

Nuggets of Knowledge for Chapter 3 – Infrared Spectroscopy

Chem 2310

I. Introduction to Spectroscopy

Characterizing compounds

- It is often important for organic chemists to be able to identify an organic compound. In order to know its identity, we must know the complete structure of the compound. Chemists often describe this as “characterizing” a compound. The following are some examples:
 - When you run a chemical reaction, you need to be able to determine if the compound you have recovered is the expected product of the reaction.
 - If an important compound is isolated from a natural source, say, a new cancer-fighting compound from a plant, you need to be able to determine its identity.
 - If an organic compound were found as a pollutant in a lake or stream, it would be important to determine its identity.
- There are three principle ways to identify a compound: physical properties, chemical properties, and spectroscopy.
 - Physical properties include melting point, boiling point, solubility, color, etc. They are useful for confirming the identity of a compound if you already think you know what it is, but aren't much help if you are starting from scratch, since so many compounds have similar properties.
 - Chemical properties involve how a compound behaves in the presence of other chemicals. Chemical tests make use of these properties to determine the functional group of a compound, but they don't tell you the actual structure of the compound.
 - Spectroscopy involves the interaction of the compound with various kinds of light. It can give different information, depending on the type of light used.
 - Infrared spectroscopy (IR) uses infrared light and gives information about the bonds in a compound, which can be used to determine the functional group of organic compounds.
 - Nuclear magnetic resonance spectroscopy (NMR) uses radio waves, and gives information about the environment of the H's in a compound, which can be used to determine its structure.
 - Ultraviolet spectroscopy (UV) uses ultraviolet light and gives information about pi bonds in a molecule, which is helpful for certain kinds of compounds.

- Mass spectrometry (MS) uses a beam of electrons rather than light and gives information about the molecular weight of a compound as well as some structural information.
- NMR and IR will be the two that we will be concerned with in this class.

The Electromagnetic Spectrum

- Many different kinds of light are contained in the electromagnetic spectrum. The only difference is the frequency (and therefore wavelength) of the light.
 - From highest to lowest energy, the types of light include: gamma rays, x-rays, UV light, visible light, infrared light, microwaves, and radio waves.
 - Gamma rays (the highest energy light) have the shortest wavelengths and the highest frequencies. Radio waves (the lowest energy light) have the longest wavelengths and the lowest frequencies.
 - Gamma rays and x-rays are considered ionizing radiation, because they have enough energy to cause electrons to jump out of an atom, creating an ion. This is very dangerous to living tissue.
 - UV and visible light can cause electrons to jump up into higher energy levels, then fall back down again. This is how atomic absorption and UV spectroscopy work.
 - Infrared light causes changes in the vibrational energy of bonds. This is why IR spectroscopy tells you about bonds in the molecule.
 - Microwave radiation causes changes in the rotational energy of bonds. There is a spectroscopy based on this called Raman spectroscopy.
 - Radio waves can cause transitions in the energy levels of the nucleus of the atom, which is why NMR tells you about the atoms in a compound.
- The units used in IR spectroscopy to measure the frequency of the light are called wavenumbers. A wavenumber is the number of waves in a centimeter, so wavenumber has the units $1/\text{cm}$, or cm^{-1} .
 - The frequency range that we will be looking at is 4000 cm^{-1} to 400 cm^{-1} . 4000 cm^{-1} is the high energy end of the range, while 400 cm^{-1} is the low energy end of the range.

The IR Spectrometer and an IR Spectrum

- An IR spectrometer is the instrument used to take an IR spectrum (plural: spectra). IR light is shined through a sample, and the spectrum shows which frequencies of light the sample absorbed, and which passed through.

- The infrared spectrometer contains the following essential components:
 - a highly tunable laser to give out specific frequencies of infrared light
 - a sample cell which allows the light to pass through a sample of the compound
 - a detector that senses how much of each frequency of light passed through the compound without being absorbed
 - a computer which takes the information from the detector and displays it as a spectrum.
- The original IR spectrometers slowly went through all of the frequencies of IR light, recording how much passed through for each frequency. Now, however, all of the frequencies are used at once, and a complex mathematical operation called a Fourier transform separates out the frequencies afterwards, which speeds things up a lot. Infrared spectroscopy is often abbreviated FTIR because of this, even though the old kind isn't used anymore.
- On an IR spectrum, the x-axis is frequency (in wavenumbers) and the y-axis is % transmittance. The line goes across the top (where all of the light goes through), and dips down as certain frequencies are absorbed – these are called bands.
- In order for a spectrum to be taken, light must pass through the sample. Liquids are transparent and cause no difficulties, but solids are opaque, and there are several techniques which can be used to create a sample that light can pass through. The method used is often written on the spectrum, since this can have an effect on the spectrum's appearance.
 - “Thin film” or “neat”: This label is used for liquids. A few drops of the compound are placed on a transparent crystal, or between two clear plates made of salt (which doesn't absorb IR light). This makes a thin film of liquid for the light to pass through; neat simply means that nothing was mixed with the solvent.
 - “Melt”: If the solid melts near room temperature, it can be melted on a salt plate and taken while the compound is in a liquid state.
 - “Nujol mull”: A solid may also be mulled (mashed) in a hydrocarbon oil called Nujol until it becomes a transparent paste. The hydrocarbon bonds from the oil will appear in the spectrum, so you have to take this into account when reading a spectrum taken with this method.
 - “KBr pellet”: A solid may also be finely ground with potassium bromide, then pressed to become a transparent pellet. These spectra often have a flattened look on one side.

II. Molecular Vibrations

Types of Vibrations

- The reason why molecules absorb IR light is that their bonds are vibrating at the same frequency as the light. Therefore it is important to understand the vibrations that a molecule can undergo.
- There are two types of vibrations that a molecule can undergo.
 - Stretching vibrations involve changes in the length of a bond. The bond stretches and shortens at a certain frequency, like two balls connected by a spring.
 - When two bonds are attached to the same atom, their vibrations are related. There is a symmetrical stretch, in which they are in sync, and an unsymmetrical stretch, in which they are exactly opposite each other.
 - Bending vibrations involve changes in the angle between two bonds. The angles can change in the same plane as the bond, or at right angles to the bond, and can be symmetrical and unsymmetrical. The actual motion of the atoms is a combination of all of these vibrations.
 - In the plane of the bond, the symmetrical vibration is called a scissor vibration, while the unsymmetrical vibration is called a rocking vibration.
 - At right angles to the bond, the symmetrical vibration is called the wagging vibration, and the unsymmetrical vibration is called a twisting vibration.
- The more atoms in a molecule, the more complex vibrations it can have. Rather than trying to identify every vibration in a molecule, we will be looking for the ones that give us useful information.

Factors which effect a band

- There are two factors which affect how much light is absorbed (how deep the band goes down).
 - Dipole – A bond with a stronger dipole absorbs more light than a bond with a weaker dipole. In fact, a totally nonpolar bond absorbs no light, and doesn't create a band. However, even very small dipoles created by nearby atoms can cause a small band to be created.
 - Number of bonds – if the molecules contains more than one bond with the same frequency, more of this frequency of light will be absorbed.
- There are three factors which affect the frequency of a vibration (where the band falls on the spectrum).
 - Mass – bonds between lighter atoms vibrate more frequently than bonds between heavier atoms. This is most noticeable when one of the atoms is hydrogen.

- Bond order – stronger bonds vibrate faster, so triple bonds vibrate at a higher frequency than double bonds, and double bonds are at a higher frequency than single bonds.
- Type of vibration – stretching vibrations are faster than bending vibrations.

Regions of the IR Spectrum

- In practice, there are two major regions of the frequency axis – the functional group region, and the fingerprint region.
 - The functional group region goes from 4000 cm^{-1} to about 1300 cm^{-1} . This is where you can find most of the bands that indicate the functional group of the compound.
 - The fingerprint region goes from about 1300 cm^{-1} to 400 cm^{-1} . This region contains bands which are unique to the compound and are difficult to interpret. However, they can be used to match up two compounds to see if they are the same (like a fingerprint).

III. Identifying Functional Groups

- The bands which are useful for identifying functional groups occur at known frequencies, and usually have a similar appearance. All of them are stretching bands unless otherwise indicated.

<i>frequency</i>	<i>bond</i>	<i>appearance</i>
3400-3200 cm^{-1}	N-H	1 or 2 bands
3400-3200 cm^{-1}	O-H	broad, rounded, long
3400-2400 cm^{-1}	O-H on C=O	very broad, covers C-H band
$\sim 3300 \text{ cm}^{-1}$	C-H on C \equiv C (triple bond)	sharp, long
3100-3000 cm^{-1}	C-H on C=C or aromatic ring	small
3000-2850 cm^{-1}	C-H	long, sharp
2790-2720 cm^{-1}	C-H on C=O	small, often two
$\sim 2700 \text{ cm}^{-1}$	carboxylic acid dimer	small, often two, overlap O-H
2260-2200 cm^{-1}	C \equiv N	sharp, long
2200-2100 cm^{-1}	C \equiv C	sharp, small
2000-1660 cm^{-1}	aromatic overtones	4 small bands
1680-1620 cm^{-1}	C=C	small, sharp
1800-1650 cm^{-1}	C=O	large, deep
$\sim 1600 \text{ cm}^{-1}$	NH ₂ bending	wide, rounded, small
1600-1500 cm^{-1}	C=C in an aromatic ring	sharp, may be hard to find
1460, 1380 cm^{-1}	CH ₂ bending	multiple bands
1300-1000 cm^{-1}	C-O	large, deep
730-960 cm^{-1}	C=C bending	large, deep
850-500 cm^{-1}	C-Cl, C-Br	often difficult to locate

- Most compounds contain C-H and CH₂ bending bands. They can therefore serve as references. There are five general ranges that you should look at.
 - left of the C-H band (3400-3200 cm^{-1})
 - O-H, N-H, C-H on C \equiv C
 - around the C-H band (3100-2700 cm^{-1})
 - C-H on C=C or aromatic, C-H on C=O, O-H on C=O, and carboxylic acid dimer
 - in between the C-H and CH₂ bending bands (2500-2000)
 - C \equiv C, C \equiv N
 - just to the left of the CH₂ bending band (2000-1500)
 - aromatic overtones, C=O, C=C, NH₂ bending
 - to the right of the CH₂ bending band, in the fingerprint region (1300-400 cm^{-1})
 - C-O, C=C bending, C-X

- Each functional group has one or more identifying bands that you should look for:
 - alkane: C-H; CH₂ bending
 - alkene: C-H on C=C; C=C; C=C bending
 - alkyne: C-H on C≡C; C≡C
 - aromatic: C-H on C=C; C=C aromatic; aromatic overtones
 - alcohol: O-H; C-O
 - carboxylic acid: O-H on C=O; C=O; carboxylic acid dimer
 - ether: C-O
 - ketone: C=O
 - aldehyde: C-H on C=O; C=O
 - ester: C=O; C-O
 - anhydride: C=O (2); C-O
 - amine: N-H (2, 1, or 0); NH₂ bending
 - amide: N-H (2, 1, or 0); NH₂ bending; C=O
 - nitrile: C≡N
 - alkyl halide: C-X (not always visible)

IV. Interpreting an IR Spectrum

- There are so many bands on an IR spectrum that it can seem overwhelming if you don't have a step-by-step strategy for dealing with them.
- When dealing with the spectrum of a compound that you think you know what is, first identify all of the bands that should be there, then look for them.
- When dealing with the spectrum of a compound that you don't know what is, scan the spectrum from left to right, looking for the larger or more obvious bands that can give you someplace to start. Then look for other bands that narrow it down or confirm what the more obvious bands told you.
 - Examples of bands that stand out include O-H, O-H on C=O, N-H, C=O, and C---C or C---N.
 - An example of bands that narrow down the options include, when you see a C=O, look for C-H on C=O to tell you it is an aldehyde, or a C-O to tell you it is an ester.
 - An example of a band that confirms your choice is looking for a C-O band when you have found an O-H band.
- Remember that in order for a compound to have a certain functional group, it must have ALL of the bands for that functional group.
 - For example, you can't have a C-H on C=O if there is no C=O band!
- When using IR to characterize the product of a reaction, look for the bands that the product compound should have to see if that product was made. Then look for the bands that the starting material(s) should have to see if there is any left that didn't react.

IR Frequency Table by Functional Group

Alkanes	C-H 3000-2850 cm^{-1} CH ₂ bending 1460, 1380 cm^{-1}
Alkenes	C-H on C=C 3100-3000 cm^{-1} C=C 1680-1620 cm^{-1} C=C bending 960-730 cm^{-1}
Alkynes	C-H on C \equiv C ~3300 cm^{-1} C \equiv C 2200-2100 cm^{-1}
Aromatic	C-H on C=C 3100-3000 cm^{-1} C=C aromatic 1600, 1500 cm^{-1} overtones 2000-1660 cm^{-1}
Alcohols	O-H 3400-3200 cm^{-1} C-O 1300-1000 cm^{-1}
Ethers	C-O 1300-1000 cm^{-1}
Carboxylic Acids	O-H on C=O 3400-2400 cm^{-1} COOH dimer ~2700 cm^{-1} C=O 1800-1650 cm^{-1}
Esters	C=O 1800-1650 cm^{-1} C-O 1300-1000 cm^{-1}
Anhydrides	C=O 1800-1650 cm^{-1} (2 bands) C-O 1300-1000 cm^{-1}
Amines	N-H 3400-3200 cm^{-1} (2 bands if NH ₂ , 1 band if NH, no bands if N) NH ₂ bending ~1600 cm^{-1} (if NH ₂)
Amides	N-H 3400-3200 cm^{-1} (2 bands if NH ₂ , 1 band if NH, no bands if N) C=O 1800-1650 cm^{-1} NH ₂ bending ~1600 cm^{-1} (if NH ₂)
Alkyl halides	C-X 850-500 cm^{-1}