehydes or ketones.

When carbonyls (or other multiple bonds) are in conjugation with another double or triple bond a resonance form can be drawn in which the carbonyl oxygen bears a negative charge. The contribution of this resonance form reduces the double bond character of the carbonyl shifting the absorption to a lower frequency. (See Figure 5)

The characteristic bands observed for alcohols result from O-H stretching in addition to C-O stretching. The carbon-oxygen stretching vibration of alcohols appears in a region complicated by many other absorptions, the fingerprint region. The presence of a hydroxyl is better established by the O-H stretching. The shape and frequency of an O-H band depends on hydrogen bonding. As hydrogen bonding becomes stronger, O-H stretches appear at lower frequencies. In the vapor phase or in dilute solution in nonpolar solvents “free” hydroxyl group of alcohols absorbs strongly around 3600 cm-1. As the concentration of the solution increases intermolecular hydrogen bonding increases and we see additional bands start to appear at lower frequencies, 3550-3200 cm-1 and the “free” hydroxyl band decreases. When the hydrogen of a hydroxyl group is involved in a hydrogen bond a resonance form can be drawn in which the oxygen bears a negative charge. The contribution of this resonance form reduces the single bond character of the hydroxyl bond shifting the absorption to a lower frequency. (See Figure 6)

Carboxylic acids tend to form strongly hydrogen bonded dimers which shift the O-H stretch to frequencies lower than 3000, however, carboxylic O-H stretches can occur anywhere between 2500-3300 depending upon the strength of hydrogen bonding.

A process of elimination can identify ethers. If a compound contains oxygen and the infrared spectrum lacks absorptions characteristic of a carbonyl group or a hydroxyl group, we may conclude that the compound is an ether.

Activity Five

As we talk about the characteristic bands for functional groups students will be given actual IR spectra that illustrate each of the bands being discussed. At the culmination of the activity they will be given the spectra of carefully selected unknown compounds and will be asked to determine which functional groups are present and/or absent.

Activity Six

Students will be given the IR spectrum and other data about a particular compound, such as elemental analysis and molecular mass. They will be asked to draw a structural formula for the compound consistent with the information given and be required to justify their choice of structure.

Investigation 1: What factors affect the frequency of oscillation of a swing?

Work with a partner to design and conduct an experiment to determine what factors, if any, affect the frequency of oscillation of a swing. Frequency is defined as the number of complete oscillations per unit of time. For the purposes of comparison report your frequency in oscillations/minute. As you plan keep in mind the variables you want to control and the ones you want to test. The experiment will be conducted across the street at College Woods.

After gathering your data address the following questions in the results and conclusions section of your lab report.

1. From your data, which factor(s) affect the frequency of oscillation of a swing?

2. For each factor that you found affected the frequency, describe the relationship between frequency and the factor. In other words, how does varying the factor change the frequency?

Investigation 2: Masses on a spring

The bonds between atoms may be modeled using masses connected by springs. If one mass is held stationary and the other is allowed to move, the stretching vibration of a bond between the two atoms may be modeled by stretching the spring and releasing it.

Using the model above investigate the effect of mass on the frequency of vibration and the effect of bond strength on the frequency of vibration.

After gathering your data, address the following questions in the results and conclusions section of your lab report.

1. Did the mass affect the frequency of vibration? If so, quantitatively describe the relationship between mass and frequency?

2. Did the number of springs or spring tightness affect the frequency of vibration? If so, describe the relationship between spring tightness and the frequency.

3. Relate what you discovered about the effects of mass and spring strength to atoms joined by a chemical bond. Make a statement about the relationship between atomic mass and frequency and bond strength and frequency.

4. Compare your results from this investigation to the results for the swing in Investigation 1.

Worksheet 1: Predicting Vibrational Frequencies

Consider the following hypothetical diatomic molecules C-H, C-C, and C-I. The carbon atom is common to the molecules. If we were to hold the carbon atom in a clamp and represent the bond by a spring we could attach masses representing the H, C, and I atoms one by one and measure the frequency of vibration as we did in investigation 2. In your investigation you found that the frequency of vibration was inversely related to the mass (as mass increased the frequency decreased). In the infrared spectrum the infrared vibrations of these atoms will occur at:

C-H, 3000 cm-1 C-C, 1000 cm-1 C-I, 500 cm-1

This is consistent with our observation that as we increased the mass the frequency decreased.

If the diatomic grouping consisted of C-O, near to which of the three frequencies would you expect to find the absorption band?

Would the frequency of the absorption band be higher or lower than this frequency? Why?

Suppose now we connect two of these diatomic groupings having sufficiently different frequencies to make a hypothetical triatomic grouping. We now have two bond springs and there will be two ways to stretch each grouping.

((((
H - C - C C - C - I
((((
H - C - C C - C - I
((: direction of motion of the atoms when the two springs are vibrating.

The bonds in the H-C-C grouping are found to vibrate practically independently, when the C-H bond vibrates the C-C hardly changes, and the spectrum of this compound would show two absorption bands at 3000 cm-1 and 1000 cm-1. Similarly in the C-C-I grouping the two vibrations are shown to be almost independent of each other and to occur very close to their diatomic positions.

Where would you expect to find the absorption bands for the C-C-I grouping?

Worksheet 1

Where would you expect to find the absorption bands for the grouping H-C-I ?

If we were to link two identical bonds together to make a C-C-C grouping we would still get two absorption bands but these would involve both of the bonds vibrating. The two frequencies would arise from an in-phase and an out-of-phase vibrational motion.

(

C- C- C C- C- C
((((
symmetric asymmetric
in-phase out-of-phase

The two vibrations are termed symmetric and asymmetric. The two bonds do not move independently of each other, therefore, we say there is interaction between the groups and the frequencies of vibration will be displaced from the diatomic frequency.

In which of these groupings will there be symmetric and asymmetric vibrations?

H-C-I C- C- I O- C- O

If each bond is represented by a spring then the C-N will have one spring, the C=N will have two springs and the C(N will have three. This means the strength of the bond has been increased as you go from C-N to C(N. If the strength of the spring has been increased and the atoms remain constant the frequency of the vibration will also be increased. The frequencies of these groups are approximately:

C-N, 1070 cm-1 C=N, 1650 cm-1 C(N, 2250 cm-1

Consider the following triatomic groupings, which will have symmetric and asymmetric vibrations? Why?

N-C=N N=C=N N-C(N

Worksheet 2: Deformations

Vibrations other than the stretching of a bond also occur. These vibrations are called deformations and they refer to the bond angle changing between the atoms of a molecule. These deformations occur at frequencies lower than those of the stretching vibrations. If we consider groups of atoms of the type XY2 there are some general descriptions of the deformational vibrations we can apply to these groups.

The terms used are scissors, rock, wag, and twist. These four motions may be further divided into in-plane and out-of-plane motions of the atoms.

H(In-plane symmetric deformation
C (scissors)
H(
If you think of the C as the pivot and the H as the points of a pair of scissors then there is a plane through all of the atoms and the motion is in-plane.
C In-plane asymmetric deformation
(rock)
H H

Consider the hydrogens to be the tips of a rocker on a rocking chair and the carbon is sitting on the chair. There is a plane through all of the atoms. This is a poor group frequency because all of the atoms move.

H + Out-of-plane symmetric deformation
C (wag)
H +
Consider the C to be the body of a horse and the H to be the tail. When the horse wags its tail the motion is from side to side and out of the plane of the horse (in the diagram the plane of the paper). The "+" indicates motion perpendicular to the plane of the paper. This is also a poor group frequency.
+ H H - Out-of-plane asymmetric deformation
C (twist)
Look at the diagram of the CH2ClBr molecule and consider the CH2 part only. What is the total number of vibrations that may occur?

Worksheet 2

The infrared spectrum has in its composition three types of absorption bands, fundamental, combination, and overtone. When we stretched the masses on the springs we observed that they vibrated at a certain frequency, this is the fundamental frequency for that system. The masses were vibrating with simple harmonic motion.

If a molecule with a fundamental vibration occurring at a frequency (1 is subjected to radiation at a frequency 2(1 , an absorption may also be observed at this frequency and is called an overtone absorption band. This does not mean that the molecule itself is vibrating at 2(1 , but the fundamental is being excited by the radiation at twice its frequency and such bands are generally much weaker than the fundamental. If a molecule has two different fundamental absorptions at (a and (b it is possible that an absorption may be observed at frequencies corresponding to (a + (b and (a -(b and these are called combination bands. Combination bands will usually be weaker than the fundamentals involved.

What would be the frequency of the fundamental absorption if its first overtone absorption was observed at 2000 cm-1?

Teacher Bibliography

Atkins, P.W. Physical Chemistry. 2nd Ed. San Francisco: W.H. Freeman and Company, 1982. Discussion of vibrational spectra from a quantum mechanical view. Cook, B.W. and K. Jones. A Programmed Introduction to Infrared Spectroscopy. New York: Heyden & Son Inc., 1972. Excellent resource for the beginning spectroscopist.

http://chemistry.gsu.edu/post_docs/koen/wir.html

Provides links to IR spectroscopy related websites.

http://www.aist.go.jp/RIODB/SDBS

Searchable database of spectra. Can be searched by compound name, CAS No., or number of atoms of each element in the molecule. Will allow you to view and download spectra.

http://www.chem.uni-potsdam.de/tools/index.html

Allows you to enter a wavenumber and returns possible structures.

Morrison, Robert T. and Robert N. Boyd. Organic Chemistry. 5th Ed. Boston: Allyn and Bacon, Inc., 1987. Provides a brief description of spectroscopy. Includes relevant IR spectra for each family of organic compounds. Shriner, Ralph L., Fuson, Reynold C., Curtin, David Y., and Terence C. Morrill. The Systematic Identification of Organic Compounds. 6th Ed. New York: Wiley, 1980. Contains a brief section on IR spectroscopy. Mainly a text for identification of compounds by chemical tests. Silverstein, Robert M., Bassler, G. Clayton, and Terence C. Morrill. Spectrometric Identification of Organic Compounds. 4th Ed. New York: Wiley, 1981. Description of mass spectrometry, IR spectrometry, 1H NMR spectrometry, 13C spectrometry, and UV spectrometry. Smith, A. Lee. Applied Infrared Spectroscopy: Fundamentals, Techniques, and Analytical Problem-Solving. New York: Wiley, 1979. Comprehensive treatment of IR spectroscopy. Includes history, instrumentation, sampling techniques, qualitative and quantitative applications. Socrates, George. Infrared Characteristic Group Frequencies. 2nd Ed. Chichester: Wiley, 1994. A comprehensive reference of correlation tables. Streitweiser, Jr., Andrew and Clayton H. Heathcock. Introduction to Organic Chemistry. 2nd Ed. New York: Macmillan Publishing Co., Inc., 1981. Introductory organic text with a section on IR spectroscopy. Includes spectroscopic information as each family is presented. Student Reading List

Morrison, Robert T. and Robert N. Boyd. Organic Chemistry. 5th Ed. Boston: Allyn and Bacon, Inc., 1987, pp573-576.

Classroom Materials

The following materials should be available for student use for the investigations: stopwatches, swings of various lengths, springs with different force constants or many springs with the same force constant, masses of different magnitude (washers may be used if commercial masses are not available), measuring tape, triple beam balances. If computers are available MacSpartan for the Macintosh or PC Spartan for Windows brings the vibrational motion of atoms within specific molecules to life.

Answer: 1000 cm-1 and 500 cm-1