

Infrared Spectroscopy

Most of us are quite familiar with infrared radiation. We have seen infrared lamps keep food hot and often associate infrared radiation with heat. While the generation of heat is a probable event following the absorption of infrared radiation, it is important to distinguish between the two. Infrared is a form of radiation that can travel through a vacuum while heat is associated with the motion and kinetic energy of molecules. The concept of heat in a vacuum has no meaning because of the lack of molecules and molecular motion. Infrared spectroscopy is the study of how molecules absorb infrared radiation and ultimately convert it to heat. By examining how this occurs, we will not only learn about how infrared radiation is absorbed, but we will also learn about molecular structure and how the study of infrared spectroscopy can provide information about the structure of organic molecules. An infrared spectrum of a chemical substance, is very much like a photograph of a molecule. However, unlike a normal photograph which would reveal the position of nuclei, the infrared spectrum will only reveal a partial structure. It is the purpose of this narrative to provide you with the tools necessary to interpret infrared spectra, successfully. In some respects, this process is similar to reading an X-ray of the chest. While most of us could easily identify the gross structural features of the chest such as the ribs, most of us would need some guidance in identifying those features of the X-ray associated with disease.

In order to interpret infrared spectra, having some idea or model of the physical process involved when a molecule interacts with infrared radiation would be useful. You may recall in introductory chemistry, the discussion of how atoms interact with electromagnetic radiation led to the development of quantum theory and the introduction of quantum numbers. The interaction of infrared radiation with molecules requires a similar treatment. While the use of quantum theory is necessary to explain this interaction, most of us live in a world that appears continuous to us and we do not have much experience discussing phenomena that occur in discrete steps. The discussion that follows will attempt to develop a model of how molecules interact with infrared radiation that is based as much as possible on classical physics. When necessary, we will insert the modifications required by quantum mechanics. This model, while perhaps oversimplified, will contain the physical picture that is useful to understand the phenomena and will be correct from a quantum mechanical standpoint.

Let's begin first by considering two isolated atoms, a hydrogen and a bromine atom moving toward each other from a great distance. What do you suppose will happen once the atoms approach each other and can feel each others presence? The potential energy curve for the H-Br molecule is shown in Figure 1. As the two atoms approach each other notice that the potential energy drops. If we recall that energy must be conserved, what must happen to the kinetic energy? The two atoms must attract each other and accelerate toward each other, thereby increasing their kinetic energy. The change in kinetic energy is illustrated by the dotted line in the figure. At some point they will "collide" as indicated by the part of the potential energy curve that rises steeply at small interatomic distances and then the atoms will begin to move away from each other. At this point, we might ask, "Will the molecule of HBr survive the collision"? Unless some energy from this system is lost, say by emission of a photon of light or collision by a third body to remove some energy, these are two ships passing in the night. The kinetic energy resulting from the coulombic attraction of the two atoms will exactly equal the drop in potential energy and the two atoms will

fly apart. The spontaneous emission of a photon of light is improbable, so this mechanism is unlikely to drop the HBr molecule into the well. Most Probable from a physical perspective, is the

Potential Energy Diagram for HBr

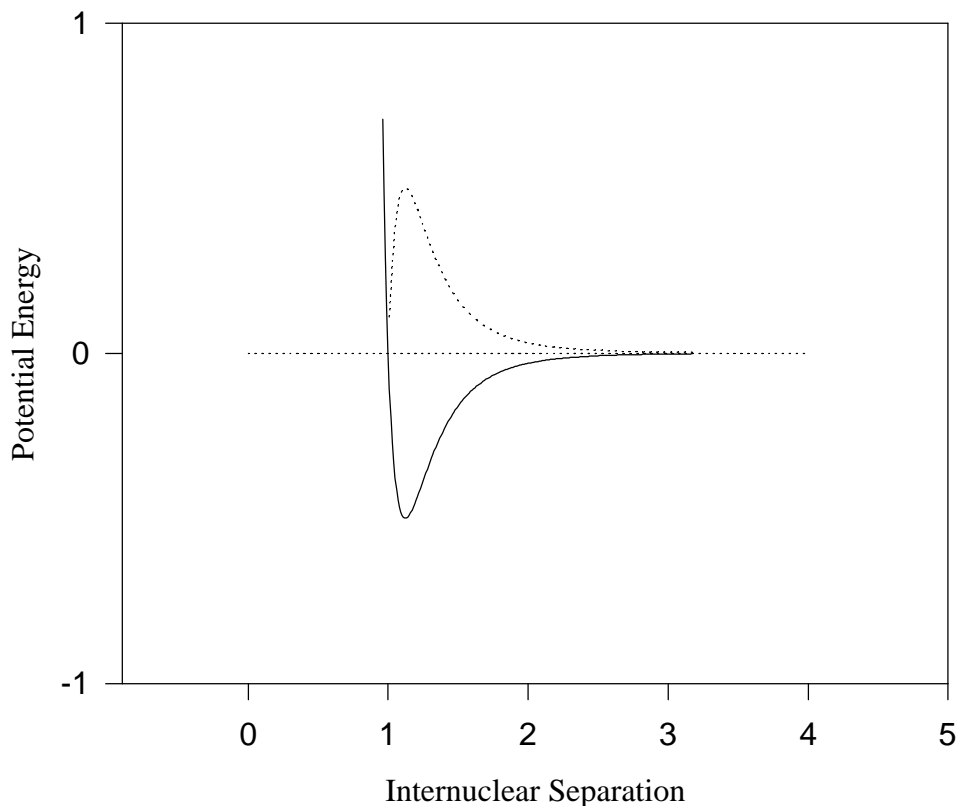


Figure 1. The potential (solid line) and kinetic energy (dotted line) of HBr as a function of the separation of the two nuclei. The kinetic energy at every point illustrated by the dotted line is equal to the potential energy plus the small amount of kinetic energy associated with initial motion of the two nuclei when separated at large distances.

collision of our HBr with a third body which will remove some energy and result in the trapping of the HBr molecule in the well. Though very excited, this molecule will now survive until other collisions with less energetic molecules leads to an HBr molecule at the bottom of the well and the generation of heat (kinetic energy) that would be experienced in the exothermic reaction of hydrogen and bromine atoms to form hydrogen bromide. Let us now consider a hydrogen bromide molecule that has lost a little kinetic energy by collision and has been trapped in the potential energy well of Figure 1. We might ask, "How would a molecule that does not have enough kinetic energy to escape the well behave in this well? A molecule with some kinetic energy below this threshold value (total energy slightly less than 0 in Fig. 1) will be able to move within this well. The internuclear separation will vary within the limits governed by the available kinetic energy.

Since this motion involves a stretching or compression of the internuclear distance it is usually described as a vibration. Additional collisions with other molecules will eventually lead to the dissipation of the energy associated with formation of the hydrogen bromide bond. At this point we might ask the following question. If we remove all the excess kinetic energy from HBr, what will be its kinetic and potential energy? Alternatively we might ask, "Will the hydrogen bromide molecule reside at the very bottom of the well when it is cooled down to absolute zero Kelvin?" Before we answer this question, let's digress for a little and discuss the relative motions of the hydrogen and bromine atoms in terms of the physics of everyday objects. Once we learn how to describe the classical behavior of two objects trapped in a potential energy well, we will return to the question we have just posed.

One model we can use to describe our hydrogen bromide molecule is to consider our HBr molecule to be made up of balls of uneven mass connected to each other by means of a spring. Physicists found many years ago some interesting properties of such a system which they referred to as a harmonic oscillator. Such a system repeatedly interconverts potential and kinetic energy, depending on whether the spring is exerting a force on the balls or the momentum of the balls is causing the spring to be stretched or compressed. The potential energy of this system (PE) is given by the parabola,

$$PE = k(x-x_0)^2 \quad 1$$

where $x-x_0$ is the displacement of the balls from their equilibrium condition when the system is at rest and k is a measure of the stiffness of the spring. While this simple equation does not apply to molecules, please notice how similar the potential energy surface of the parabola (Figure 3) is to the bottom of the surface of Figure 1. The constant k is used to describe chemical bonds and is referred to as the **force constant**. As you might imagine, it is a measure of the stiffness of the chemical bond.

Several other relationships were observed that do carry over in describing molecular systems. For example, they found that when a ball was suspended on a spring from a horizontal wall, the frequency of vibration or oscillation, ν , depended only on the mass of the ball and the stiffness of the spring. The term A is a constant of the proportionality. By varying the mass of the ball and the stiffness of the spring, they were able to uncover the following simple relationship between frequency, mass and force constant:

$$\nu = A\sqrt{\frac{k}{m}} \quad 2$$

Suspending a ball and spring from a horizontal surface is a special case of the more general situation when you have two more comparable masses attached to each other. Under these circumstances, when two similar masses are attached to a spring, the relationship between frequency of vibration, mass and force constant is given by:

$$n = A \sqrt{\frac{k}{m}}$$

3

where μ , represents the product of the masses divided by their sum ($m_1 m_2 / (m_1 + m_2)$). This latter term is found in other physical relationships and has been given the name, the **reduced mass**. It can easily be seen that equation 2 is a special case of the more general relationship given by equation 3. If we consider m_1 to be much larger than m_2 , the sum of $m_1 + m_2 \approx m_1$ and substituting this approximation into ($m_1 m_2 / (m_1 + m_2) \approx m_2$). Substituting m_2 into equation 3 where m_2 is the smaller of the two masses gives us exactly the same relationship as we had above when the ball was suspended from a horizontal wall. The horizontal wall is much more massive than the ball so that the vibration of a smaller ball has very little effect on the wall. Despite their simplicity, equations 2 and 3 play an important role in explaining the behavior of molecular systems. However, before we discuss the important role these equations play in our understanding of infrared spectroscopy, we need to review some of the properties of electromagnetic radiation, particularly radiation in the infrared range.

The electromagnetic spectrum is summarized in Figure 2. On the extreme right we find radiowaves and scan from right to left we encounter terms which have become familiar to us; microwave, infrared, visible ultraviolet and X-rays. All of these forms of electromagnetic radiation

Wavenumbers, cm^{-1}

10^{10} 10^8 10^6 2×10^5 1×10^5 4000 650 12 5×10^{-2} 10^{-3} 10^{-6}

Gamma Rays	X-Rays	Ultra violet	Visible Light	Near IR	Infra red	Far Infrared	Micro wave	TV Waves	Radio
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10^{-6} 10^{-4} 10^{-2} 4×10^{-2} 4×10^{-2} 2.5 15.4 830 4×10^5 10^7 10^{10}

Wavelength (microns)

Figure 2. The electromagnetic spectrum.

are related to each other in a simple and obvious way. First let us discuss why we refer to these different forms of light as electromagnetic radiation. Simply stated, all these forms of radiation have an electric and magnetic field associated with them that varies as shown for the standing wave in Figure 3. Only the electric field is shown in this figure. If we were to include the magnetic field it would look exactly as the electric field but would be rotated 90° out of the plane of the paper and would oscillate above and below the plane of the paper like a sin or cos wave. In infrared spectroscopy, only the electric field associated with the electromagnetic radiation is important and we will limit our present discussion to how this field varies with time. We called the light wave associated with Figure 4 a standing wave because this is how the electric field would

Electric Field of Light

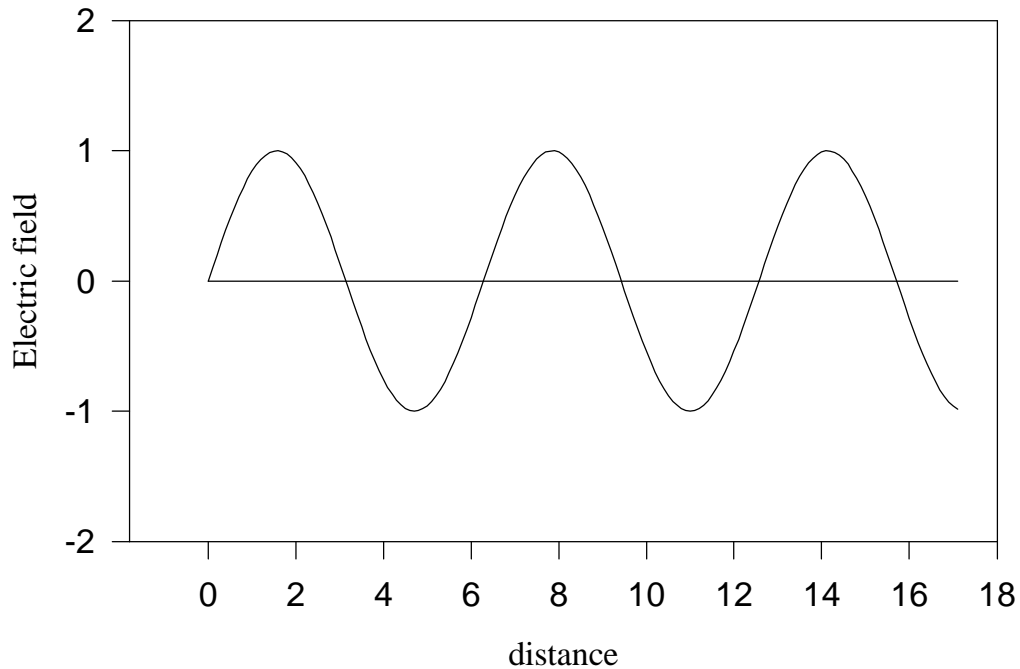


Figure 3. The electric field of light associated with a standing wave with a fixed wavelength.

vary if we took a picture of the wave. One of the properties of all electromagnetic radiation is that it travels in a vacuum at the speed of 3×10^{10} cm/sec. Therefore, if we were to turn this standing wave "on" we would observe this oscillating field rapidly passing us by. If we examine the electric field (or the magnetic field which is not shown), we observe that the field is repetitive, varying as a cos or sin wave. The length of the repeat unit along the x axis is called the wavelength, λ , and it is this property which varies continuous from 10^6 cm (10^{10} microns) for radio waves down to 10^{-13} cm (10^{-6} microns) for cosmic radiation. A unit of length that is frequently used in infrared spectroscopy is the micron. A micron is equivalent to 10^{-4} cm. If we were to "stand on the corner and watch all the wavelengths go by", since all electromagnetic radiation would be traveling at 3×10^{10} cm/sec, the frequency, ν , at which the shorter wavelengths would have to pass by would have to increase in order to keep up with the longer wavelengths. This relationship can be described in the following mathematical equation:

$$\lambda\nu = c; (c = 3 \times 10^{10} \text{ cm/sec}). \quad 4$$

The frequency of the light times the wavelength of the light must equal the speed at which the light is traveling.

In addition to having wave properties such as the ones we have been discussing, electromagnetic radiation also has properties we would normally attribute to particles. These “particle like” properties are often referred to as characteristics of **photons**. We can discuss the wave properties of photons by referring to the wavelength (eqn. 4) and frequency associated with a photon. The energy of a single photon is a measure of a property we would normally associate with a particle. The relationship which determines the energy associated with a single photon of light, E , and the total energy incident at on a surface by monochromatic light, E_T , is given by:

$$E = h \nu \quad (\text{or equivalently, } E = h c / \lambda, \text{ from equation 4}), \quad 5$$

$$E_T = n h \nu \quad 6$$

where h is Planck's constant and is numerically equal to 6.6×10^{-27} erg s and n is the number of photons. Equations 4 and 5 tell us that photons with short wavelengths, in addition to having higher frequencies associated with them, also carry more punch! The energy associated with a photon of light is directly proportional to its frequency.

At this point we are ready to return to a discussion of how infrared radiation interacts with molecules. Following our discussion of balls and springs, you have probably figured that infrared spectroscopy deals with the vibration of molecules. Actually, both rotation and vibration of molecules is involved in the absorption of infrared radiation, but since molecular rotation is not usually resolved in most infrared spectra of large organic molecules, we will ignore this additional consideration. In order to derive the relationship between vibrational energy and molecular structure, it is necessary to solve the Schoedinger equation for vibrational-rotational interactions. Since solution of this equation is beyond the scope of this treatment, we will simply use the relationship that is derived for a harmonic oscillator from this equation. As you see, the quantum mechanical solution of a harmonic oscillator, equation 7, is remarkably simple and very similar to the relationship we obtained from considering the classical model of balls and springs.

$$E = \frac{h}{2\pi} \sqrt{\frac{k}{m}} \left(n + \frac{1}{2}\right) \quad 7$$

Before discussing the implications of equation 7, let's take a moment to see how similar it is to equations 3 and 5. From equation 5, we see that substituting equation 3 for ν results in equation 7 except for the $(n + 1/2)$ term. However we should point out that we have substituted the vibrational frequency of two masses on a spring for a frequency associated with the number of wave maxima (or minima, null points. *etc.*) passing a given point (or street corner) per unit time. We are able to do this because of the presence of the $(n + 1/2)$ term. Let's discuss the significance of the $(n + 1/2)$ term before we returning to answer this question. The previous time you encountered the Schroedinger equation was probably when studying atomic spectra in Introductory Chemistry. An important consequence of this encounter was the introduction of quantum numbers, at that time the principle quantum number, N , the azimuthal quantum number, l , the magnetic, m_l , and spin quantum number, s . This time is no exception. Meet n , the vibrational quantum number. These numbers arise in a very similar manner. The Schroedinger equation is a

differential equation which vanishes unless certain terms in it have very discrete values. For n , the allowed values are 0,1,2,... Let us now consider the energy of vibration associated with a molecule in its lowest energy of vibration, $n = 0$. According to equation 6, the energy of vibration is given by $E = \frac{h}{4\pi} \sqrt{\frac{k}{m}}$, when $n = 0$, the zero point energy. This equation allows us to answer the question posed earlier about what would happen to the vibrational energy of a molecule at absolute zero. According to quantum theory the molecule would continue to vibrate. From the relationship $E = h \nu$, we can evaluate the vibrational frequency as $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$, the same as found by classical physics for balls and springs. This equation states that the vibrational frequency of a given bond in a molecule depends only on the stiffness of the chemical bond and the masses that are attached to that bond. Similarly, according to equation 7, once the structure of a molecule

Potential Energy Surface for HBr

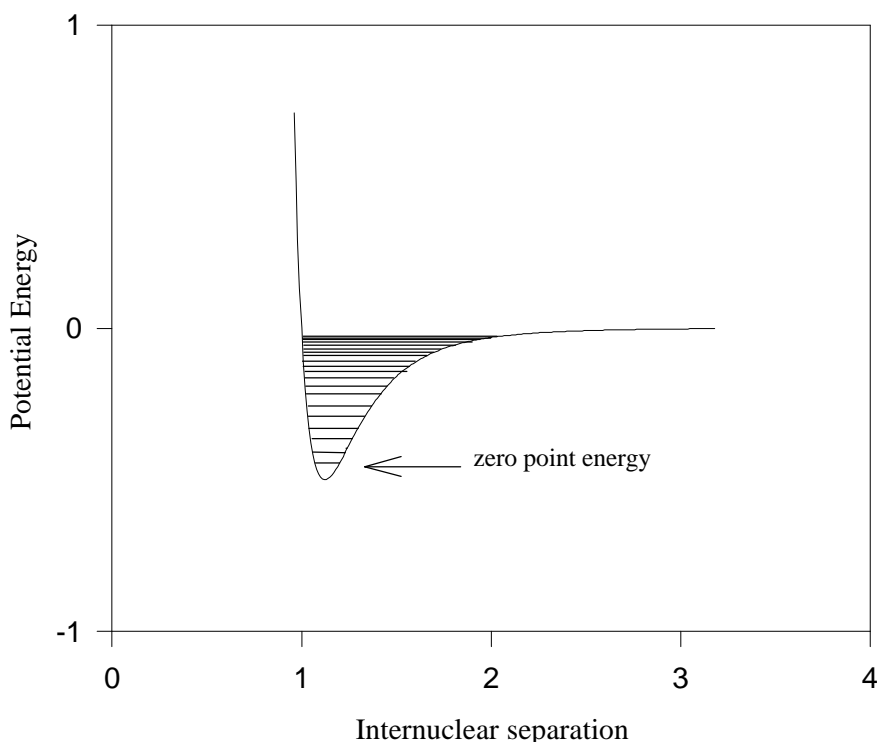


Figure 4. The potential energy surface for a HBr molecule illustrating how the vibrational energy levels vary in energy with increasing vibrational quantum number.

is defined, the force constants and reduced mass are also defined by the structure. This also defines the vibrational frequencies and energy of absorption. Stated in a slightly different manner, a molecule will not absorb vibrational energy in a continuous fashion but will do so only in discrete steps as determined by the parameters in equation 7 and illustrated for the HBr molecule in Figure 4. We have pointed out that the vibrational quantum number can have positive integer values including a value of zero. Upon absorption of vibration energy, this vibrational quantum number can change by +1 unit. At room temperature, most molecules are in the $n = 0$ state.

Figure 4 illustrates the real vibrational levels for HBr. Notice that equation 7 predicts that the energy level spacings should all be equal. Notice according to Figure 4, the spacings actually converge to a continuum for large values of n . For small values of n , $n = 0, 1, 2$, equation 7 gives a good approximation of the vibrational energy levels for HBr. Equation 7 was derived from the approximation that the potential energy surface is like a parabola. Near the minimum of this surface, around the zero point energy, this is a good approximation. As you go up from the minimum, the resemblance decreases and the assumptions made in solving the Schrodinger equation no longer are valid.

Let us now return and question the wisdom of substituting the vibrational frequency of a molecule for the frequency of electromagnetic radiation in equation 5. I hope at this point of the discussion this does not seem so absurd. If the vibrational frequency of the molecule, as determined by the force constant and reduced mass, equals the frequency of the electromagnetic radiation, then this substitution makes good sense. In fact, this gives us a mechanism by which we can envision why a molecule will absorb only distinct frequencies of electromagnetic radiation. It is known that symmetrical diatomic molecules like nitrogen, oxygen and hydrogen, do not absorb infrared radiation, even though their vibrational frequencies are in the infrared region. These homonuclear diatomic molecules have no permanent dipole moment and lack a mechanism of interacting with the electric field of the light. Molecules like HBr and HCl which have a permanent dipole, resulting from an unequal sharing of the bonding electrons, have a dipole which oscillates as the bond distance between the atoms oscillate. As the frequency of the electric field of the infrared radiation approaches the frequency of the oscillating bond dipole and the two oscillate at the same frequency and phase, the chemical bond can absorb the infrared photon and increase its vibrational quantum number by +1. This is illustrated in Figure 5. Of course, some HBr molecules may not be correctly oriented toward the light to interact and these molecules will not absorb light. Other factors will also influence the intensity and shape of the absorption. However, when the frequency of the electromagnetic radiation equals the vibrational frequency of a molecule, absorption of light does occur and this leads to an infrared spectrum that is characteristic of the structure of a molecule.

Up to now we have discussed molecules changing their vibrational quantum number by +1. A change of -1 is also equally possible under the influence of infrared radiation. This would lead to emission of infrared radiation. The reason why we have not discussed this possibility is that most molecules at room temperature are in the ground vibrational level ($n=0$) and cannot go any lower. If we could get a lot of molecules, let say with $n = 1$, use of infrared could be used to stimulate emission. This is how an infrared laser works.

Electric Field of Light

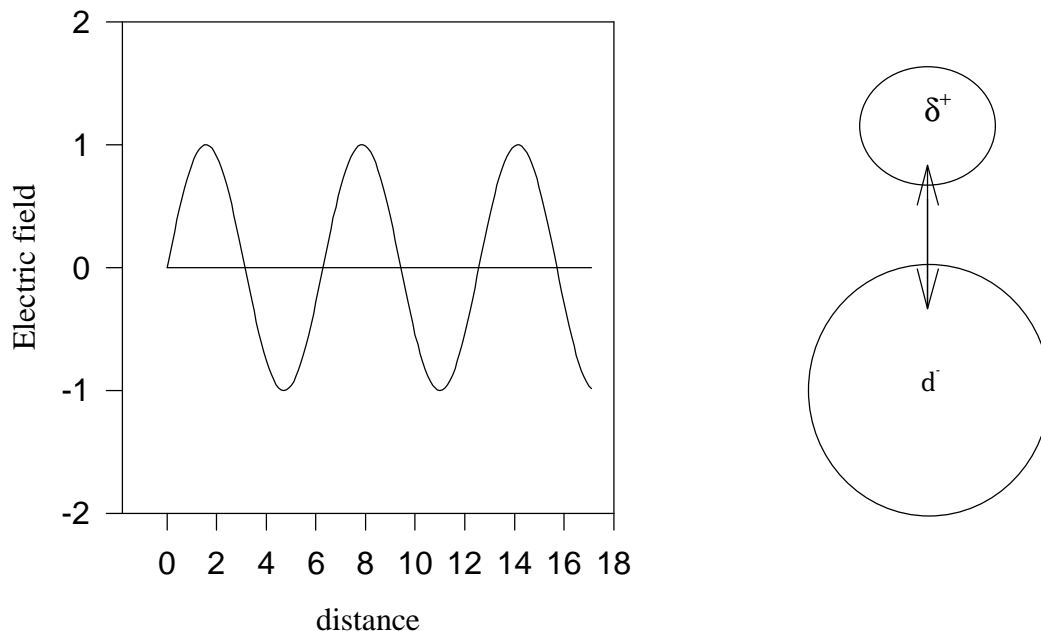


Figure 5. An HBr molecule interacting with electromagnetic radiation. In order for this interaction to occur successfully, the frequency of the light must equal the natural vibrational frequency of the HBr and the electric field must be properly orientated.

We have previously discussed the infrared region of the electromagnetic spectrum in terms of the wavelength of the light that is involved, $1\text{-}40\ \mu$ ($(1\text{-}40)\times 10^{-4}\ \text{cm}$) (Figure 3). According to equation 4, we can also express this region of the electromagnetic spectrum in terms of the frequency of the light. There is an advantage to discussing the absorption of infrared radiation in frequency units. According to equation 5, energy is directly proportional to frequency. The energy associated with an absorption occurring at twice the frequency of another can be said to require twice the energy. Occasionally, weak bands occur at twice the frequency of more intense bands. These are called overtones and result when the vibrational quantum number changes by +2. While these transitions are weak and are theoretically forbidden (i.e. they occur with an intensity of less than 5 % of the same transition that involves a change of +1 in the vibrational quantum number) they are easy to identify when units of frequency are used. Sometimes absorption bands involving a combination of frequencies occur. There is no physical significance to adding together wavelengths - there is a physical significance to the addition of frequencies since they are directly proportional to energy. To convert wavelength to frequency according to equation 4, we need to multiply the speed of light by the reciprocal of wavelength. Since the speed of light is a universal constant, a curious convention of simply using the reciprocal of wavelength has evolved. Thus a peak at 5

μ would be expressed as $1/(5 \times 10^{-4} \text{ cm})$ or 2000 cm^{-1} . You will note that 2000 cm^{-1} is not a true frequency. A true frequency would have units of cycles/sec. To convert 2000 cm^{-1} to a true frequency one would need to multiply by the speed of light (cm/sec). However, 2000 cm^{-1} is proportional to frequency and this is how frequency units in infrared spectroscopy are expressed.

At this point we are ready to leave diatomic molecules and start talking about complex organic molecules. Before doing so, it should be pointed out that the discussion that follows is an over simplification of the true vibrational behavior of molecules. Many vibrational motions of molecules are motions that involve the entire molecule. Analyze of such motions can be very difficult if you are dealing with substances of unknown structure. Fortunately, the infrared spectrum can be divided into two regions, one called the functional group region and the other the fingerprint region. The functional group region is generally considered to range from 4000 to approximately 1500 cm^{-1} and all frequencies below 1500 cm^{-1} are considered characteristic of the fingerprint region. The fingerprint region involves molecular vibrations, usually bending motions, that are characteristic of the entire molecule or large fragments of the molecule. Hence the origin of the term. Used together, both regions are very useful for confirming the identity of a chemical substance. This is generally accomplished by comparison to an authentic spectrum. As you become more proficient in analyzing infrared spectra, you may begin to assign bands in this region. However, if you are just beginning to interpret spectra of organic molecules, it is best to focus on identifying the characteristic features in the functional group region. The functional group region tends to include motions, generally stretching vibrations, that are more localized and characteristic of the typical functional groups found in organic molecules. While these bands are not very useful in confirming identity, they do provide some very useful information about the nature of the components that make up the molecule. Perhaps most importantly, the frequency of these bands are reliable and their presence or absence can be used confidently by both the novice and expert interpreter of infrared spectra. The discussion which follows focuses primarily on the functional group region of the spectrum. Some functional groups are discussed in more detail than others. You will find that all this information is summarized in Table 1 which should prove useful to you when you try to interpret an unknown spectrum. Finally, you should bear in mind that although we have developed a model that can help us understand the fundamental processes taking place in infrared spectroscopy, interpretation of spectra is to a large extent an empirical science. Information about the nature of a compound can be extracted not only from the frequencies that are present but also by peak shape and intensity. It is very difficult to convey this information in Table form. It is only by examining real spectra will you develop the expertise to accurately interpret the information contained within. Be sure to examine the spectra contained in this handout carefully. Whenever you interpret a spectrum and extract structural information, check your assignments by examining the spectrum of a known substance that has similar structural features.

Carbon-Hydrogen Stretching Frequencies

Let's take one more look at equation 6 and consider the carbon-hydrogen stretching frequencies. Since k and m_H are the only two variables in this equation, if we assume that all C-H stretching force constants are similar in magnitude, we would expect the stretching frequencies of all C-H bonds to be similar. This expectation is based on the fact that the mass of a carbon atom

Table 1. A summary of the principle infrared bands and their assignments. R is an aliphatic group.

Functional Group	Type		Frequencies cm ⁻¹	Peak Intensity	Examples Figure No.
C-H	sp ³ hybridized	R ₃ C-H	2850-3000	M(sh)	6, 18, 22
	sp ² hybridized	=CR-H	3000-3250	M(sh)	7, 13, 42
	sp hybridized	≡C-H	3300	M-S(sh)	13
	aldehyde C-H	H-(C=O)R	2750, 2850	M(sh)	14, 15
N-H	primary amine, amide	RN-H ₂ , RCON-H ₂	3300, 3340	S,S(br)	18, 19
	secondary amine, amide	RNR-H, RCON-HR	3300-3500	S(br)	20, 21
	tertiary amine, amide	RN(R ₃), RCONR ₂	none		22, 23
O-H	alcohols, phenols	free O-H	3620-3580	W(sh)	17, 24, 25
		hydrogen bonded	3600-3650	S(br)	24, 25, 28
C≡N	carboxylic acids	R(C=O)O-H	3500-2400	S(br)	26, 27, 29, 30
	nitriles	RC≡N	2280-2200	S(sh)	31
C≡C	acetylenes	R-C≡C-R	2260-2180	W(sh)	32
		R-C≡C-H	2160-2100	M(sh)	13
C=O	aldehydes	R(C=O)H	1740-1720	S(sh)	14
	ketones	R(C=O)R	1730-1710	S(sh)	35
	esters	R(CO ₂)R	1750-1735	S(sh)	33, 34
	anhydrides	R(CO ₂ CO)R	1820, 1750	S, S(sh)	36
	carboxylates	R(CO ₂)H	1600, 1400	S,S(sh)	37
C=C	olefins	R ₂ C=CR ₂	1680-1640	W(sh)	10, 39, 40
		R ₂ C=CH ₂	1600-1675	M(sh)	9, 35
		R ₂ C=C(OR)R	1600-1630	S(sh)	41
-NO ₂	nitro groups	RNO ₂	1550, 1370	S,S(sh)	28

and whatever else is attached to the carbon is much larger the mass of a hydrogen. The reduced mass for vibration of a hydrogen atom would be approximately the mass of the hydrogen atom which is independent of structure. All C-H stretching frequencies are observed at approximately 3000 cm⁻¹, exactly as expected. Fortunately, force constants do vary some with structure in a fairly predictable manner and therefore it is possible to differentiate between different types of C-H bonds. You may recall in your study of organic chemistry, that the C-H bond strength increased as the s character of the C-H bond increased. Some typical values are given below in Table 2 for various hybridization states of carbon. Bond strength and bond stiffness measure different properties. Bond strength measures the depth of the potential energy well associated with a C-H. Bond stiffness is a measure of how much energy it takes to compress or stretch a bond. While these are different properties, the stiffer bond is usually associated with a deeper potential energy surface. You will note in Table 2 that increasing the bond strength also increases the C-H bond stretching frequency.

Table 2. Carbon Hydrogen Bond Strengths as a Function of Hybridization

Type of C-H bond		Bond Strength kcal/mol	IR Frequency cm ⁻¹
sp ³ hybridized C-H	CH ₃ CH ₂ CH ₂ -H	99	<3000
sp ² hybridized C-H	CH ₂ =CH-H	108	>3000
sp hybridized C-H	HC≡C-H	128	3300

C-H sp³ hybridization

Methyl groups, methylene groups and methine hydrogens on sp³ carbon atoms all absorb between 2850 and 3000 cm⁻¹. While it is sometimes possible to differentiate between these types of hydrogen, the beginning student should probably avoid this type of interpretation. It should be pointed out however, that molecules that have local symmetry, will usually show symmetric and asymmetric stretching frequencies. Take, for example, a CH₂ group. It is not possible to isolate an individual frequency for each hydrogen. These two hydrogens will couple and will show two stretching frequencies, a symmetric stretching frequency in which stretching and compression of both hydrogens occurs simultaneously, and an asymmetric stretching frequency in which stretching of one hydrogen is accompanied by compression of the other. While these two motions will occur at different frequencies, both will be found between the 2850-3000 cm⁻¹ envelope. This behavior is found whenever this type of local symmetry is present. We will find other similar examples in the functional groups we will be discussing. Some examples of spectra containing only sp³ hybridization can be found in Figures 5-6, and located at the end of this discussion. These peaks are usually sharp and of medium intensity. Considerable overlap of several of these bands usually results in absorption that is fairly intense and broad in this region.

C-H sp² hybridization

Hydrogens attached to sp² carbons absorb at 3000-3250 cm⁻¹. Both aromatic and vinylic carbon hydrogen bonds are found in this region. Examples of spectra that contain only sp² hybridization can be found in Figure 7. Examples of molecules that contain only sp² C-H bonds along with other functional groups include Figures 23, 24 and 25. Examples of hydrocarbons that contain both sp² and sp³ hybridization can be found in Figures 8-12. These peaks are usually sharp and of low to medium intensity.

check fig 23-25

C-H sp hybridization

Hydrogens attached to sp carbons absorb at 3300 cm⁻¹. An examples of a spectrum that contains sp hybridization can be found in Figure 13. These peaks are usually sharp and of medium to strong intensity.

C-H aldehydes

Before concluding the discussion of the carbon hydrogen bond, one additional type of C-H stretch can be distinguished, the C-H bond of an aldehyde. The C-H stretching frequency appears as a doublet, at 2750 and 2850 cm^{-1} . Examples of spectra that contain a C-H stretch of an aldehyde can be found in Figures 14 and 15.

C-H exceptions

In summary, it is possible to identify the type of hydrogen based on hybridization by examining the infrared spectra in the 3300 to 2750 cm^{-1} region. Before concluding, we should also mention some exceptions to the rules we just outlined. Cyclopropyl hydrogens which are formally classified as sp^3 hybridized actually have more s character than 25 %. Carbon-hydrogen frequencies greater than 3000 cm^{-1} are observed for these stretching vibrations. Halogen substitution can also affect the C-H stretching frequency. The C-H stretching frequencies of hydrogens attached to a carbon also bearing halogen substitution can also be shifted beyond 3000 cm^{-1} . This is illustrated in Figure 16. The last exception we will mention is an interesting case in which the force constant is increased because of steric interactions. The infrared spectrum of tri-*t*-butylcarbinol is given in Figure 17. In this case, the hydrogens are sp^3 hybridized but stretching the C-H bonds leads to increased crowding and bumping, and this is manifested by a steeper potential energy surface and an increase in k , the force constant in equation 6.

Nitrogen Hydrogen Stretching Frequencies

Much of what we have discussed regarding C-H stretching frequencies is also applicable here. There are three major differences between the C-H and N-H stretching frequencies. First, the force constant for N-H stretching is stronger, there is a larger dipole moment associated with the N-H bond, and finally, the N-H bond is usually involved in hydrogen bonding. The stronger force constant leads to a higher frequency for absorption. The N-H stretching frequency is usually observed from 3500-3200 cm^{-1} . The larger dipole moment leads to a stronger absorption and the presence of hydrogen bonding has a definite influence on the band shape and frequency position. The presence of hydrogen bonding has two major influences on spectra. First, its presence causes the a shift toward lower frequency of all functional groups that are involved in hydrogen bonding and second, the peaks are generally broadened. Keep these two factors in mind as you examine the following spectra, regardless of what atoms and functional groups are involved in the hydrogen bonding.

The N-H stretching frequency is most frequently encountered in amines and amides. The following examples will illustrate the behavior of this functional group in a variety of circumstances.

Primary amines and amides derived from ammonia

The N-H stretching frequency in primary amines and in amides derived from ammonia have the same local symmetry as observed in CH_2 . Two bands, a symmetric and an asymmetric stretch

are observed. It is not possible to assign the symmetric and asymmetric stretches by inspection but their presence at approximately 3300 and 3340 cm^{-1} are suggestive of a primary amine or amide. These bands are generally broad and a third peak at frequencies lower than 3300 cm^{-1} , presumably due to hydrogen bonding, is also observed. This is illustrated by the spectra in Figures 18 and 18 for n-butyl amine and benzamide.

Secondary amines and amides

Secondary amines and amides show only one peak in the infrared. This peak is generally in the vicinity of 3300 cm^{-1} . This is illustrated in Figures 20 and 21. Again notice the effect of hydrogen bonding on the broadness of the N-H peak.

Tertiary amines and amides

Tertiary amines and amides from secondary amines have no observable N-H stretching band as is illustrated in Figures 22 and 23.

N-H bending motions

You may recall that we will be ignoring most bending motions because these occur in the fingerprint region of the spectrum. One exception is the N-H bend which occurs at about 1600 cm^{-1} . This band is generally very broad and relatively weak. Since many other important bands occur in this region it is important to note the occurrence of this absorption lest it be mistakenly interpreted as another functional group. Figure 18 illustrates the shape and general intensity of the bending motion. Most other functional groups absorbing in this region are either sharper or more intense.

Hydroxyl Stretch

The hydroxyl stretch is similar to the N-H stretch in that it hydrogen bonds but does so more strongly. As a result it is often broader than the N-H group. In those rare instances when it is not possible to hydrogen bond, the stretch is found as a relative weak to moderate absorption at 3600-3650 cm^{-1} . In tri-t-butylmethanol where steric hindrance prevents hydrogen bonding, a peak at 3600 cm^{-1} is observed as shown in Figure 17. Similarly for hexanol, phenol, and hexanoic acid, Figures 24, 25, and 26, gas phase and liquid phase spectra illustrate the effect of hydrogen bonding on both the O-H stretch and on the rest of the spectrum. It should be pointed out that, in general, while gas phase spectra are usually very similar, frequencies are generally shifted to slightly higher values in comparison to condensed phase spectra. Gas phase spectra that differ significantly from condensed phase spectra are usually taken as evidence for the presence of some sort of molecular association in the condensed phase.

The hydroxyl group in phenols and alcohols usually is found as a broad peak centered at about 3300 cm^{-1} in the condensed phase as noted above and in the additional examples of Figures 24, 28, and 29. The O-H of a carboxylic acid, so strongly associated that the O-H absorption in these materials, is often extended to approximately 2500 cm^{-1} . This extended absorption is clearly

observed in Figures 26, 27, and 29 and serves to differentiate the O-H stretch of a carboxylic acid from that of an alcohol or phenol. In fact, carboxylic acids associate to form intermolecular hydrogen bonded dimers both in the solid and liquid phases.

The nitrile group

The nitrile group is another reliable functional group that generally is easy to identify. There is a significant dipole moment associated with the $C\equiv N$ bond which leads to a significant change when it interacts with infrared radiation usually leading to an intense sharp peak at 2200-2280 cm^{-1} . Very few other groups absorb at this region with this intensity. The only exception to this is if another electronegative atom such as a halogen is attached to the same carbon as the nitrile group. The spectrum in Figure 31 illustrates the typical behavior of this functional group.

The carbon-carbon triple bond

The $C\equiv C$ bond is not considered to be a very reliable functional group. This stems in part by considering that the reduced mass in equation 6 is likely to vary. However it is characterized by a strong force constant and because this stretching frequency falls in a region where very little else absorbs, 2100-2260 cm^{-1} , it can provide useful information. The terminal carbon triple bond ($C\equiv C-H$) is the most reliable and easiest to identify. We have previously discussed the C-H stretching frequency; coupled with a band at 3300 cm^{-1} , the presence of a band at approximately 2100 cm^{-1} is a strong indication of the $-C\equiv C-H$ group. The spectrum in Figure 13 illustrates the presence of this group.

An internal $-C\equiv C-$ is more difficult to identify and is often missed. Unless an electronegative atom such as nitrogen or oxygen is directly attached to the sp hybridized carbon, the dipole moment associated with this bond is small; stretching this bonds also leads to a very small change. In cases where symmetry is involved, such as in diethyl acetylenedicarboxylate, Figure 32, there is no change in dipole moment and this absorption peak is completely absent. In cases where this peak is observed, it is often weak and difficult to identify with a high degree of certainty.

The carbonyl group

The carbonyl group is probably the most ubiquitous group in organic chemistry. It comes in various disguises. The carbonyl is a polar functional group that frequently is the most intense peak in the spectrum. We will begin by discussing some of the typical acyclic aliphatic molecules that contain a carbonyl group. We will then consider the effect of including a carbonyl as part of a ring and finally we will make some comments of the effect of conjugation on the carbonyl frequency.

Acyclic aliphatic carbonyl groups

Esters, aldehydes, and ketones

Esters, aldehydes, and ketones are frequently encountered examples of molecules exhibiting a C=O stretching frequency. The frequencies, 1735, 1725, 1715 cm^{-1} respectively, are too close to allow a clear distinction between them. However, aldehydes can be distinguished by examining both the presence of the C-H of an aldehyde (2750, 2850 cm^{-1}) and the presence of a carbonyl group. Examples of some aliphatic esters, aldehydes and ketones are given in Figures 14, 33, 34, 36, and 36, respectively.

Carboxylic acids, amides and carboxylic acid anhydrides

Carboxylic acids, amides and carboxylic acid anhydrides round out the remaining carbonyl groups frequently found in aliphatic molecules. The carbonyl frequencies of these molecules, 1700-1730 (carboxylic acid), 1640-1670 (amide) and 1800-1830, 1740-1775 cm^{-1} (anhydride), allow for an easy differentiation when the following factors are also taken into consideration.

A carboxylic acid can easily be distinguished from all the carbonyl containing functional groups by noting that the carbonyl at 1700-1730 cm^{-1} is strongly hydrogen bonded and broadened as a result. In addition it contains an O-H stretch which shows similar hydrogen bonding as noted above. Spectra which illustrate the effect of hydrogen bonding include Figures 27, and 29.

Amides are distinguished by their characteristic frequency which is the lowest carbonyl frequency observed for an uncharged molecule, 1640-1670 cm^{-1} (Amide I). In addition, amides from ammonia and primary amines exhibit a weaker second band (Amide II) at 1620-1650 cm^{-1} and 1550 cm^{-1} respectively, when the spectra are run on the solids. Amides from secondary amines do not have a hydrogen attached at nitrogen and do not show an Amide II band. The Amide I band is mainly attributed to the carbonyl stretch. The Amide II involves several atoms including the N-H bond. We will return to the frequency of the amide carbonyl when we discuss the importance of conjugation and the effect of resonance on carbonyl frequencies. The spectra of benzamide, a conjugated amide (Figure 19), and N-methyl acetamide (Figure 21) clearly identify the Amide I and II bands. The spectrum of N,N dimethyl acetamide (Figure 23) illustrates an example of an amide from a secondary amine.

Anhydrides can be distinguished from other simple carbonyl containing compounds in that they contain and exhibit two carbonyl frequencies. However, these frequencies are not characteristic of each carbonyl. Rather they are another example of the effects of local symmetry similar to what we have seen for the CH_2 and NH_2 groups. The motions involved here encompass the entire anhydride ($-\text{O}=\text{C}-\text{O}-\text{C}=\text{O}-$) in a symmetric and asymmetric stretching motion of the two carbonyls. The two carbonyl frequencies often differ in intensity. It is not possible to assign the peaks to the symmetric or asymmetric stretching motion by inspection nor to predict the more intense peak. However, the presence of two carbonyl frequencies and the magnitude of the higher frequency (1800 cm^{-1}) are a good indication of an anhydride. Figure 36 contains a spectrum of an aliphatic anhydride.

Cyclic aliphatic carbonyl containing compounds

The effect on the carbonyl frequency as a result of including a carbonyl group as part of a ring is usually attributed to ring strain. Generally ring strain is believed to be relieved in large rings because of the variety of conformations available. However as the size of the ring gets smaller, this option is not available and a noticeable effect is observed. The effect of increasing ring strain is to increase the carbonyl frequency, independent of whether the carbonyl is a ketone, part of a lactone, anhydride or lactam. The carbonyl frequencies for a series cyclic compounds is summarized in Table 3.

Table 3. The Effect of Ring Strain on the Carbonyl Frequencies of Some Cyclic Molecules

Ring Size	ketone:	cm ⁻¹	lactones:	cm ⁻¹	lactams:	cm ⁻¹
3	cyclopropanone:	1800				
4	cyclobutanone:	1775	β-propiolactone:	1840		
5	cyclopentanone:	1751	γ-butyrolactone:	1750	γ-butyrolactam:	1690
6	cyclohexanone:	1715	δ-valerolactone:	1740	δ-valerolactam:	1668
7	cycloheptanone:	1702	ε-caprolactone:	1730	ε-caprolactam:	1658

Carbon carbon double bond

Like the C≡C bond, the C=C bond stretch is not a very reliable functional group. However, it is also characterized by a strong force constant and because of this and because the effects of conjugation which we will see can enhance the intensity of this stretching frequency, this absorption can provide useful and reliable information.

Terminal C=CH₂

In simple systems, the terminal carbon carbon double bond (C=C-H₂) is the most reliable and easiest to identify since the absorption is of moderate intensity at 1600-1675 cm⁻¹. We have previously discussed the C-H stretching frequency of an sp² hybridized C-H. The spectrum in Figure 9 illustrates the presence of this group. In addition the terminal C=CH₂ is also characterized by a strong band at approximately 900 cm⁻¹. Since this band falls in the fingerprint region, some caution should be exercised in its identification.

Internal C=C

An internal non-conjugated C=C is difficult to identify and can be missed. The dipole moment associated with this bond is small; stretching this bonds also leads to a very small change. In cases where symmetry is involved, such as in 4-octene, Figure 10, there is no change in dipole moment and this absorption peak is completely absent. In cases where this peak is observed, it is often weak. In 2,5-dihydrofuran, Figure 39, it is difficult to assign the C=C stretch because of the presence of other weak peaks in the vicinity. The band at approximately 1670 cm⁻¹ may be the

C=C stretch. In 2,5-dimethoxy-2,5-dihydrofuran, Figure 40, the assignment at 1630 cm^{-1} is easier but the band is weak.

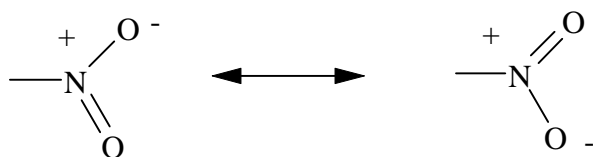
There is one circumstance that can have a significant effect on the intensity of both internal and terminal olefins and acetylenes. Substitution of a heteroatom directly on the unsaturated carbon to produce, for example, a vinyl or acetylenic ether, or amine leads to a significant change in the polarity of the C=C or C \equiv C bond and a substantial increase in intensity is observed. The C=C in 2,3-dihydrofuran is observed at 1617.5 cm^{-1} and is one of the most intense bands in the spectrum (Figure 41). Moving the C=C bond over one carbon gives 2,5-dihydrofuran attenuates the effect and results in a weak absorption (Figure 39).

Aromatic ring breathing motions

Benzene rings are encountered frequently in organic chemistry. Although we may write benzene as a six membered ring with three double bonds, most are aware that this is not a good representation of the structure of the molecule. The vibrational motions of a benzene ring are not isolated but involve the entire molecule. To describe one of the fundamental motions of benzene, consider imaginary lines passing through the center of the molecule and extending out through each carbon atom and beyond. A symmetric stretching and compression of all the carbon atoms of benzene along each line is one example of what we might describe as a ring breathing motion. Simultaneous expansions and compressions of these six carbon atoms lead to other ring breathing motions. These vibrations are usually observed between 1450 and 1600 cm^{-1} and often lead to four observable absorptions of variable intensity. As a result of symmetry, benzene, Figure 7, does not exhibit these bands. However most benzene derivatives do and usually 2 or 3 of these bands are sufficiently separate from other absorptions that they can be identified with a reasonable degree of confidence. The least reliable of these bands are those observed at approximately 1450 cm^{-1} where C-H bending motions are observed. Since all organic molecules that contain hydrogen are likely to have a C-H bond, absorptions observed at 1450 cm^{-1} are not very meaningful and should usually be ignored. Two of the four bands around 1600 cm^{-1} are observed in *ortho* and *meta* xylene, identified by the greek letter ϕ and a third band at about 1500 cm^{-1} is assigned (Figure 11 and 12). We will return to a discussion of these bands when we discuss the effects of conjugation on the intensities of these motions.

Nitro group

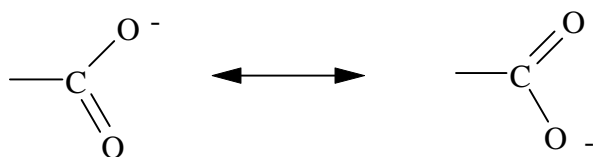
The final functional group we will include in this discussion is the nitro group. In addition to being an important functional group in organic chemistry, it will also begin our discussion of the importance of using resonance to predict effects in infrared spectroscopy. Let's begin by drawing a Kekule or Lewis structure for the nitro group. You will find that no matter what you do, it will be necessary to involve all 5 valence



electrons of nitrogen and use them to form the requisite number of bonds to oxygen. This will lead to a positive charge on nitrogen and a negative charge on one oxygen. As a result of resonance, we will delocalize the negative charge on both oxygens and as shown, this leads to an identical structure. Since the structures are identical, we would expect the correct structure to be a resonance hybrid of the two. In terms of geometry, we would expect the structure to be a static average of the two geometric structures both in terms of bond distances and bond angles. Based on what we observed for the CH_2 and NH_2 stretch, we would expect a symmetric and an asymmetric stretch for the N-O bond in the nitro group halfway between the $\text{N}=\text{O}$ and $\text{N}-\text{O}$ stretches. Since both of those functional groups are not covered in this discussion, we will need to assume for the present that this is correct. Two strong bands are observed, one at $1500\text{-}1600\text{ cm}^{-1}$ and a second between $1300\text{-}1390\text{ cm}^{-1}$, Figure 28.

Effect of resonance and conjugation on infrared frequencies

Let's continue our discussion of the importance of resonance but shift from the nitro group to the carboxylate anion. The carboxylate anion is represented as a resonance hybrid by the following figure:

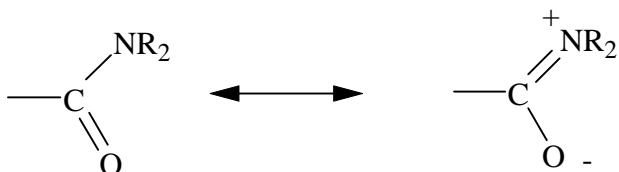


Unlike the nitro group which contained functional groups we will not be discussing, the carboxyl group is made up of a resonance hybrid between a carbon oxygen single bond and a carbon oxygen double bond. According to resonance, we would expect the C-O bond to be an average between a single and double bond or approximately equal to a bond and a half. We can use the carbonyl frequency of an ester of 1735 cm^{-1} to describe the force constant of the double bond. We have not discussed the stretching frequency of a C-O single bond for the simple reason that it is quite variable and because it falls in the fingerprint region. However the band is known to vary from 1000 to 1400 cm^{-1} . For purposes of this discussion, we will use an average value of 1200 cm^{-1} . The carbonyl frequency for a bond and a half would be expected to fall halfway between 1735 and 1200 or at approximately 1465 cm^{-1} . The carboxyl group has the same symmetry as the nitro and CH_2 groups. Both a symmetric and asymmetric stretch should be observed. The infrared spectrum of sodium benzoate is given in Figure 42. An asymmetric and symmetric stretch at 1410 and 1560 cm^{-1} is observed that averages to 1480 cm^{-1} , in good agreement with the average frequency predicted for a carbon oxygen bond with a bond order of 1.5. While this is a qualitative argument, it is important to realize that the carboxylate anion does not show the normal carbonyl and normal C-O single bond stretches (at approximately 1700 and 1200 cm^{-1}) suggested by each of the static structures above.

In the cases of the nitro group and the carboxylate anion, both resonance forms contribute equally to describing the ground state of the molecule. We will now look at instances where two or more resonance forms contribute unequally to describing the ground state and how these resonance forms can effect the various stretching frequencies.

Carbonyl frequencies

Most carbonyl stretching frequencies are found at approximately 1700 cm^{-1} . A notable exception is the amide carbonyl which is observed at approximately 1600 cm^{-1} . This suggests that the following resonance form makes a significant contributions to describing the ground state of amides:



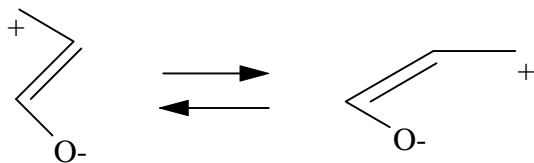
You may recall that resonance forms that lead to charge separation are not considered to be very important. However the following information support the importance of resonance in amides. X-ray crystal structures of amides show that in the solid state the amide functional group is planar. This suggests sp^2 hybridization at nitrogen rather than sp^3 . In addition the barrier to rotation about the carbon nitrogen bond has been measured. Unlike the barrier of rotation of most aliphatic C-N bonds which are of the order of a few kcal/mol, the barrier to rotation about the carbon nitrogen bond in dimethyl formamide is approximately 18 kcal/mol. This suggests an important contribution of the dipolar structure to the ground state of molecule and the frequency of 1600 cm^{-1} , according to the arguments given above for the carboxylate anion, is consistent with more C-O single bond character than would be expected otherwise.

Conjugation of a carbonyl with an C=C bond is thought to lead to an increase in resonance interaction. Again the resonance forms lead to charge separation which clearly de-emphasizes their importance.



However this conjugative interaction is useful in interpreting several features of the spectrum. First it predicts the small but consistent shift of approximately 10 cm^{-1} to lower frequency, observed when carbonyls are conjugated to double bonds or aromatic rings. This feature is summarized in Table 4 for a variety of carbonyl groups. Next the dipolar resonance form suggests a more polar C=C than that predicted for an unconjugated C=C. In terms of the change in dipole moment, contributions from this structure suggests that the intensity of infrared absorption of a C=C double bond would increase relative to an unconjugated system. Comparison of Figures 9, 10 and 35 with Figures 43, and 44-47 shows this to be the case. Conjugation is associated with an increase in intensity of the C=C stretching frequency. Finally, examination of Figures 43-46 reveals an intricacy not previously observed with simple non-conjugated carbonyls. The carbonyls of Figures 43-46 which are all conjugated appear as multiplets while those unconjugated carbonyls such as those in Figures 14 and 35 appear as single frequencies. Note however that not all conjugated carbonyls appear as multiplets (Figures 15 and 47. Resolution of this additional complicating feature can be achieved if we consider that conjugation requires a fixed conformation. For most

conjugated carbonyls, two or more conformations are possible. The *s-cis* form is shown above and the *s-trans* form is shown below.



If the resonance interaction in these two forms differ, the effect of resonance on the carbonyl will differ leading to similar but different frequencies. The presence of multiple carbonyl frequencies is a good indication of a conjugated carbonyl. In some conjugated systems such as benzaldehyde and benzyl 4-hydroxyphenylketone (Figures 15 and 47), only one conformation by symmetry is possible and conjugation does not lead to any additional carbonyl frequencies.

Table 4. The effect of conjugation on carbonyl frequencies.

Non-conjugated Compound	Frequency cm ⁻¹	Conjugated Compound	Frequency cm ⁻¹	Frequency cm ⁻¹	
butanal	1725	2-butenal	1691	benzaldehyde	1702
2-butanone	1717	methyl vinyl ketone	1700, 1681	acetophenone	1685
propanoic acid	1715	propenoic acid	1702	benzoic acid	1688
ethyl propionate	1740	ethyl acrylate	1727	ethyl benzoate	1718
butanoic anhydride	1819	2-butenic anhydride	1782	benzoic anhydride	1786
	1750		1722		1726
<i>cis</i> -cyclohexane-1,2-dicarboxylic anhydride	1857	1-cyclohexene-1,2-dicarboxylic anhydride	1844	phthalic anhydride	1852
	1786		1767		1762

Experimental infrared spectra

Up to now we have been focusing in on theory and interpretation of infrared spectra. At this point we should spend some time discussing the practical aspects of how infrared spectra are obtained and the factors to take into consideration when trying to interpret the results. Let's first start by considering gas phase spectra.

Cells and gas phase spectra

These type of spectra were more a curiosity and of theoretical interest until the introduction of the combined techniques of gas chromatography-Fourier transfer infrared spectroscopy (GC-FTIR). The major advantages of this method is that spectra can be obtained on micrograms of material and the spectra do not show the effects of interactions between molecules characteristic of condensed phase spectra. These spectra are usually obtained at elevated temperatures. Condensed phase spectra however will continue to be important because of the fact that many compounds do not survive injection into a gas chromatograph. Currently, most

frequency correlations for various functional groups are reported for the condensed phase. Frequencies observed in the gas phase are usually slightly higher than those observed for the same functional group in the condensed phase.

Gas phase spectra can also be taken at room temperature. All that is needed is a sample with a vapor pressure of several millimeters and a pathlength of about a decimeter (10 cm). Cells with NaCl or KBr windows are commercially available or can be built easily. Crystals of KBr are transparent from 4000-250 cm^{-1} and are perfectly acceptable for most uses. They have the disadvantage of being hygroscopic and must be stored in a desiccator. Cells of sodium chloride are transparent from 4000-600 cm^{-1} , less expensive and less hygroscopic. These cells are also acceptable for routine spectra.

Cells and condensed phase spectra

Condensed phase spectra can be taken as a solid or as a liquid. Comparison of the same sample in the liquid and solid phase will differ. However the major differences observed will be in the fingerprint region. In cases where infrared spectroscopy is used as a criteria of identity, the spectra under comparison should be obtained under identical experimental conditions. Liquid phase spectra are the easiest to obtain. All that is needed are two polished disks of NaCl or KBr, both commercially available. A thin film is prepared by depositing a drop of the liquid between the two plates and mounting them in the beam of the spectrometer. This is referred to as a neat liquid. Glass is not a useful material in infrared spectroscopy because of the strong absorptions due to the Si-O group. The infrared spectrum of quartz is shown in Figure 49.

Spectra of solids can be obtained in a variety of ways. The method of choice varies depending on the physical properties of the material under consideration. We will list several methods that can be used satisfactorily along with the limitations and advantages of each.

Neat Spectra (thin film)

In order to obtain an infrared spectrum of a solid, it is necessary to get light, mainly infrared through the sample. This can be achieved in various ways and we will outline some that have proven successful in the past. A thin layer of a solid deposited as a solution on an infrared cell and allowed to evaporate has proven successful with many solids. Solvents such as CHCl_3 , CH_2Cl_2 and CCl_4 have been frequently used. The solid sample should have an appreciable solubility in one of these solvents. A drop of a solution left to evaporate will deposit a thin film of crystal that will often transmit sufficient light to provide an acceptable infrared spectrum. This method suffers from the disadvantage that a spectrum of the solvent must also be run to determine whether all the solvent has evaporated.

Nujol mull

A mull is a suspension of a solid in a liquid. Under these conditions, light can be transmitted through the sample to afford an acceptable infrared spectrum. The commercial sample of Nujol, or mineral oil, which is a long chain hydrocarbon is often used for this purpose. Most solids do not dissolve in this medium but can be ground up in its presence. A small mortar and

pestle is used for this purpose. If the grinding process gives rise to small particles of solid with diameters roughly the same as the wavelength of the infrared radiation being used, 2-5 microns, these particles will scatter rather than transmit the light. The effect of poor grinding is illustrated in Figures 29 and 30 for a sample of benzoic acid. If you find this type of band distortions with either a Nujol mull or a KBr pellet (discussed below), simply continue grinding the sample up until the particles become finer.

The major disadvantage of using a Nujol mull is that the information in the C-H stretching region is lost because of the absorptions of the mulling agent. A spectrum of Nujol is shown in Figure 5. To eliminate this problem, it may be necessary to run a second spectrum in a different mulling agent that does not contain any C-H bonds. Typical mulling agents that are used for this purpose are perfluoro- or perchlorohydrocarbons. Examples include perchlorobutadiene, perfluorokerosene or a perfluorohydrocarbon oil (Figure 48).

KBr pellets

A KBr pellet is a dilute suspension of a solid in a solid. It is usually obtained by first grinding the sample in anhydrous KBr at a ratio of approximately 1 part sample to 100 parts KBr. Although it is best to weigh the sample (1 mg) in the KBr (100mg), with some experience it is possible to use your judgment in assigning proportions of sample to KBr. The mixture is the ground up in an apparatus called a Wiggle-Bug, frequently used by dentists to prepare amalgams. The ground up sample mixture is then placed on a steel plate containing a paper card with a hole punched in it. The sample is placed in the hole, making sure that some sample also overlaps the paper card. Paper the thickness and consistency of a postcard is usually used and the hole is positioned on the card so that it will lie in the infrared beam when placed on the spectrometer. A second steel plate is placed over the sample and card and the steel sandwich is placed in a hydraulic press and subjected to pressures of 15000 psi for about 20 seconds. Removal of the paper card following decompression usually results in a KBr pellet that is reasonably transparent both to visible light and infrared radiation. Some trial and error may be necessary before quality pellets can be obtained routinely. Samples that are not highly crystalline sometimes prove difficult and do not produce quality pellets. However good quality spectra can be obtained on most samples. The only limitation of KBr is that it is hygroscopic. Because of this, it is usually a good idea to obtain a spectrum run as a Nujol mull on your sample as well. The two spectra should be very similar and since Nujol is a hydrocarbon and has no affinity for water, any absorption in Nujol between 3400-3600 cm^{-1} can be attributed to the sample and not to the absorption of water by KBr.

PE 1600 FT Infrared Spectrometer

The operation of the Perkin Elmer 1600 FTIR, the instrument that you will be using in this laboratory, will be demonstrated. However before learning how to use it you should familiarize yourself with some of the general operating features of the instrument and its capabilities and limitation. In addition this brief tutorial will serve as a useful reminder once you have learned how to use the instrument. A discussion of the performance of a Fourier Transfer infrared spectrometer is beyond the scope of this publication. However the following will summarize some of the

essential features of the PE 1400. To begin with the PE 1400 is a single beam instrument. Unlike a double beam instrument that simultaneously corrects for absorptions due to atmospheric water vapor and carbon dioxide, most FTIR spectrometers correct for the background absorption by storing an interferogram and background spectrum before recording your spectrum. An interferogram contains the same information as a regular spectrum, frequency vs. intensity, but this information is contained in the form of intensity vs. time. The Fourier Transform is the mathematical process which converts the information from intensity and time to intensity and frequency. One of the major advantages of a FTIR instrument, is that it takes on the order of a second to record an entire spectrum. This makes it very convenient to record the same spectrum a number of times and display an average spectrum. Since the signal to noise ratio varies as the square root of the number of scans averaged, it is easy to obtain good signal to noise on this type of instrument, even if you have very little sample. On a typical spectrum you should average at least four spectra. Be sure you average a similar number of background spectra.

Looking at the keyboard of the instrument you will find keys with a permanent function. Two functions are defined on some keys and these functions can be accessed by pressing the key directly or by a combination of the shift + function key. A number of other keys, those directly under the monitor, are defined by the screen and their function may vary depending on the screen. The instrument has four active memory sites where spectra can be stored and retrieved. These are called the background, x, y and z. Once the instrument has been turned on and has passed the self tests, it is usually a good idea to allow the infrared source to warm up for 5 min. With the sample pathway empty, pressing "scan + background + the key under the monitor prompt consistent with the number of scans you wish to average" will produce a background interferogram. Placing your sample in the beam and pressing "scan x, y, or z + the number of scans you desire" will produce an interferogram with the requisite number of scans that will be corrected for the background and displayed on the screen. You may wish to record a spectrum, make some adjustments to see if they improve the quality of the spectrum. Storing the second spectrum in a different memory region allows you to evaluate the adjustments. If the first spectrum was stored in x and the second in y, pressing x or y allows you to retrieve either.

To plot your spectrum on the HP plotter, simply turn the plotter on, load paper on the plotter, and make sure the plotter is equipped with at least one pen. Press "plot" and the monitor will tell you the number of peaks the instrument has detected that satisfy the current settings. The frequency of each peak identified as meeting these criteria will be printed out. If the number of peaks is too large or too few peaks are identified, it may be necessary to change the current setting on the instrument. Simply press "cancel + plot (the key is located on the monitor)".

To change the peak threshold, press the following keys located on the monitor: press "setup", "view", "peaks". You can change the threshold value using the number pad on the left of the console. Increasing the threshold will decrease the number of peaks while decreasing the existing value will include more peaks. Next press "execute"; and exit. Additional details and instructions are generally available at the instrument.

When you are first learning to make KBr pellets, you will be using a paper punch to produce a hole on a paper card. You will need to adjust the size and position of the hole properly

so that it will allow sufficient infrared light to pass through the card. To monitor how much radiation is reaching the detector, press "shift + monitor and then the energy key under the monitor". This will let you know how much energy is reaching the detector. With nothing else in the beam except the paper card with the hole punched in, at least 60-70% of the energy should reach the detector. If you observe a reading much less than this, you may either have to adjust the position of the aperture or enlarge it or both. The cancel key under the monitor will return you to normal mode.

The Degree of Unsaturation

Once the molecular formula of an unknown is known, it is a simple matter to determine the degree of unsaturation. The degree of unsaturation is simply the sum of the number of carbon-carbon multiple bonds and rings. Each reduces the number of hydrogens (or any other element with a valence of one) by two. There is a general formula that can be memorized and used:

unsaturation number, $U = \#C + 1 - 1/2 (X-N)$ where X=monovalent atoms, N=trivalent atoms, and C=tetravalent atoms. Note that divalent atoms are not counted.

Consider C_6Cl_6 as an example: $U = 6 + 1 - 1/2 (6-0) = 7 - 3 = 4$; the degree of unsaturation is four. An unsaturation factor of four is required for a single benzene ring.

Consider C_5H_9NO as another example. $U = 5 + 1 - 1/2 (9-1) = 2$. Clearly this compound cannot have a benzene ring but the oxygen atom could be part of a carbonyl group.

Application of the degree of unsaturation to the interpretation of an infrared spectrum is quite straightforward. Clearly some functional groups can be eliminated by composition. Amines, amides, nitriles and nitro groups can be eliminated if the molecule does not contain any nitrogen. Alternatively everything but amines can be eliminated if the molecular formula contains nitrogen and no degrees of unsaturation.

Interpretation of Infrared Spectra--A Beginner's Guide

We have just concluded a discussion of a large number of frequencies and the functional groups that are generally associated with these frequencies. At this point you may be asking yourself how to begin to interpret these frequencies with regards to obtaining information of molecular structure. There are a number of different approaches that can be used and often the best approach to use depends on the nature of the information you would like to obtain from your infrared spectrum. For example, if you are repeating a synthesis in the laboratory and you wish to determine whether you have successfully isolated the material you intended to prepare, you may be able to compare your spectrum to an infrared spectrum of an authentic sample. In this case, you are using infrared analysis for establishing the identity of your sample. Assuming that your spectrum has been run under the same conditions, as your reference, i.e. neat sample, KBr pellet, etc., you should be able to reproduce the spectrum of the reference material, peak for peak. The presence of some additional peaks in your spectrum may indicate a contamination with solvent, starting material or an impurity that has not been removed. The presence of fewer peaks than your reference is of more concern. This generally indicates a failure to obtain the desired material.

If the structure of the material of interest is unknown, then a more systematic analysis of your spectrum will be necessary. You should be aware that it is not usually possible to determine molecular structure from the infrared spectrum alone. Usually, some supplemental spectroscopic and/or structural information (such as molecular formula) is also necessary. For the unknowns in this course, you will generally be using infrared spectroscopy to differentiate between a few possible compounds. Frequently, this can be achieved by an analysis of the functional groups in your spectrum. The discussion which follows, uses a more generalized approach to analyze spectra. This approach should be applicable in a variety of different circumstances. If a portion of the discussion is not relevant to you, simply skip it and continue until it does become relevant.

The following steps should serve as a general protocol to follow and should prove useful regardless of the structure of your unknown or whether the degree of unsaturation is known.

1. Look in the carbonyl region, typically $1800\text{-}1620\text{ cm}^{-1}$, for a strong absorption band. So many classes of compounds contain a carbonyl group (carboxylic acids, esters, amides, ketones, aldehydes, etc) and the absorption is so obvious that it is the perfect starting point. If there is no carbonyl absorption, you have eliminated a large number of possibilities.

2. Examine the C-H stretching frequencies at 3000 cm^{-1} . Absorption bands at frequencies slightly larger than 3000 cm^{-1} are indicative of vinyl or/and aromatic hydrogens. The presence of these peaks should be consistent with the degree of unsaturation of your molecule. The absence of absorption above 3000 cm^{-1} but the presence of some unsaturation in the molecular formula are consistent with a cyclic compound.

If your degree of unsaturation is 4 or greater, look for 2 to 4 absorption peaks between $1600\text{-}1450\text{ cm}^{-1}$ and weak peaks at $2000\text{-}1667\text{ cm}^{-1}$. These are characteristic of aromatic compounds.

3. Next look for a doublet at 2750 and 2850 cm^{-1} characteristic of an aldehyde. The presence of these two bands should also be accompanied by a strong absorption at approximately 1700 cm^{-1} . Most spectra display strong absorption in the $1800\text{-}1700\text{ cm}^{-1}$ region. If your spectrum does, check to see if the carbonyl is a closely spaced doublet or multiplet. Closely spaced multiplicity in the carbonyl region accompanied by C-H absorption at $3000\text{-}3100\text{ cm}^{-1}$ is frequently characteristic of an α, β -unsaturated carbonyl compounds. Check to make sure that the carbonyl frequency is consistent with conjugation.

4. If your unknown contains broad absorption from $3600\text{-}3000\text{ cm}^{-1}$, your molecule could have an O-H or N-H stretch. Check the multiplicity of this peak. A doublet is characteristic of a primary amine or and amide derived from ammonia. Check the carbonyl region at around $1650\text{-}1600\text{ cm}^{-1}$. Two bands in this region are consistent of an amide from ammonia or a primary amine. Remember a broad and relatively weak band at about 1600 cm^{-1} is characteristic of N-H bending. Usually you will only see this band in amines, since that carbonyl group of the amide will interfere. Be sure to look for the effect of hydrogen bonding which usually results in a general broadening of the groups involved.

5. If the broad band starting at 3600 cm^{-1} expands to nearly 2400 cm^{-1} , look for the presence of a broad carbonyl at approximately 1700 cm^{-1} . This extremely broad OH band is only observed in carboxylic acids and enols from β -diketones. The presence of a relatively intense but broad band at approximately 1700 cm^{-1} is good evidence for a carboxylic acid.

6. Don't try to over-interpret your spectrum. Usually, it is not possible to arrive at a unique structure based on infrared analysis alone. Your goal is to determine the class of compound and other possible functional groups (eg, double bonds, benzene rings). These can be confirmed with classification tests. Sometimes, the information is confusing and you will have to determine which tests and which data are most reliable. You can learn a great deal about your unknown from your spectrum but be sure to use other important physical data such as melting point, boiling point and solubility characteristics of your unknown to assist you in narrowing down the different structural possibilities.

Question:

For a C_3H_6O compound, what is the degree of unsaturation? Write several possible structures for a compound with this molecular formula.