## Infrared Spectroscopy

BACKGROUND INFORMATION

Before introducing the subject of IR spectroscopy, we must first review some aspects of the electromagnetic spectrum. The electromagnetic spectrum is composed of energy that may behave both as a particle and as a wave. When we describe this energy as a particle, we use the word **photon**. When we describe this energy as a wave, we use the terms **frequency** (v) and **wavelength** (λ). Frequency is the number of wave troughs that pass a given point in a second and wavelength is the distance from one crest of a wave to an adjacent crest. Frequency and wavelength are inversely related, according to the equation $E = hv = hc / \lambda$. Therefore, as frequency increases, wavelength decreases. When we discuss IR spectroscopy, we introduce a new unit of measurement called the **wavenumber** (v). The wavenumber is the number of waves in one centimeter and has the units of reciprocal centimeters (cm^{-1}). Since the wavenumber is inversely proportional to wavelength, it is directly proportional to frequency and energy which makes it more convenient to use.

I. Bond Vibrations: The Basis of IR Spectroscopy

Spectroscopy is the study of matter and its interaction with electromagnetic radiation. All matter contains molecules; these molecules have bonds that are continually vibrating and moving around. These bonds can vibrate with stretch motions or bend motions. Imagine two balls attached by a spring, representing a diatomic molecule. The movement of each ball toward or away from the other ball along the line of the spring represents a **stretching vibration** (fig. 1). Stretching can either be symmetric or asymmetric. A molecule with three or more atoms can experience a **bending vibration**, a vibrational mode where the angle between atoms changes (fig. 2). In the following examples, imagine a triatomic molecule ABC.

Fig. 1: *Stretching Vibrations*

Symmetric Stretch: allows molecule to move through space

A————— B—————C

←   ←

OR

A————— B—————C

→   →
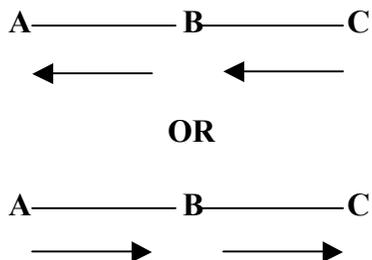
<u>Asymmetric Stretch</u>: leads to an increase or decrease in bond length

A————————B————————C

OR

A————————B————————C

Fig. 2: *Bending Vibrations*

A
  B   OR   A
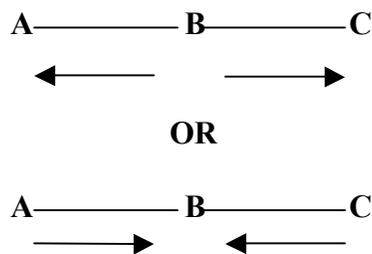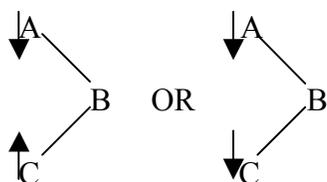C   B
                 C

Each excited vibrational state is reached when a molecule is exposed to a specific frequency. In order for a bond to be promoted to the excited state, it must be exposed to radiation of the exact same frequency as the energy difference between ground and excited states (ΔE). Determining these frequencies and representing them allows us to determine the bonds that exist in a molecule. These frequencies all lie within the **infrared** region of the electromagnetic region, a region of lower wavelength than visible light. A machine called an **IR Spectrometer** passes infrared radiation through a sample of an unknown compound and uses a detector to plot percent transmission of the radiation through the molecule versus the wavenumber of the radiation. A downward peak on the plot represents absorption at a specific wavenumber. In sum, IR spectroscopy is useful in determining chemical structure because energy that corresponds to specific values allows us to identify various functional groups within a molecule. An IR spectrum usually extends from radiation around 4000 cm^{-1} to 600 cm^{-1} and can be split into the **functional group region** and the **fingerprint region**. The fingerprint region is different for each molecule just like a fingerprint is different for each person. Two different molecules may have similar functional group regions because they have similar functional groups, but they will always have a different fingerprint region. In this course, we will only focus on the functional group region when identifying the structures of molecules. This is because the fingerprint region, which extends from about 1450 cm^{-1} to 400 cm^{-1}, is very complex. It has many absorptions and makes it quite difficult for students and scientists to make precise bond assignments. Additionally, since stretching vibrations are typically found in the functional group region, they are the most convenient vibrations to analyze when determining the types of bonds a molecule has. Thus, we tend to ignore bending vibrations because they are usually found in the fingerprint region.

II. Intensity and Position of Absorption bands

IR spectra look quite complex because the bond vibrations create **absorption bands**. The **intensity** of an absorption band depends on the change in the dipole moment of the bond and the number of the specific bonds present. The bond dipole results from two things: the bond length and the charge difference between the two atoms. When the molecule absorbs a photon, it stretches and the bond length changes. So that only leaves the charge difference, which can be derived from the electronegativity values of the atoms involved. If we have two different atoms, there will be an electronegativty difference and a photon will be absorbed. If there is no electronegativity difference, such as in an O_2 or an N_2 molecule, then a photon will not be absorbed, and the molecule will not be excited to a higher vibrational state. On the other hand, the bigger the electronegativity difference, the more intense the absorption is. Additionally, the number of the specific bond also determines the intensity of a peak. For example, if you compare the IR spectra of methane to that of octane, the octane molecule will have a much more intense C-H peak because it has many more C-H bonds than methane.

Since an IR spectrum is a plot of % transmittance vs. wavenumber, the bond vibration energies vary as you move horizontally on the graph. Thus, the horizontal position of the absorption band corresponds to a different **energy**. What molecular features determine what types of bonds or atoms exist on various positions of the spectrum? The strength of the bond and the masses of the bonded atoms are crucial in determining the stretching energy. The best way to understand the following concepts is to imagine two atoms connected by a spring. Imagine you have your bonded atoms – the stronger the bond is, the tighter the spring, and the more energy is required to stretch it. For example, triple bonds are stronger than double bonds which are in turn stronger than single bonds. Moreover, the lighter the atoms are, the more energy is required to vibrate the atoms. **Hooke's law** describes the motion of a vibrating spring and shows the relationships between the masses of the atoms (m_1, m_2), the force constant of the bond (f), and wavenumber (v):

$$ v = \frac{1}{2\pi c} \left[\frac{f\,(m_1 + m_2)}{m_1\,m_2} \right]^{1/2} $$

Hooke's Law shows that lighter atoms and stronger bonds lead to higher frequencies.

III. The Real Deal – Dr. Hardinger's Five Zone Analysis

Now the time has come – we've developed enough knowledge about molecular structure to take a look at an IR spectrum and begin to divide it into zones and analyze it for various functional groups. Ultimately, we will be able to identify the main structural features of a molecule from its IR spectrum. The following is an example of an IR spectrum. Take a look at it and become familiar with its features. Later, we will analyze this spectrum and find out what molecule it is. For now, let's break it up into five zones

and discuss the method of five zone analysis (for a more detailed explanation, refer to the thinkbook):
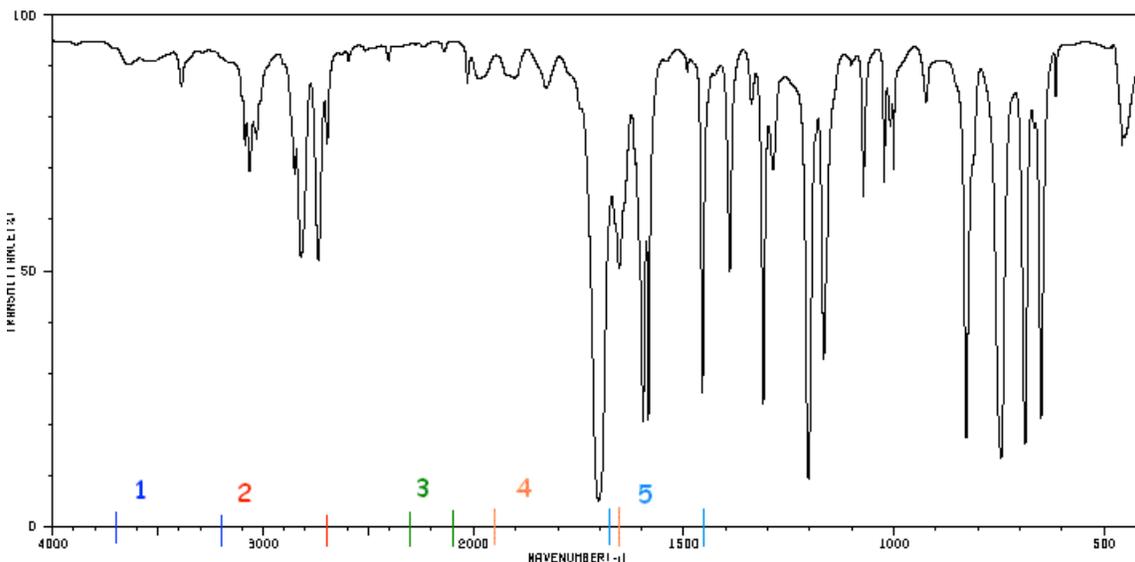
The best thing to do is become familiar with an IR spectrum before we conduct the five zone analysis. Remember, the vertical axis represents percent transmittance. The peaks show that there is low transmittance, and hence large absorption. The horizontal axis represents wavenumber, and it increases as we move to the left. Areas that do not have peaks show that photons are not being absorbed at that frequency, indicating that the specific bond at that frequency does not exist in the molecule. Now that we are familiar with the IR spectrum, let's break it up into the five zones. It may seem a little tedious, but with lots of practice, it will become like second nature. Refer to the IR spectrum above as you read. **Zone 1** extends from about 3700 to 3200 cm^{-1} and is used to locate the following bonds: the alcohol O-H, the terminal alkyne C-H, and the amine or amide N-H. The alcohol peak is usually broad and wide and can be distinguished easily. The more concentrated the solution is with O-H molecules, the more likely it is to form hydrogen bonds. Since it is easier to stretch hydrogen bonds (because the oxygen pulls away the electrons), less energy is required and the peaks appear broader. Alkyne C-H bonds have strong peaks around 3300 cm^{-1}. In **Zone 2**, absorptions by alkane C-H bonds, aryl and vinyl C-H bonds, aldehyde C-H bonds, and carboxylic acid C-H bonds can be found. The sp^3 C-H bond peaks can usually be found slightly to the right of the 3000 cm^{-1} mark. The sp^2 C-H bonds can be distinguished because they are located slightly to the left of the 3000 cm^{-1} mark. Both of these C-H bonds have many tiny peaks. Evidence of the presence of an aldehyde can be found around 2700 cm^{-1} and 2900 cm^{-1} mark. Lastly, the carboxylic acid O-H bond appears as a wide, broad peak in the spectrum. **Zone 3** reaches from 2300 to 2100 cm^{-1}. Here, we can find the absorptions of alkyne triple bonds and nitrile triple bonds. Their peaks are variable in intensity. In **Zone 4** we find absorption peaks by carbonyl double bonds. These peaks are usually very strong and intense. They allow us to identify the existence of ester, aldehyde, ketone, carboxylic acid, or amide functional groups. Here is an important note: if conjugation exists among the carbonyl group, the peak can shift 20 to 40 cm^{-1} lower because the bond has more

single bond character. Aromatic overtones, tiny peaks caused by aromatic rings, may also appear. The last zone (**Zone 5**) has absorption peaks caused by alkene double bonds and aromatic carbon –carbon bonds. Benzene has two peaks: one at around 1600 cm^{-1} and one around 1500 cm^{-1}.

IR Spectrum – Strategies

When analyzing IR spectra, it is very important to take advantage of *all* of the information you have. The best way is to prepare a chart with the five zones and the types of bonds that can be found within them. After you do this, start from the high energy end of the spectrum and begin looking for evidence. When given the chemical formula of the molecule, you can use the atomic information to eliminate functional groups. For example, if your chemical formula does not contain any nitrogen atoms, you can easily eliminate amides and amines from your zone analysis. Additionally, if you see any peaks in zone 1 but you know there are no nitrogen atoms, you will realize that the peaks are either caused by the alcohol O-H bond or the alkyne C-H bond. Another strategy is using the information you derived from one zone and applying it to another. For example, if you do not see a peak in zone 2 at approximately 2700 cm^{-1}, you automatically know that your molecule does not have any aldehyde groups; thus, if there is a peak in zone 3, you will know it wasn't caused by aldehyde because aldehyde doesn't exist! Another important tool to utilize is the double bond equivalent. If you know the molecular formula of the substance under analysis, you can use **DBE = C – H/2 + N/2 + 1** to find out the degree of unsaturation. This will tell you how many double bonds or rings the molecule will have (for more information, see the mass spectrometry section in the thinkbook). Most importantly, it is important to analyze as many IR spectrums as you can. The more you solve, the more you learn the patterns and the better you become at deriving the accurate structure.

IV. Solving the IR Spectrum Puzzle

Finally, we have acquired enough knowledge to begin analyzing IR spectra. Refer to the IR spectrum that was introduced in part **III**. Now it's your turn - get a pen and paper, write out the five zones, and begin analyzing the IR spectrum. *Here's a hint: there is only one oxygen atom in the molecule.* After your analysis is complete, look at the answer and the explanation below.

Answer: First off, we do not see anything significant in zone 1 or 3, so we can eliminate the possibility of alcohols, amines, amides, and alkynes. In zone 2, we see some important peaks. There is an sp^2 C-H peak because it's a little greater than 3000 cm^{-1}. There is a peak at 2700 cm^{-1}, telling you that there could be an aldehyde here. As we move into zone 4, we see a huge peak at around 1700 cm^{-1}. Clearly, this is the carbonyl peak. We have two important pieces of information – we know there is a peak at 2700 cm^{-1} and a carbonyl group. It is very likely that there is an aldehyde group but we cannot eliminate other possibilities just yet. In zone 2, there is no significantly broad peak so we can eliminate the possibility of there being a carboxylic acid. Let's move into zone 5. We see a peak at around 1500 cm^{-1} and around 1600 cm^{-1}. Additionally, we noted the existence of sp^2 C-H bonds in 2. This is enough information to tell us that there exists a

benzene ring in this molecule. Also, note the aromatic overtones in zone 4. Now we are faced with a little dilemma: can we be sure that we have an aldehyde? Do we have an ester, ketone, or an amide? We can safely say that we do not have an amide because there is no N-H peak in zone 1. Esters require two O atoms, and we only have one, so now we must decide between aldehyde and ketone. The peak at 2700 cm^{-1} along with the carbonyl peak is sufficient enough to tell us that we have an aldehyde. One last thing: remember the sp^2 C-H peaks? They also tell us that the molecule has an aryl group present. So what do we have? A benzene ring with an aldehyde group attached to it. Our molecule is **benzaldehyde**.

KEY TERMS
- **Photon**
- **Frequency**
- **Wavelength**
- **Wavenumber**
- **Spectroscopy**
- **Stretching vibration**
- **Bending vibration**
- **Infrared**
- **IR Spectrometer**
- **Functional group region**
- **Fingerprint region**
- **Intensity**
- **Energy**
- **Hooke's law**
- **Absorption Bands**
- **Five Zone Analysis**
- **DBE**

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