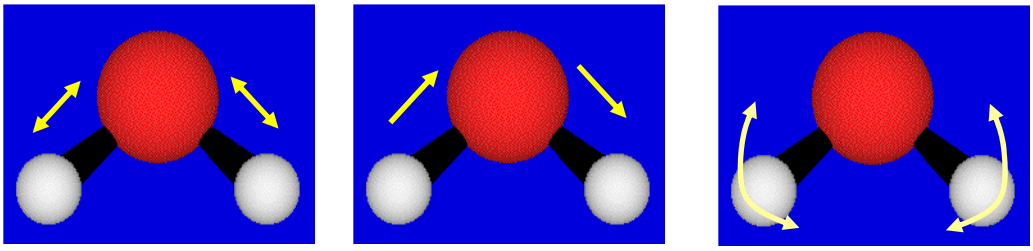
Chapter I Introduction

1. Background of Infrared Spectroscopy:

1.1 Basic Theory

The region of the infrared spectrum which is of greatest interest to organic chemists is the wavelength range 2.5 to ~15 micrometers (μm). In practice, units' proportional to *frequency*, (wave number in units of cm^{-1}) rather than wavelength, are commonly used and the region 2.5 to ~15μm corresponds to approximately 4000 to 600 cm^{-1}. Absorption of radiation in this region by a typical organic molecule results in the excitation of vibrational, rotational and bending modes, while the molecule itself remains in its electronic ground state.

Take H_2O as example, there are two vibrational modes and one bend mode as shown below:



Symmetric Stretch **Asymmetric Stretch** **Symmetric Bend**

Symmetric stretch: The movement represented by this arrowhead is the **symmetric O-H stretch** in water. In this mode, the two bonds vibrate in a coupled manner such that both shorten lengthen together.

Asymmetric Stretch: The movement represented by this arrowhead is the **asymmetric O-H stretch** in water. In this mode, the two bonds vibrate in a coupled, yet opposite manner; i.e., one shortens while the second coupled vibration lengthens.

Symmetric Bend: The movement represented by this arrowhead is the **symmetric O-H bend** in water. In this mode, the two bonds bend up and down in a coupled manner.

The fully symmetric molecules do not display absorbances in molecular asymmetry and in bending region. Molecular asymmetry and symmetric bending are requirement for excitation by infrared radiation.

For the purpose of routine organic structure determination, the most important absorptions in the infrared region are the simple stretching vibrations. For simple systems, these can be approximated by considering the atoms as point masses, linked by a 'spring' having a force constant *k* and following Hooke's Law. Using this simple approximation, the Hooke's Law equation shown below can be utilized to

approximate the characteristic stretching frequency (in cm^{-1}) of two atoms of masses m and m_2, linked by a bond with a force constant *k*:

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{\kappa}{\mu}}$$

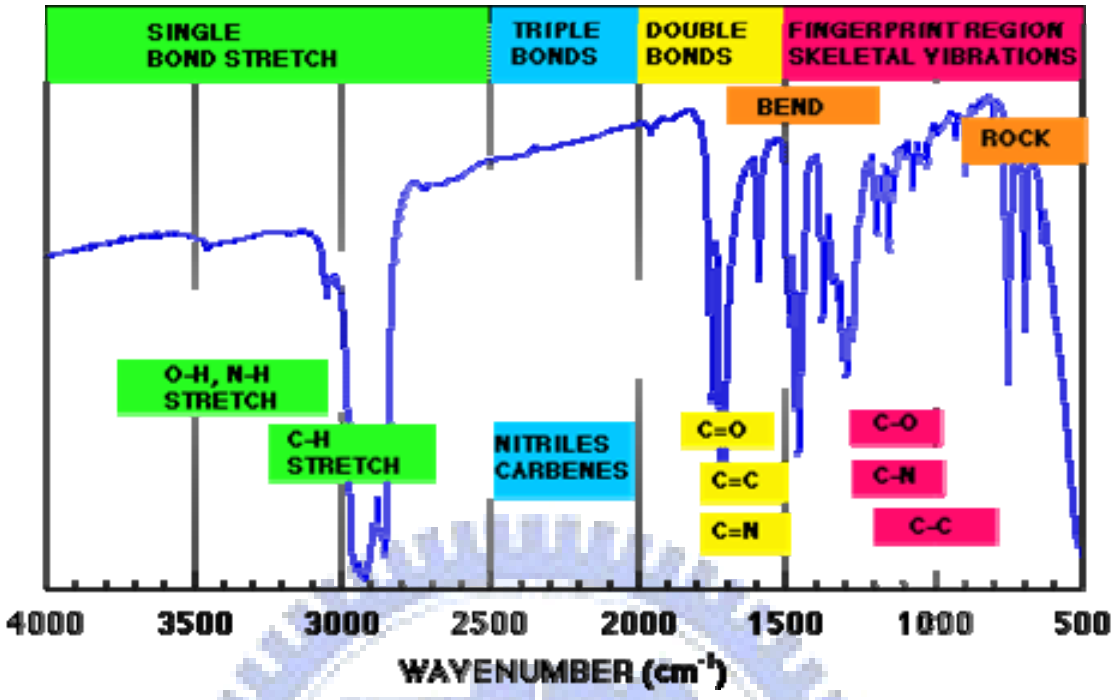
where $\mu = m_1m_2/(m_1+m_2)$ (termed the 'reduced mass'), and *c* is the velocity of light. By looking at this equation, we can see that if there is a high value of k, i.e. the bond is strong, it absorbs a higher frequency of light. So, a C=C double bond would absorb a higher frequency of light than a C-C single bond. Also, the larger the two masses, the lower the frequency of light absorbed.

1-2 Interpreting the Spectrum:

The graph produced show percentage transmission against wave number. If no radiation is absorbed at a particular frequency, then the line on the graph will be at 100% at the corresponding wave number. The stretching vibrations of typical organic molecules tend to fall within distinct regions of the infrared spectrum, as shown below:

- 3700 - 2500 cm^{-1}: X-H stretching (X = C, N, O, S)
- 2300 - 2000 cm^{-1}: C-X stretching (X = C or N)
- 1900 - 1500 cm^{-1}: C-X stretching (X = C, N, O)
- 1300 - 800 cm^{-1} : C-X stretching (X = C, N, O)

Different types of bonds have characteristic regions of the spectrum where they absorb:



Most functional groups absorb above 1500 cm^{-1}. The region below 1500 cm^{-1} is known as the "fingerprint region". Every molecule produces a unique pattern here, so if an unknown sample produces a spectrum which matches that of a known compound, the sample can be confirmed to be that compound.

1-3 Qualitative Analysis

FTIR can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum.

1-4 Quantitative Analysis

Because the strength of the absorption is proportional to the concentration, FTIR can be used for some quantitative analyses. Usually these are rather simple types of tests in the concentration range of a few ppm up to the percent level in solution. In this study, we would focus on the quantitative analysis of polymer.

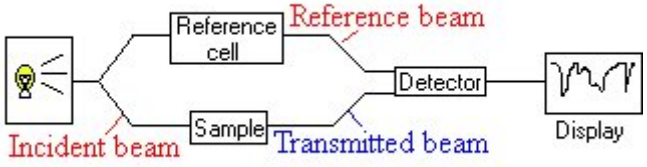
1-5 Sample Preparation

Samples for FTIR can be prepared in a number of ways. For liquid samples, the easiest is to place one drop of sample between two plates of sodium chloride (salt). Salt is transparent to infrared light. The drop forms a thin film between the plates. Solid samples can be milled with potassium bromide (KBr) to form a very fine powder. This powder is then compressed into a thin pellet which can be analyzed. KBr is also transparent in the IR. Alternatively, solid samples can be dissolved in a solvent such as methylene chloride, and the solution placed onto a single salt plate. The solvent is then evaporated off, leaving a thin film of the original material on the plate. This is called a casting film, and is frequently used for polymer identification. Solutions can also be analyzed in a liquid cell. This is a small container made from NaCl (or other IR-transparent material) which can be filled with liquid, such as the

extract for EPA 418.1 analysis. This creates a longer path length for the sample, which leads to increased sensitivity.

1-6 Experimental Procedure:

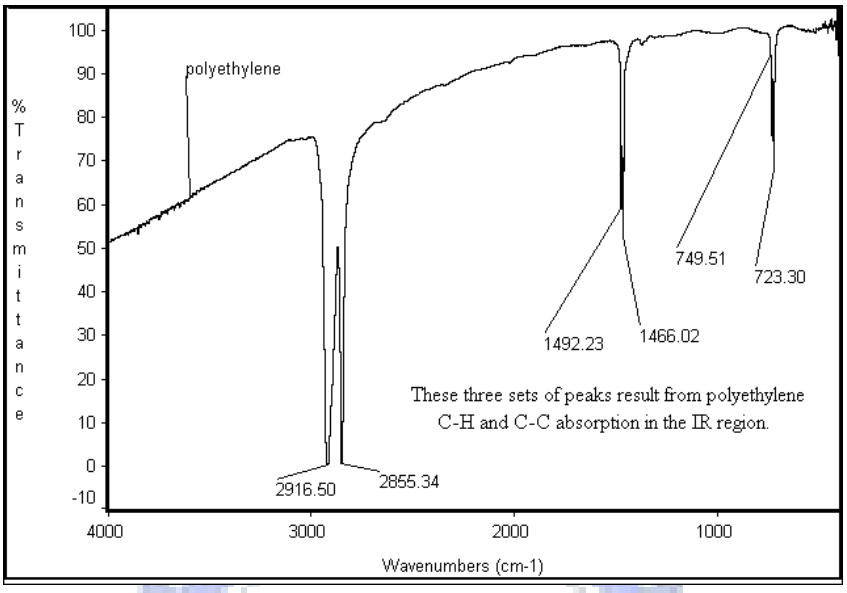
If the sample is a liquid, it can be tested straight away. If it is a solid, then it is ground up to a fine powder, and mixed with a few drops of liquid paraffin (Nujol) to form a paste. A thin layer of the liquid or paste is then spread between two sodium chloride plates, and placed in the machine. Sodium chloride is used as it does not absorb strongly in the infrared region whereas glass does, however it does dissolve readily in water, so it must be cleaned with CH_2CL_2. The sample is then placed in the machine.



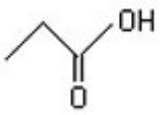
The reference cell is an identical rock salt plate, with a similar amount of holder. The detector then compares the two beams it receives, and can remove any peaks due to the holder or the plates.

1-7 Example Spectrum:

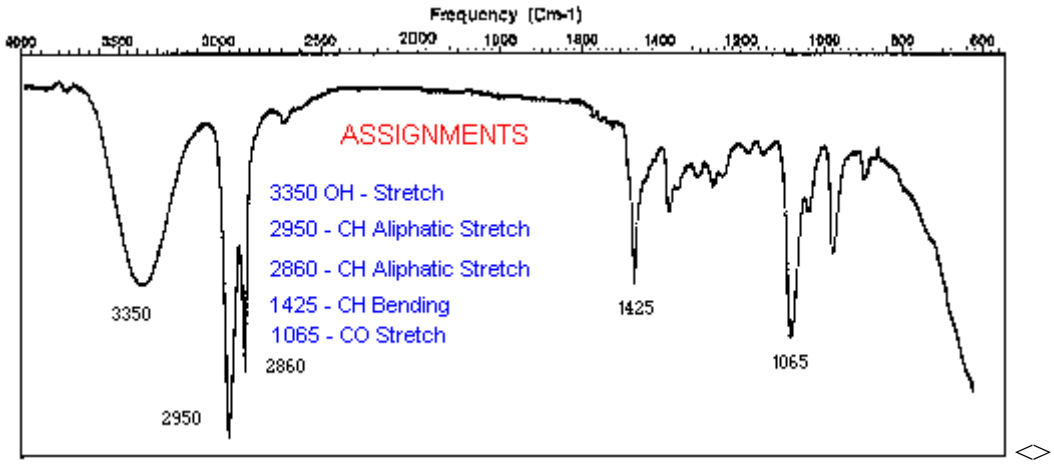
A sample with Polyethylene ($-C_2H_4-$) gives the following spectrum:



This shows a strong absorption at just over 1492~1466 cm^{-1} and a medium absorption at 2855-2916 cm^{-1}. These bonds correspond to the C=O and O-H groups found in a carboxylic acid. This information + the chemical formula tells us the structure must be propanoic acid:



Interpretation of Infrared Spectra



The interpretation of infrared spectra involves the correlation of absorption bands in the spectrum of an unknown compound with the known absorption frequencies for types of bonds. This table will help users become more familiar with the process. Significant for the identification of the source of an absorption band are **intensity** (weak, medium or strong), **shape** (broad or sharp), and **position** (cm^{-1}) in the spectrum. Characteristic examples are provided in the table below to assist the user in becoming familiar with the intensity and shape absorption bands for representative absorptions.

Characteristic infrared absorption frequencies:

Bond	Compound Type	Frequency range, cm^{-1}
C-H	Alkanes	2960-2850(s) stretch
		1470-1350(v) scissoring and bending
	CH_3 Umbrella Deformation	1380(m-w) - Doublet - isopropyl, *t*-butyl
C-H	Alkenes	3080-3020(m) stretch
		1000-675(s) bend
C-H	Aromatic Rings	3100-3000(m) stretch
	Phenyl Ring Substitution Bands	870-675(s) bend
	Phenyl Ring Substitution Overtones	2000-1600(w) - fingerprint region
C-H	Alkynes	3333-3267(s) stretch
		700-610(b) bend
C=C	Alkenes	1680-1640(m,w)) stretch
C C	Alkynes	2260-2100(w,sh) stretch
C=C	Aromatic Rings	1600, 1500(w) stretch

C-O	Alcohols, Ethers, Carboxylic acids, Esters	1260-1000(s) stretch
C=O	Aldehydes, Ketones, Carboxylic acids, Esters	1760-1670(s) stretch
O-H	Monomeric -- Alcohols, Phenols	3640-3160(s,br) stretch
	Hydrogen-bonded -- Alcohols, Phenols	3600-3200(b) stretch
	Carboxylic acids	3000-2500(b) stretch
N-H	Amines	3500-3300(m) stretch
		1650-1580 (m) bend
C-N	Amines	1340-1020(m) stretch
C N	Nitriles	2260-2220(v) stretch
NO_2	Nitro Compounds	1660-1500(s) asymmetrical stretch
		1390-1260(s) symmetrical stretch

v - variable, m - medium, s - strong, br - broad, w – weak

Infrared spectra: It is important to remember that the absence of an absorption band can often provide more information about the structure of a compound than the presence of a band. Be careful to avoid focusing on selected absorption bands and overlooking others. Use the examples linked to the table to see the profile and intensity of bands. Remember that the absence of a band may provide more information than the presence of an absorption band.

Look for absorption bands in decreasing order of importance:

1. the C-H absorption(s) between 3100 and 2850 cm^{-1}. An absorption above 3000 cm^{-1} indicates C=C, either alkene or aromatic. Confirm the aromatic ring by finding peaks at 1600 and 1500 cm^{-1} and C-H out-of-plane bending to give

substitution patterns below 900 cm^{-1}. Confirm alkenes with an absorption at 1640-1680 cm^{-1}. C-H absorption between 3000 and 2850 cm^{-1} is due to aliphatic hydrogens.

2. the carbonyl (C=O) absorption between 1690-1760cm^{-1}; this strong band indicates either an aldehyde, ketone, carboxylic acid, ester, amide, anhydride or acyl halide. The an aldehyde may be confirmed with C-H absorption from 2840 to 2720 cm^{-1}.
3. the O-H or N-H absorption between 3200 and 3600 cm^{-1}. This indicates either an alcohol, N-H containing amine or amide, or carboxylic acid. For $-NH_2$ a doublet will be observed.
4. the C-O absorption between 1080 and 1300 cm^{-1}. These peaks are normally rounded like the O-H and N-H peak in 3. and are prominent. Carboxylic acids, esters, ethers, alcohols and anhydrides all containing this peak.
5. the CC and CN triple bond absorptions at 2100-2260 cm^{-1} are small but exposed.
6. a methyl group may be identified with C-H absorption at 1380 cm^{-1}. This band is split into a doublet for isopropyl (*gem*-dimethyl) groups.
7. Structure of aromatic compounds may also be confirmed from the pattern of the weak overtone and combination tone bands found from 2000 to 1600 cm^{-1}.