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Basic Theory

Understanding how FTIR Works

FT-IR stands for Fourier Transform Infrared. It is a fast and dynamic technique for collecting infrared spectra of an enormous variety of compounds for a wide range of industries. Work done by Fellgett and Jacquinot during the 1950's formed the fundamental theoretical advantage of FT-IR spectrometers over traditional monochromator-based instruments. Their work laid the foundation for FT-IR spectroscopy. Work since then has expanded on the concept that FT-IR spectrometers are very fast, accurate, sensitive and reliable.

Fourier Transform Infrared Spectroscopy

Introduction

- *Electromagnetic radiation*
- *Vibrational spectroscopy*

Instrumentation

- *Michelson interferometer*
- *The Fourier transform*

Analysis

- *Qualitative – Identification*
- *Quantitative – Quantification*

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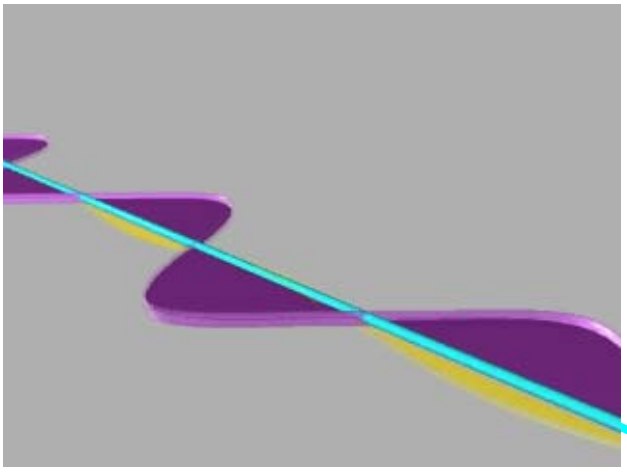
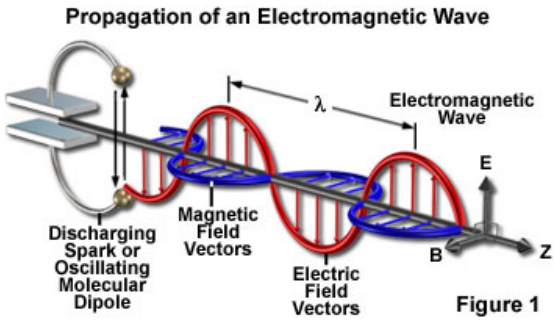
Introduction to FT Theory

In this theoretical overview, we will describe the energy states we sample and briefly how a Fourier transform spectrometer works.

Concepts which are common to all of Vibrational Spectroscopy - spectral identification, quantitative analysis, spectrometer design and function, use of spectral information. This is meant to be a general overview. Several topics are further developed in subsequent presentations.

What Is Light ?





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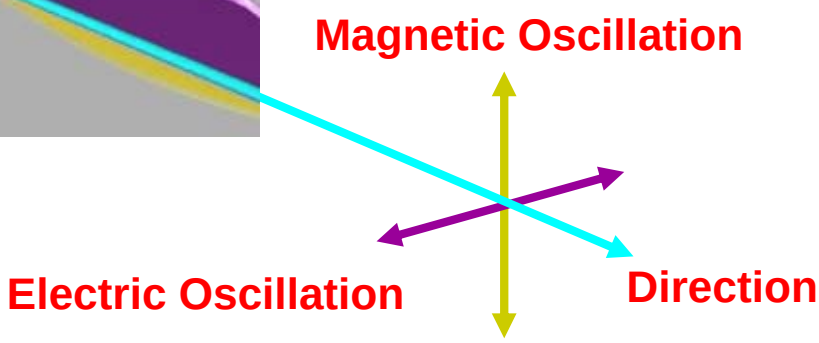
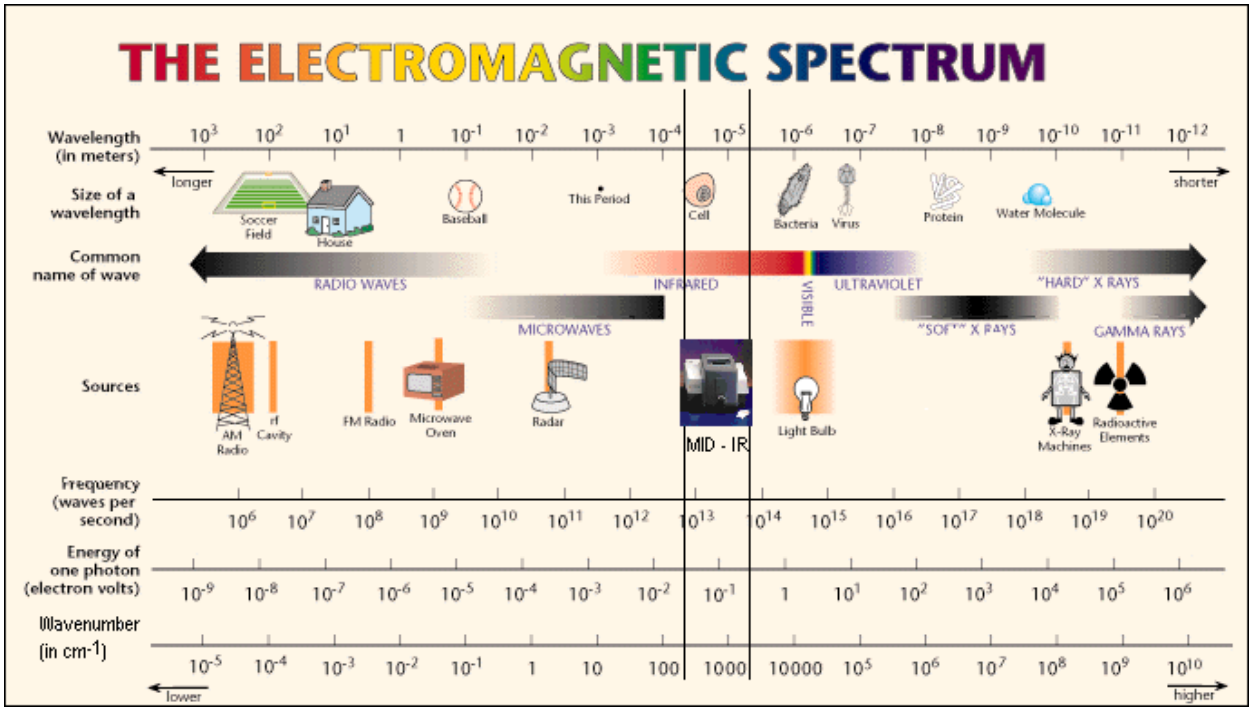


Electromagnetic Spectrum



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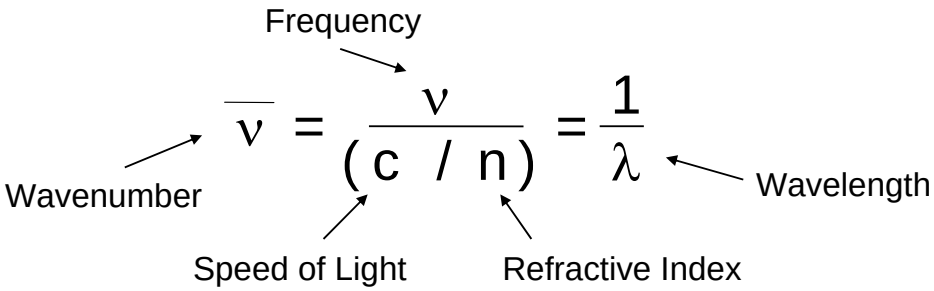
Note the low and high energy ends of the electromagnetic spectrum corresponds also to long wavelengths of light at 10^{5} cm^{-1} (radio waves) to 10^{-9} cm^{-1} (x-rays) in this chart. Note also from this chart that a molecule behaves differently when exposed to electromagnetic waves of different energy. For example when exposed to x-rays, a molecule will undergo nuclear transitions (i.e. lose a neutron) or when exposed to ultraviolet wave it may undergo an electronic transition (i.e. a transition to a higher electronic state).

NOTE: Frequency can be measured in Hertz, or re-calculated into wavelength of the light. All these values are interrelated. We like to use a unit called wavenumber, which is the number of waves per cm. One of the reasons why IR spectroscopists use this x-axis unit is because it enables us to use reasonably small numbers! Mid-Infrared covers the region from ~200 to 5000 cm^{-1}.

Our FT spectrometers allow us to measure transitions from the visible (25,000 cm^{-1}) through the far-IR (50 cm^{-1}) spectral range. The infrared regions yield specific information regarding functional groups, their associations, and relative quantity. These regions may be examined with three types of spectrometers; filter spectrometers that provide narrow bandwidths (with little, but specific information such as single gas analyzers), dispersive spectrometers and Fourier Transform spectrometers that provide broad spectral bandwidths (information rich, both non-specific and specific).

Wavenumber

- It is convenient to define the wavelength and frequency in terms of wavenumber in order to distinguish and correlate spectral features.



As a convenience, the wavelength (λ) and frequency have been defined using linear wavenumber for spectral analysis. This equation defines this relationship.

Assuming the speed of light and refractive index are constant, as wavenumber increases, wavelength becomes shorter and frequency becomes higher.

IR wavelength is commonly reported in units of mm (micrometer or microns). μm is 10^{-6} m whereas cm is 10^{-2} m.

Conversions

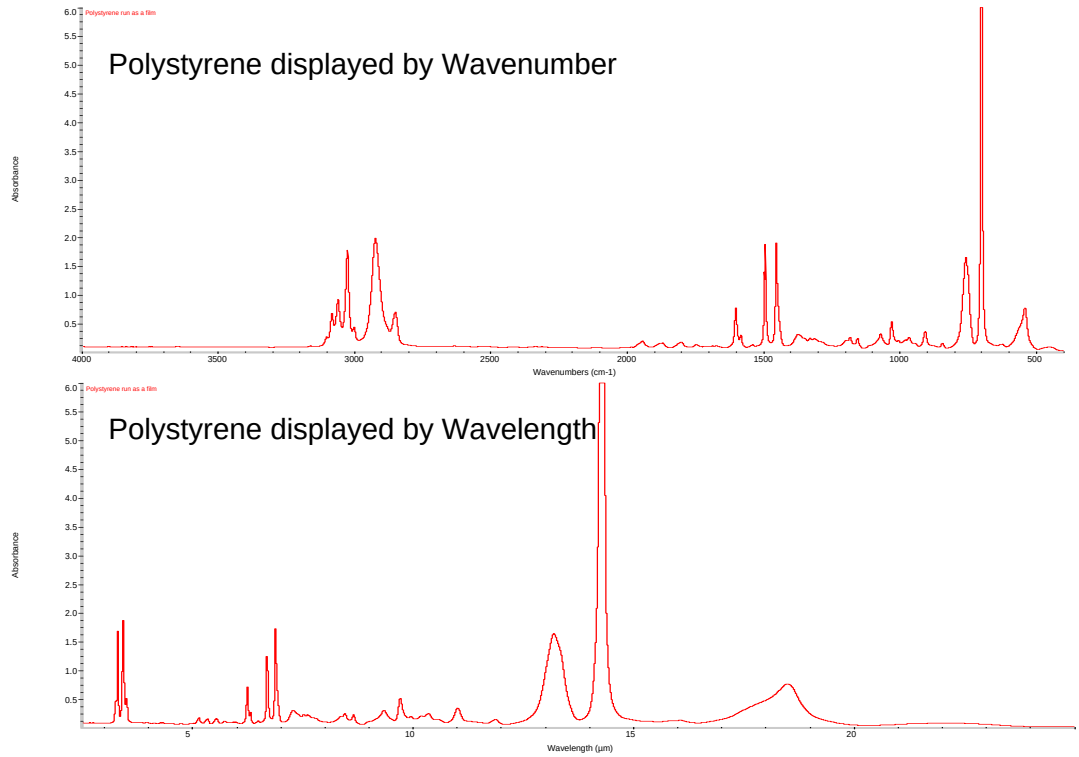
wavenumber in cm^{-1} to wavelength, λ, in μm

λ (μm) = 10^4/wavenumber

wavelength, λ, in mm to wavenumber in cm^{-1}

wavenumber (cm^{-1}) = 10^4 / λ

Wavenumber vs. Wavelength



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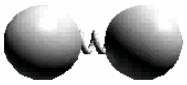
The conversion of wavelength to wavenumber eliminates the frequency dependent spacing and allows for a more detailed spectrum.

Harmonic Vibrations – Hooke's Law

- The vibration of a diatomic molecule can be approximated by the vibration of a spring with two masses attached.

- As the mass increases the vibrational frequency decreases.



- The wavenumber of the vibration equals:

Hooke's Law

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \text{where } \mu = \frac{m_1 m_2}{m_1 + m_2}$$

So why does a molecule absorb INFRARED radiation? To understand this, we need to take a closer look at what movements are made by the atoms that make up the molecule. The general term for this movement is VIBRATION.

The easiest case is that of two bodies connected together by a spring as described by Hooke's Law. If we would apply some kind of force to this system it would start vibrating. It is often thought that the external force will define the frequency of the vibration. However; it appears that to whatever length you draw the spring, the frequency, i.e. the period of the vibration will always be the same, and is determined by the strength of the spring (called the force constant or k in the equation), and the mass of the bodies (μ : reduced mass defined by the second equation).

Selection Rules for Infrared Activity

- The frequency of the light must be identical to the frequency of the vibration (resonance)
- The dipole of the molecule must change during the vibration
- The direction of the dipole change must be the same as the direction of the electric field vector

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Not all infrared light is absorbed by the molecule. Very specific frequencies are absorbed by specific groups or vibrations of the molecule.

The absorption depends on three properties:

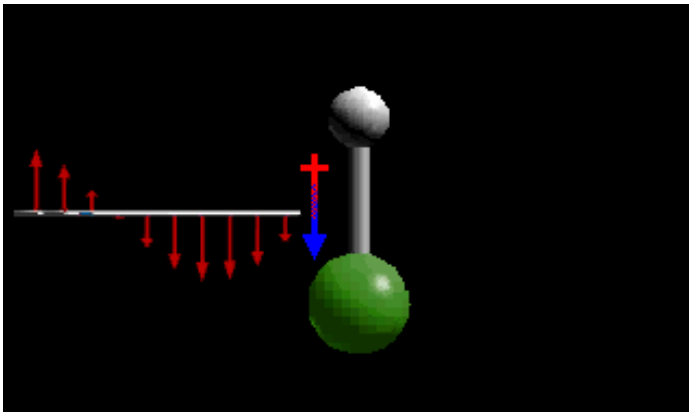
1. The frequency of the infrared radiation must be identical to the (theoretical) frequency of the vibration of the molecule. We call this resonance.

2. The dipole of the molecule, the distribution of electron density in the molecule, has to change during the vibration. This means that even though every molecule vibrates all the time, not all vibrations absorb IR radiation

3. The direction of the change of the electromagnetic field of the infrared radiation must be parallel to the direction of the change of the dipole in the molecule. This is another very interesting property because it enables us to do specific measurements on the orientation of the molecule (e.g. in the polymer industry)

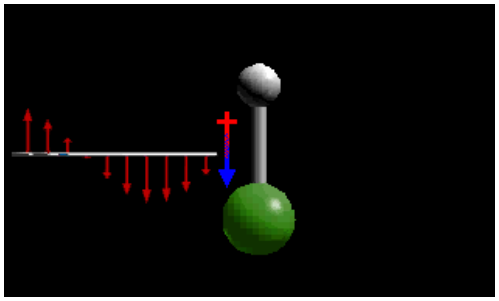
Frequency Matching

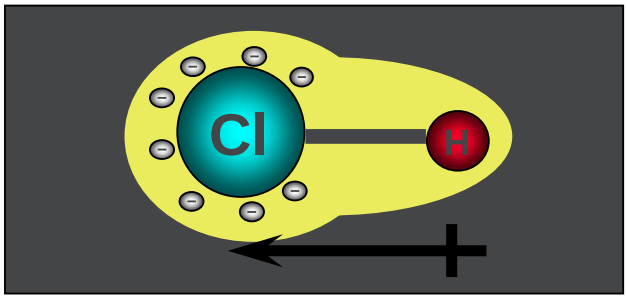
When electromagnetic radiation (light) has the same frequency as the bond vibration, some of the intensity of the light is absorbed by the bond.

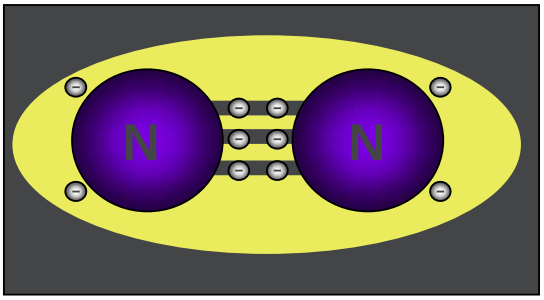


Dipole Change

- To absorb energy, the dipole must change when the transition occurs
- The intensity of the absorption is proportional to the magnitude of the dipole change







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These are two extremely simple diatomic molecules; HCl and N_2.

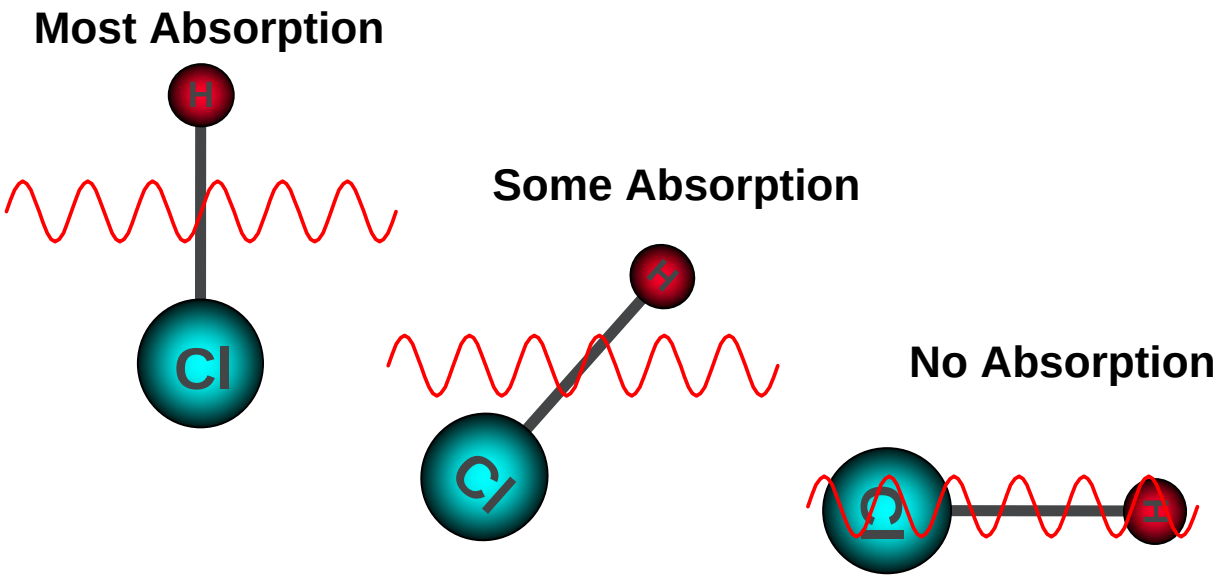
As can be seen HCl has a dipole moment: The electrons are not evenly distributed through the molecule, and there is more negative charge on the Chlorine site than there is on the Hydrogen site.

A dipole moment is charge vs. distance. As the bond stretches and shrinks, the distance between the charges changes.

Nitrogen is a homo-nuclear molecule. It is perfectly symmetrical, and the charge is divided symmetrically and so there is no dipole moment and therefore no absorption. It is important to note that this molecule is vibrating, but is not infrared active.

NOTE: The FREQUENCY of the vibration is proportional to the force constant of the bond which is determined partially by the (average) dipole of the molecule. This relationship between the molecular dipole moment and the force constant suggests that the vibrational frequency is dependent on the molecular dipole. However, it is the CHANGE of the dipole during the vibration which determines the extinction coefficient of the absorption, i.e. the INTENSITY of the absorption band!!!

The Direction of the Vibration



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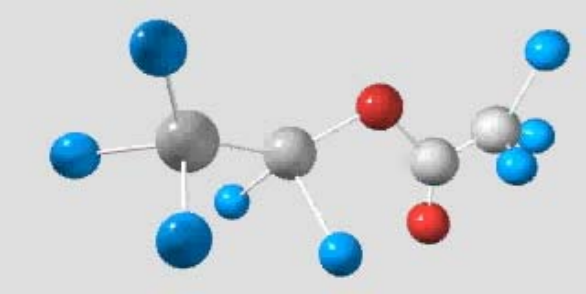
In order for maximum absorption to occur, all the chemical bonds within a molecule must be aligned with the infrared wave, specifically the electric wave. Since most materials are non-crystalline and have a statistical distribution of orientations this alignment is not crucial and the spectrometer detects the summation of all the interactions of the molecules with the infrared energy beam.

Polarizer's can be employed in order to help pass the infrared energy at a specific angle with respect to the samples orientation. This is useful in dichroic or polymer orientation studies.

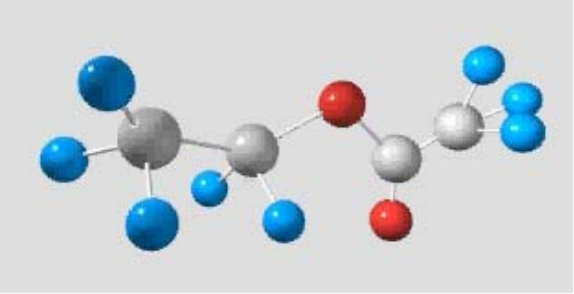
Types of Molecular Motion

Stretching



Functional groups between 4000 and ~1500 cm^{-1}

Bending



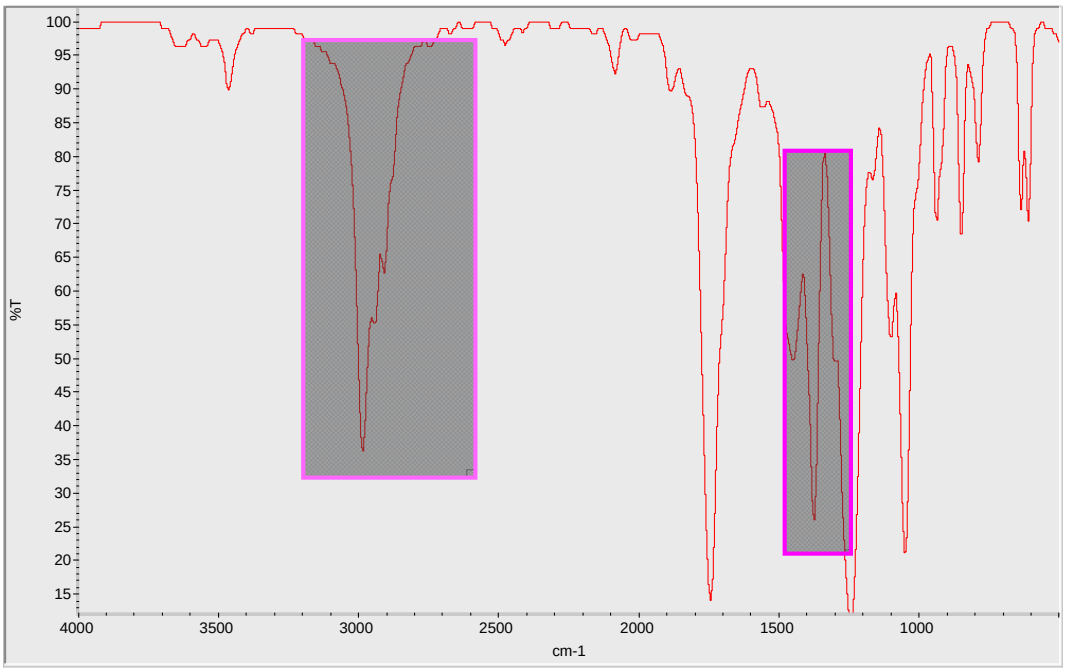
Less than ~1500 cm^{-1}

The two fundamental vibrational modes found in mid-IR spectroscopy are stretching and bending vibrations. These modes occur in different regions of the infrared spectra and therefore, relate to different vibrational energies.

Stretching vibrations require more energy and occur at the higher frequencies, larger wavenumbers.

Bending vibrations occur at lower energy and are found at lower wavenumbers, usually toward the fingerprint region (below 1500 cm^{-1}).

Molecular Vibrations



Functional groups **Fingerprint region**

Here we can see some of the absorbance's of the methyl (CH_3) and methylene (CH_2) groups in the spectrum of ethyl acetate.

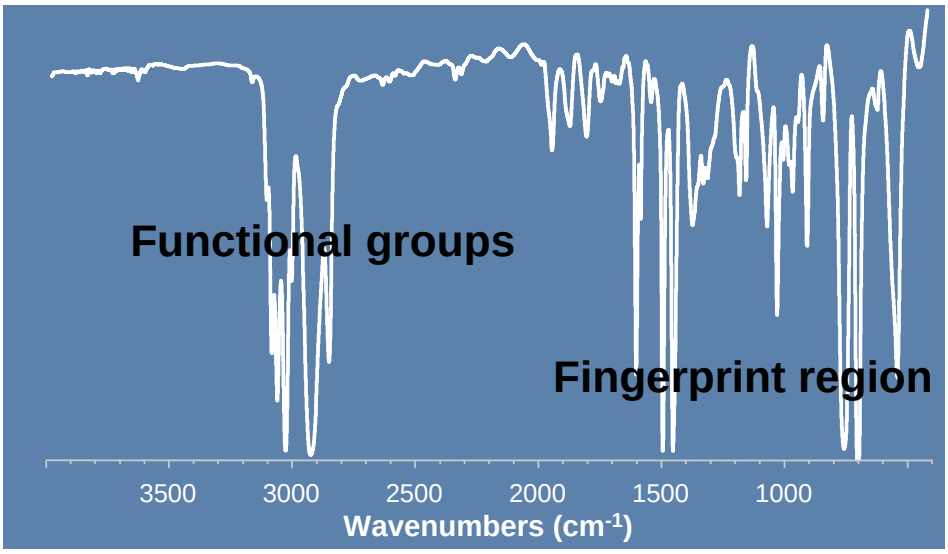
Each vibration, called a fundamental mode, has a specific energy (or frequency) which depends on the atoms involved in the motion (i.e., the mass), the type of motion, and the bond strengths (i.e., the strength of the "spring").

In this case, the carbon-hydrogen stretching appears in the higher energy region of the spectrum (about 2800-2900 cm^{-1}), with the asymmetric stretching being slightly higher in energy than the symmetric stretching mode.

There are two bending modes for the methyl group (at 1460 & 1375 cm^{-1}). The methylene scissoring, twisting, and rocking modes appear at ~1470, ~1300, and 720 cm^{-1}, respectively.

Polyatomic Molecules

- As molecules become more complex, more molecular interactions occur and the spectrum becomes more complex



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Spectral characteristics described up to this point hold for a more complicated molecule.

This is the most well-known spectrum in IR spectroscopy: polystyrene. A polymer with CH_2 and benzene groups.

For interpretation purposes, we can describe what are called functional groups which always occur at similar positions in the spectrum:

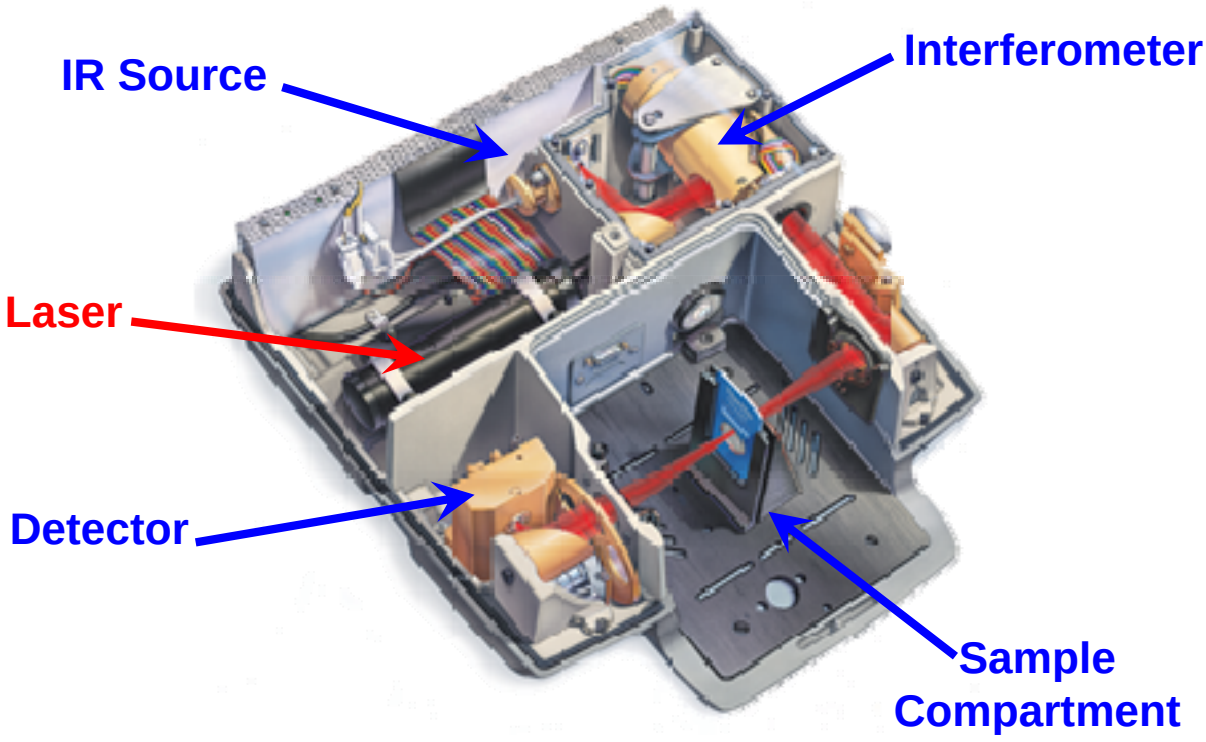
NH vibrations, OH vibrations, CH_2 vibrations, CH_3 vibrations, aromatic vibrations

These vibrations (and many more) are spread over the entire spectrum, and most of them are quite well known.

The region from 4000-1500 cm^{-1} is typically where the stretching vibrations occur. This is useful in identifying what functional groups might be present.

The region between 1500 and 400 cm^{-1} is comprised of very specific and complicated vibrations of the entire molecule. Therefore, this region is different for every molecule, and like a fingerprint, no two molecules have the same spectrum in the fingerprint region. We can use this part of the spectrum for the final identification.

FT-IR Spectrometer



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This is the internal optical layout of the Nicolet 380, one of Thermo's FT-IR spectrometers.

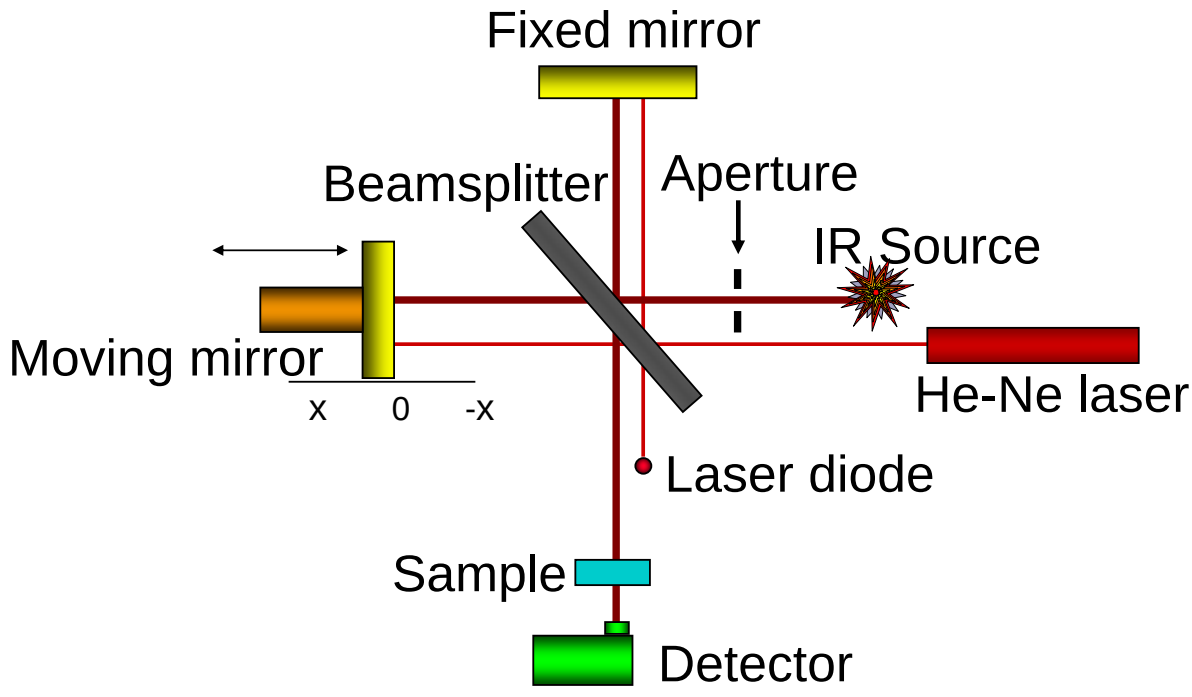
The general layout of a FT spectrometer starts at its source. The high intensity, broad band source energy is projected into the interferometer.

The interferometer consists of a beamsplitter which reflects half of the energy to a fixed mirror and half to the moving mirror. The moving mirror scans back and forth producing a path length difference with respect to the fixed mirror. This path length difference is sampled in time with respect to the internal He-Ne laser, allowing for the precise mirror position from scan to scan.

The reflected beams then combine back at the beamsplitter and are reflected into the sample compartment. The sample may absorb some of the modulated energy from the interferometer.

The detector measures the intensity of the modulated energy to produce an interferogram.

FT-IR Spectrometer Diagram



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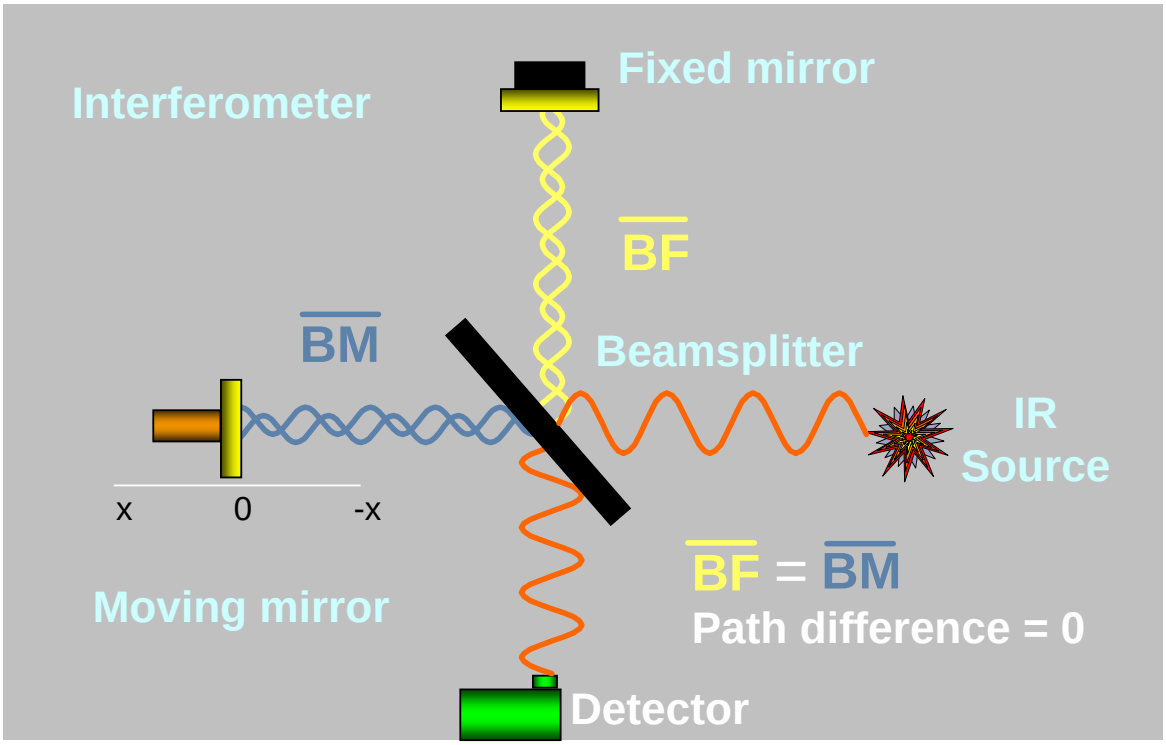
Michelson Interferometer - ZPD (Zero Path Difference)



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We can induce differences in the two pathlengths (BF and BM) by changing the position of the moving mirror while keeping the wavelength the same and thereby see an interference.

The design of a Michelson interferometer has three basic parts:

A beam splitter

A fixed mirror

A moving mirror

With the moving mirror positioned the same distance from the beam splitter as the fixed mirror, imagine one wavelength of light arriving at the beamsplitter:

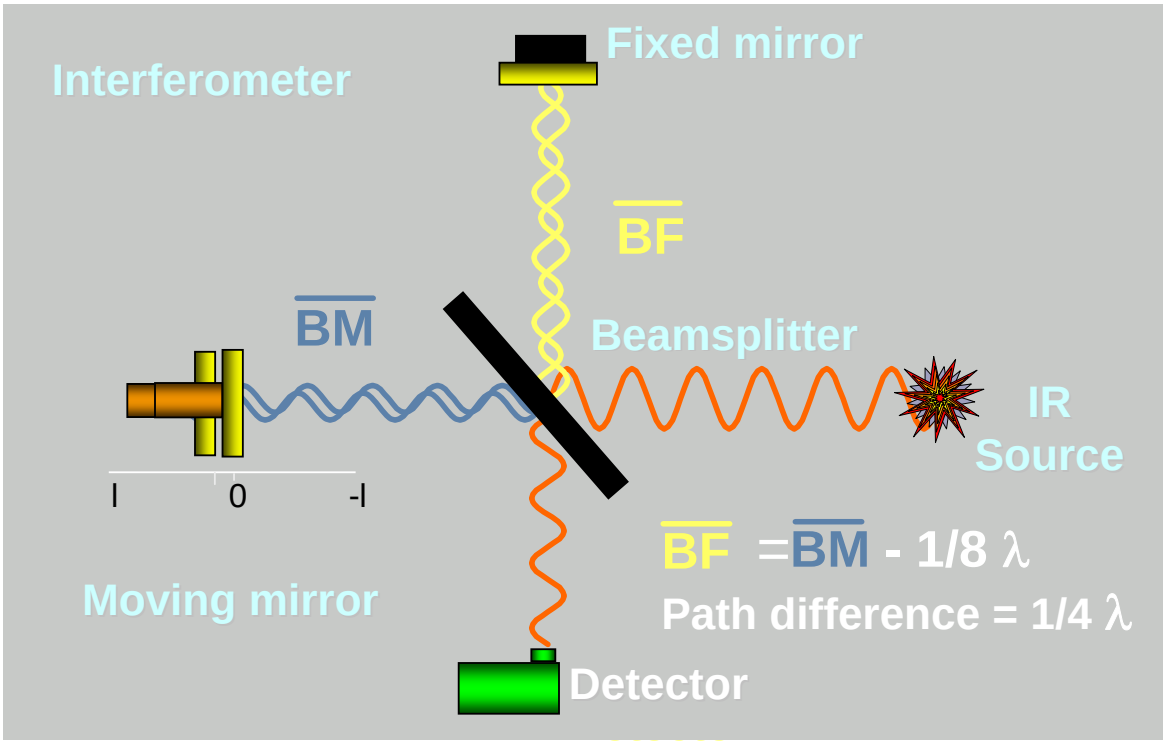
50% of the beam will be reflected to the fixed mirror

50% will be transmitted to the moving mirror

When these two beams recombine again at the beam splitter, the distance traveled by these beams is exactly the same, we will see constructive interference: there will be a large signal on the detector.

This mirror location is denoted as Zero Path Difference (ZPD).

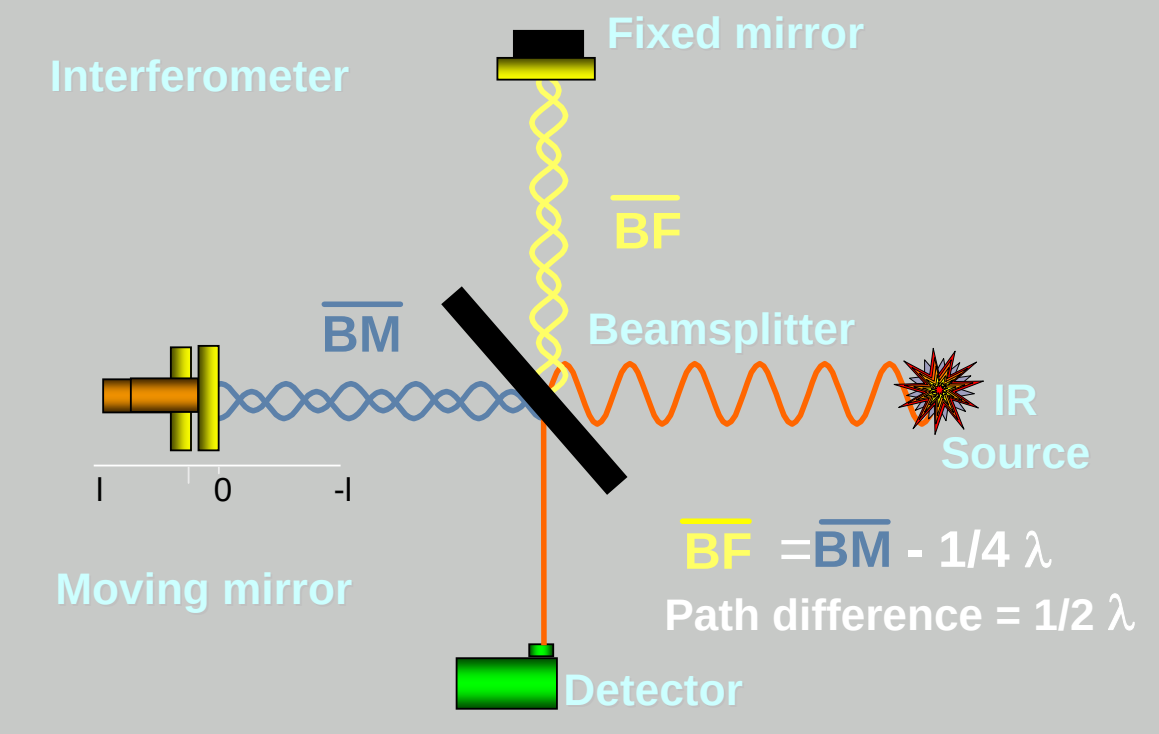
Constructive Interference



If we now move the moving mirror, the distance between beamsplitter and the moving mirror will be different than the distance between the beamsplitter and the fixed mirror. Therefore we will induce a difference in start and end of the waves, and they will start to interfere: the intensity will decrease.

In this case, the difference in the distance the beams have traveled is ¼ of the wavelength and the beams are only slightly out-of-phase.

Destructive Interference



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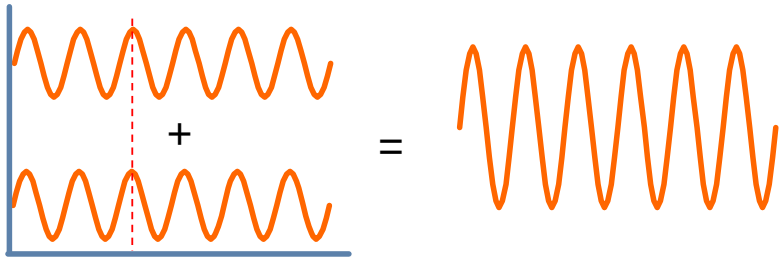
When the moving mirror is positioned at a location that causes the beams to be ½ wavelength out-of-phase, there is total destructive interference and there will be no signal on the detector at all.

If this motion is continued, the results are repeated as multiples of the wavelength distances are encountered.

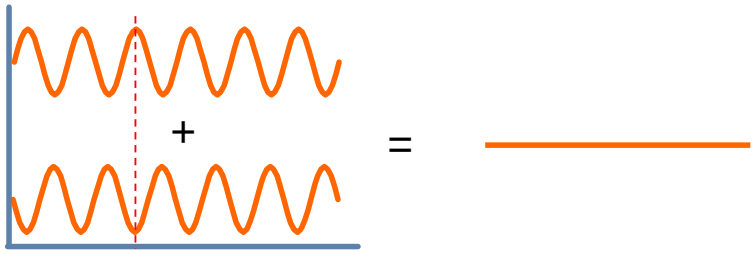
Because the effect is produced as a result of the net difference in the path of the two beams, similar information is produced when the moving mirror is positioned to produce a path shorter than the one seen in the case of the fixed mirror.

Wave Interactions (Interference)

- In-phase
  Constructive interference



- Out-of-phase
  Destructive interference

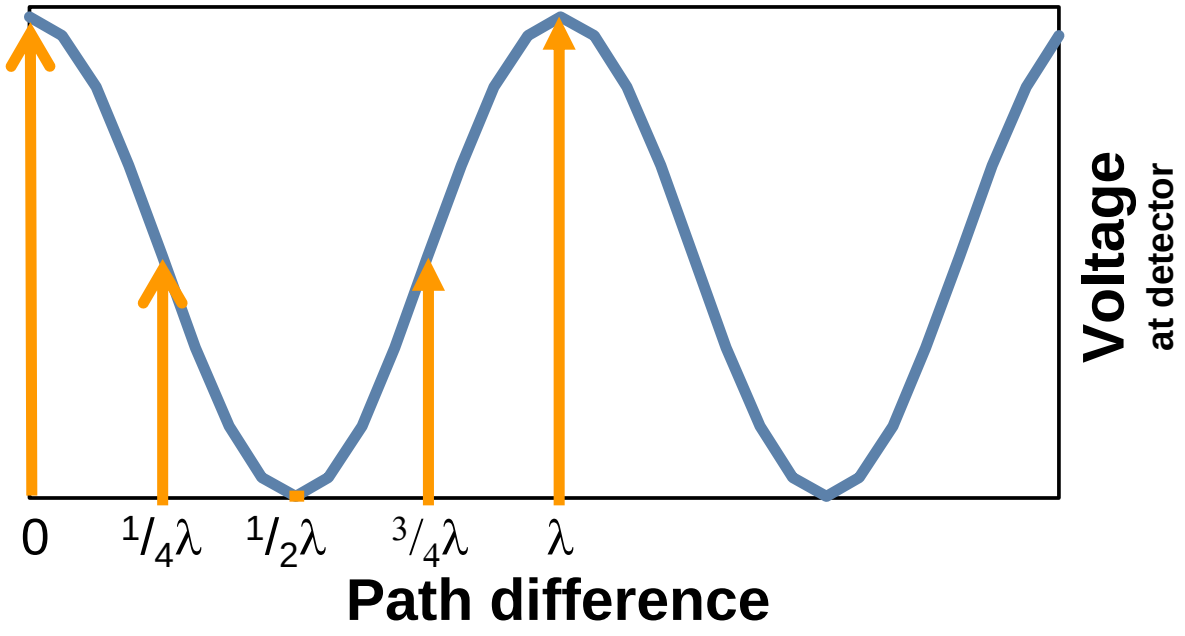


A new wave pattern is created when two or more waves are superimposed. This process is called interference. Fourier transform spectrometry is rooted in the interference of light waves.

When two waves of the same wavelength with no phase difference (starting at exactly the same moment in time) interfere with each other, the resulting wave has the same wavelength as the original wave, but its amplitude is the sum of the amplitude of original waves. This process is called CONSTRUCTIVE interference.

Similarly, if we allow two waves which are out of phase (that is one is “rising” where the other is “falling”) to interact, the resulting wave has zero amplitude. This process is called DESTRUCTIVE interference.

Signal at the Detector



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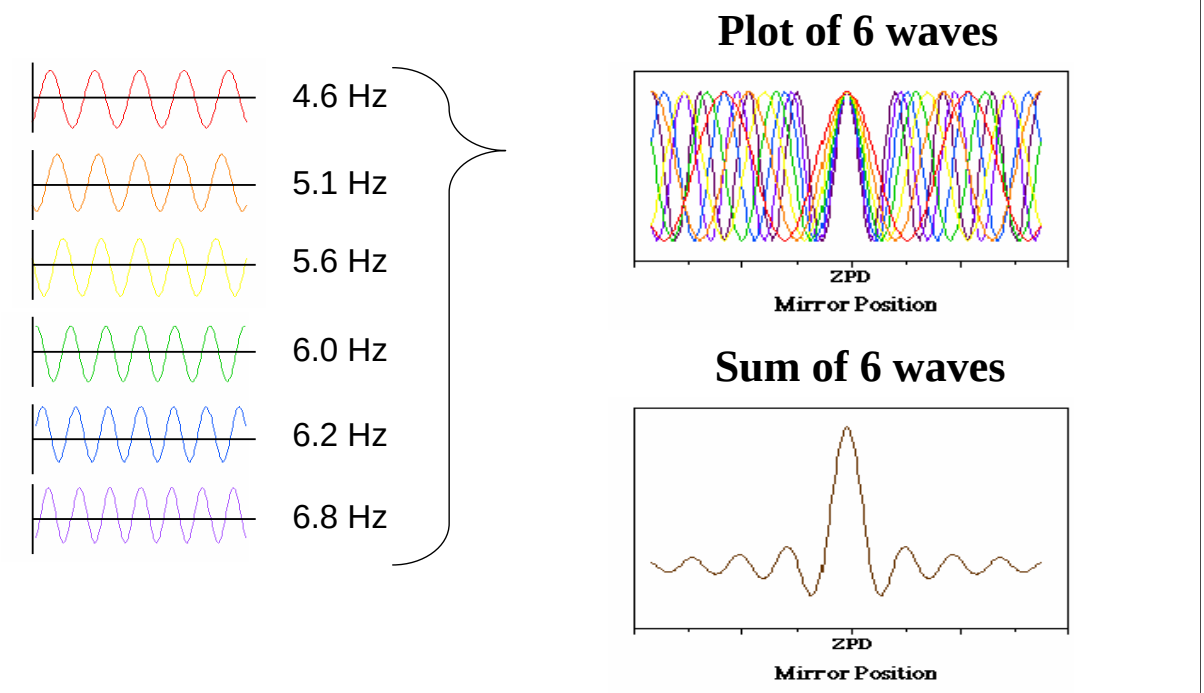
Following this in time we would measure these three points. However, if we keep moving the mirror further away from the beamsplitter we would increase the amount of light again.

So if we follow this complete process, in time we would measure a wave pattern on the detector while moving the mirror

And from this wave pattern we can calculate the wavelength of the light as long as we know how far the mirror has moved!!

Interferogram Construction



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Broad beam IR energy is made up of hundreds of frequencies of light.

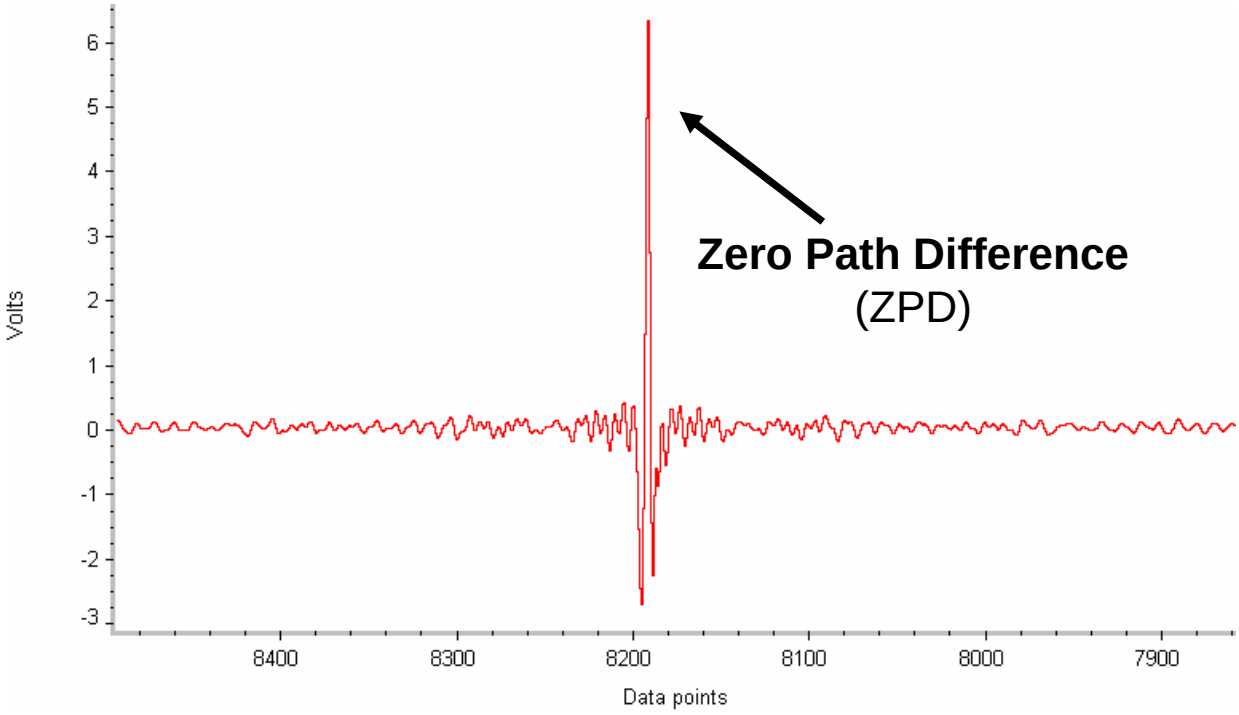
This slide demonstrates only 6 different frequencies.

Once “modulated”, these frequencies are summed together.

The lower right picture demonstrates what the summed value of the 6 frequencies look like. It is easy to see that the point at which all frequencies constructively combine is also the point of greatest intensity.

This is the point known as zero path difference (ZPD) where the optical path distance from the beam splitter to the moving mirror is equivalent to the optical path distance from the beam splitter to the fixed mirror.

FT-IR Interferogram



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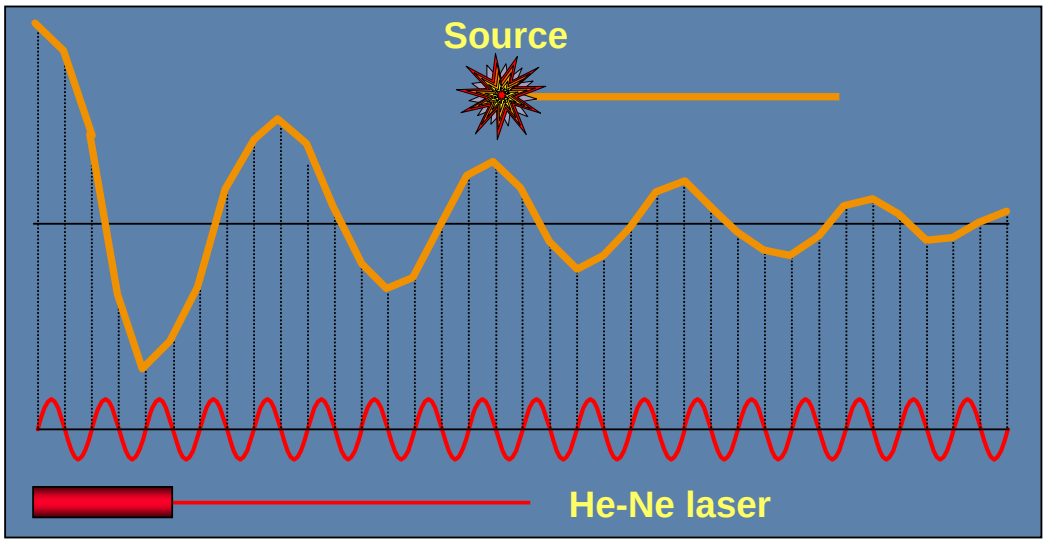
The radiation of a single frequency results in a cosine interference pattern. This same process of constructive/destructive interference occurs for every frequency emitted from the broad band infrared source. Thus, all frequencies can be sampled at the same time. The resulting signal observed by the detector is the summation of the individual interference patterns of each frequency. This signal is called an interferogram or the time domain spectrum (intensity versus time within the mirror scan).

The detector responds to the change in energy. This change in energy is plotted in terms of volts vs. data points. The data points are a function of resolution in terms of how much information the spectrometer is gathering with respect to the interferogram.

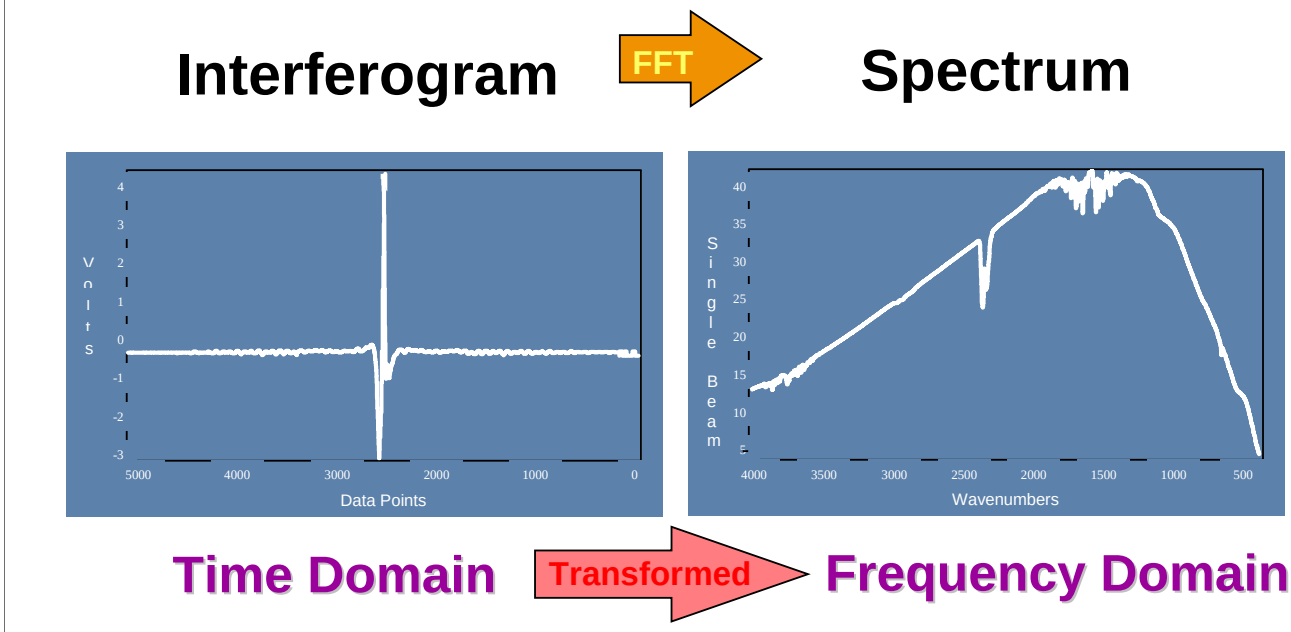
Sampling the Interferogram



To keep track of the position of the mirror we use the He-Ne laser signal. The detector is triggered to take data every time the laser signal goes through zero or every other zero-crossing.

NOTE: this means that the interferogram is built up from different points and is NOT a continuous signal

Fast Fourier Transformation



The interferogram is the raw information, but it is not in a format that is easily interpreted.

In order to obtain the spectrum, a Fast Fourier transform (FFT) is utilized. This is a method which calculates the frequencies and their intensity present from the interferogram.

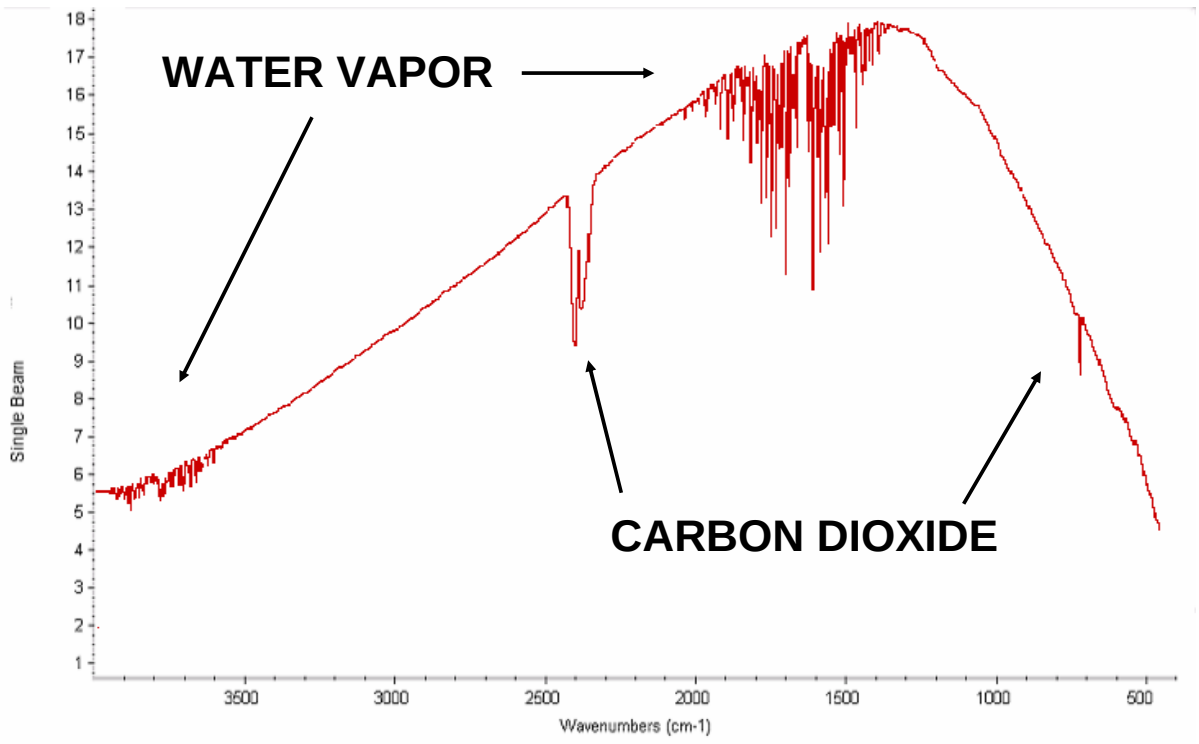
This is not too difficult when there is only 1 wave (the sine function is directly related to the frequency), but it becomes more complex when multiple waves are present. However, with the powerful computers available today, these calculations can be done in milliseconds.

Here is the example for 3601 waves (from 4000 to 400 cm^{-1}, 1 data point resolution).

The interferogram shown is a double sided interferogram which has the same information in the right part as it has in the left part and theoretically is perfectly symmetrical.

The calculated spectrum is called the background spectrum. This is amount of light falling on the detector when NO sample is present.

Single Beam Background



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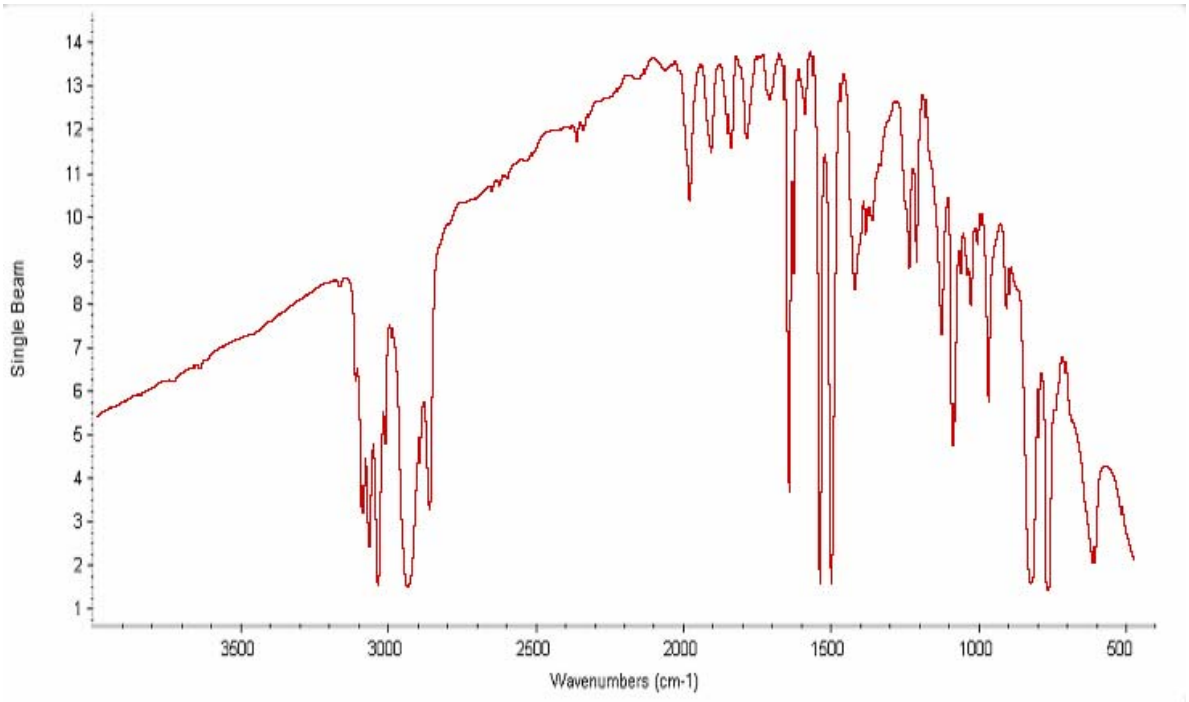
Since an interferogram has no frequency assignments, we apply a Fast Fourier transformation in order to produce a single beam spectrum. Both the sample single beam and the background single beam are generated similarly from separate Interferograms.

This is an example of a background single beam spectrum, with nothing in the sample compartment. Notice the atmospheric water vapor and carbon dioxide as well as the overall source energy distribution.

Single Beam Sample



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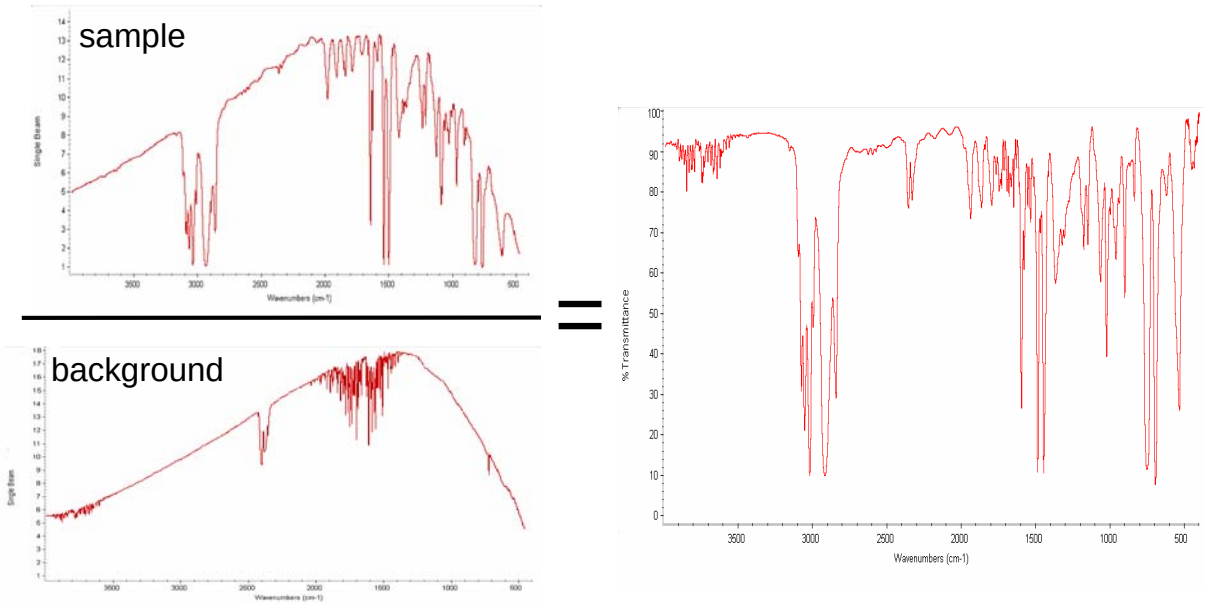
This is an example of a single beam spectrum with a sample in the sample compartment.

The single beam spectra are useful for visually determining if the instrument is working properly (Signal/Noise) and that a sample spectrum is obtainable.

Typically, the single beam spectra are viewed prior to the analysis, saving time by eliminating the unnecessary collection of bad data. Also, the single beam background can be saved and used on subsequent runs until environmental and instrumental noise change enough to warrant the collection of a new background.

Processing Single Beam

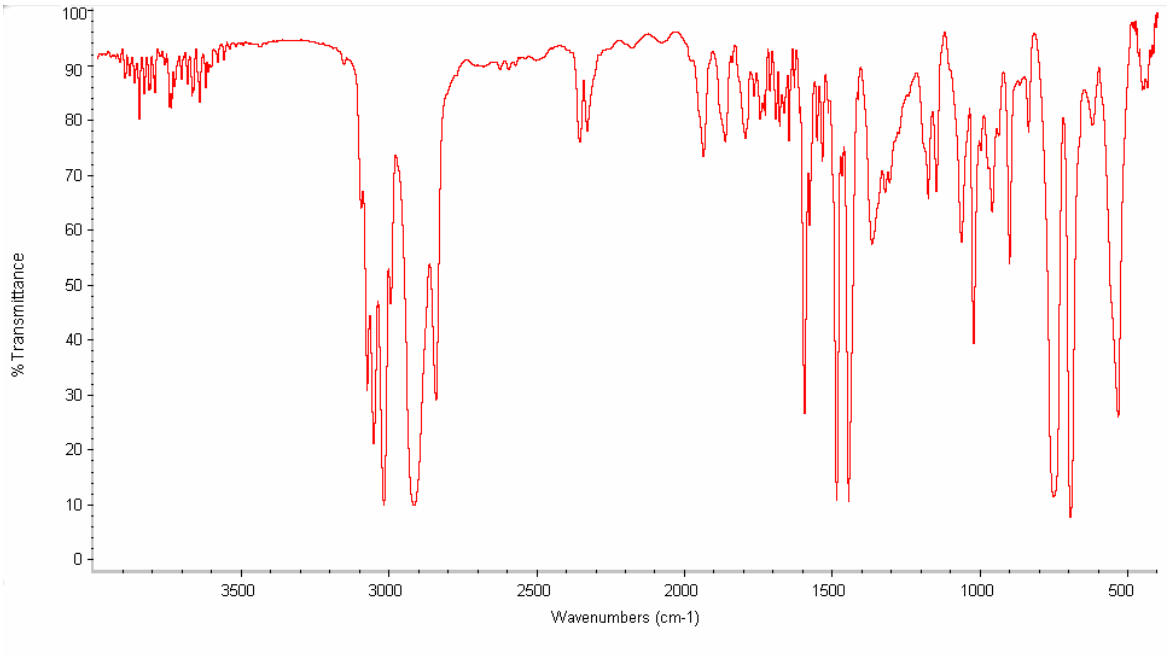
$$E_{sample} \,/\, E_{background} \times 100\% = \%Transmittance$$



%Transmission is defined as the amount of energy making it through the sample relative to the background energy. For non-interacting frequencies, this value, using the correct background, should be close to 100%T, in theory.

Baseline shift can be observed and is usually due to optical phenomena such as light scattering and refraction. Once the Fourier transformation is performed, the process is not reversible.

% Transmittance Spectrum



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The % Transmittance spectrum is typically used for spectral interpretation and/or spectral comparisons. However, the scale is logarithmic in nature and linear extrapolations normally used in quantitative analysis are not recommended using this scale. Therefore, a different scale has been developed for such work.

Qualitative Analysis

- Infrared spectrum can be used to help identify the material because of the unique information encoded in the infrared spectrum.
- Interpretation of the infrared data is a skill that can be learned. There are various tools to aid in this task.
- Searching unknown spectra against collections of spectra of known materials (libraries) can also help to identify the unknowns.

Quantitative Analysis

- There is a relationship between the intensity of peaks in the infrared spectrum and the quantity of material sampled.
- As the concentration of the compound increases, the intensity of the peaks representing the compound will also increase.
- This is described by the Beer – Lambert Law.

Beer-Lambert Law

$$A = a * b * c$$

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Converting %T to Absorbance (A)

$$A = -\log_{10}(T) = \log(1/T)$$

- **Reversible Conversion** : %T←→A
- **Ideal for Quantitative analysis**
- **Measured relative to Zero** - Easy to work with
- **Good Linearity** between 0 - 1.50 ABS units

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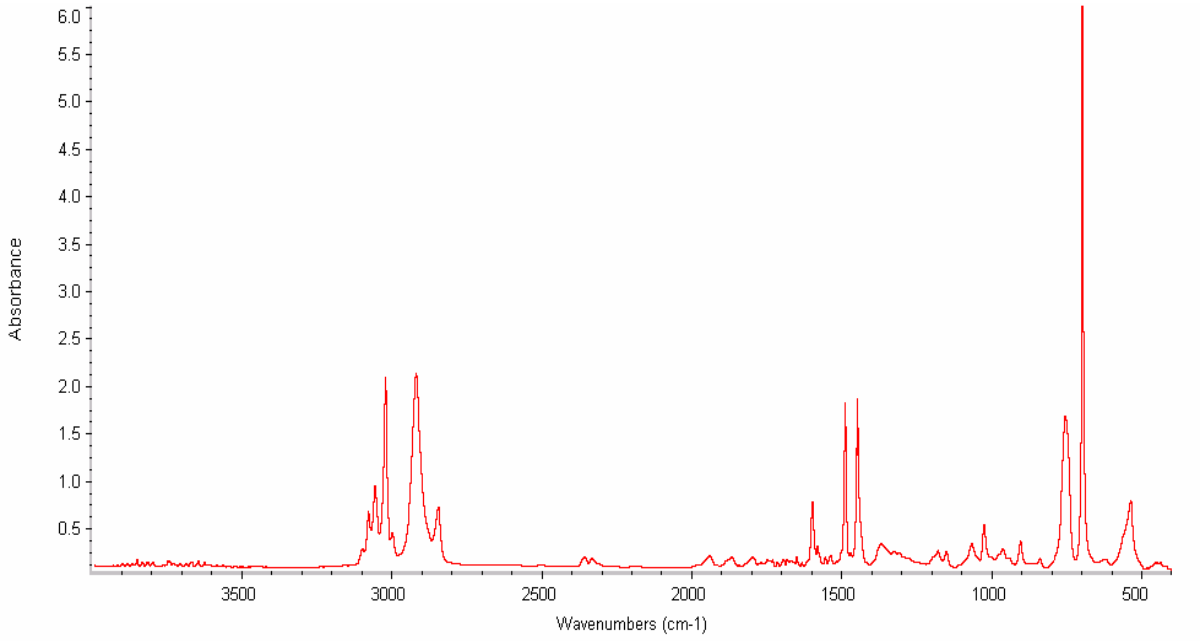
The absorbance spectrum is measured relative to zero and is extremely linear between 0-0.7ABS and relatively linear from 0.7-almost 2 ABS units. This linearity makes ABS a very useful scale for quantitative analysis and data manipulations that are linear in nature. The Absorbance conversion is a reversible process and can be converted back to %T without losing any spectral information.

Absorbance Spectrum



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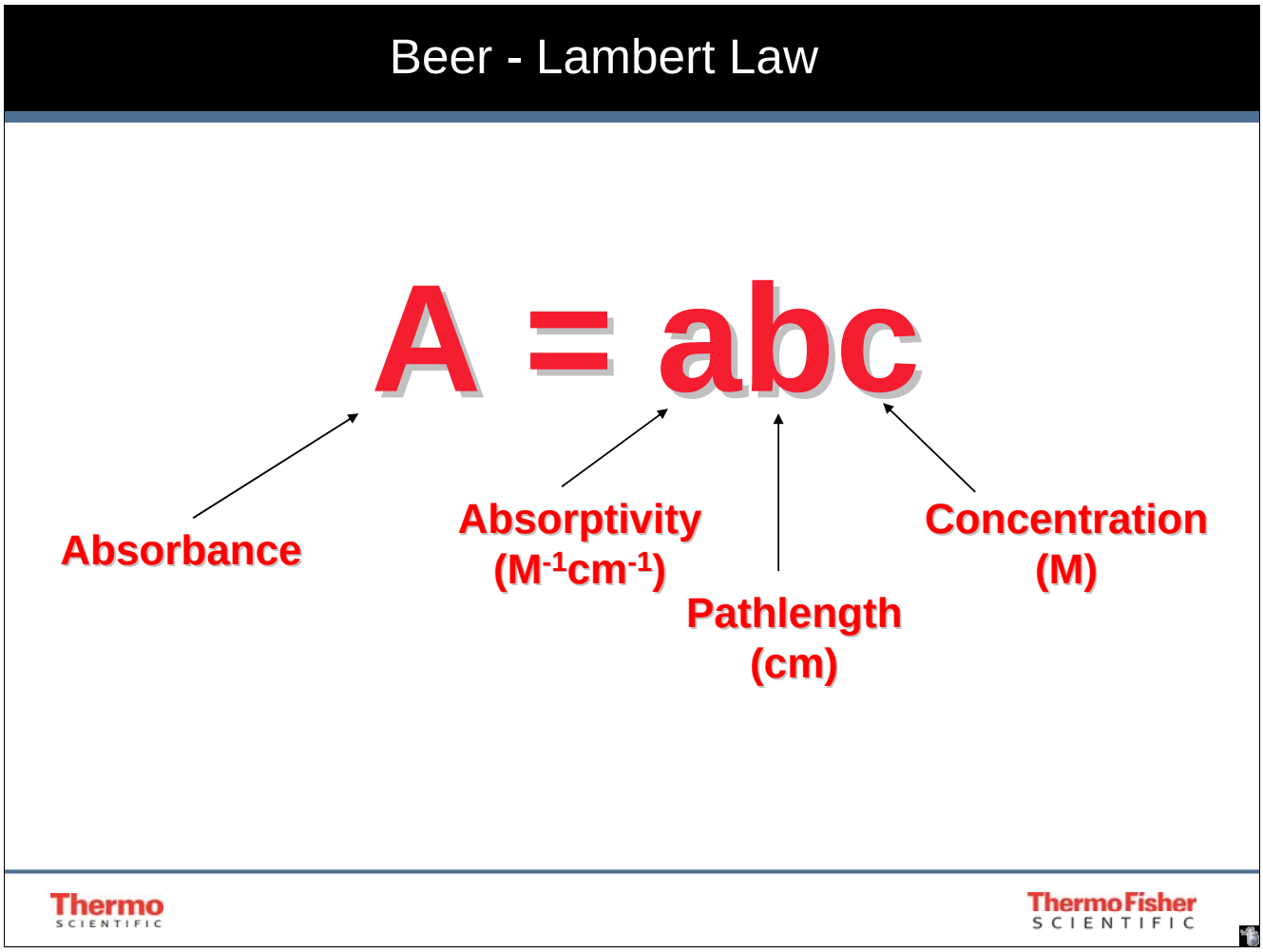
Absorbance is defined as the amount of energy interacting with the particular frequency relative to the background being used. For non-interacting frequencies this value, using the correct background, should be 0 absorbance and 100%T. In other words, none of the energy at that particular wavelength is interacting with the molecule and all the energy (in theory) is transmitted to the detector.



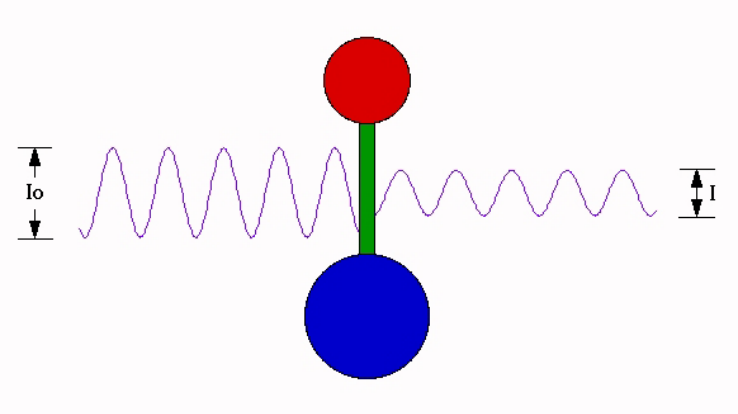
Beer-Lambert Law

The peak area and peak height tool can both be used for quantitative measurements. The principal behind using these tools for quantitative analysis is the Beer-Lambert Law.

The Beer-Lambert Law states that the concentration is proportional to the absorbance if the sample pathlength is constant. The molar absorptivity is a constant (dependent on frequency) that defines the change in the peak intensity relative to the concentration (variance of the spectra over a concentration range). The absorptivity is used to determine which frequency or peak should be used to quantitate the desired component. Since the absorptivity is constant under a given set of conditions it can be factored out of the equation. This may not be true if the frequency used to calculate the peak height or peak area changes. More importantly the pathlength must remain constant so that the concentration is proportional to the Absorbance calculation. It isn't always easy to maintain a constant pathlength, but there are several different accessories available that can help.

a = Molar Absorptivity

- A property of the material which describes how readily the compound absorbs infrared radiation at a specific wavelength
- Some species are more active in the mid-IR than others
- For normal operating conditions this term is constant



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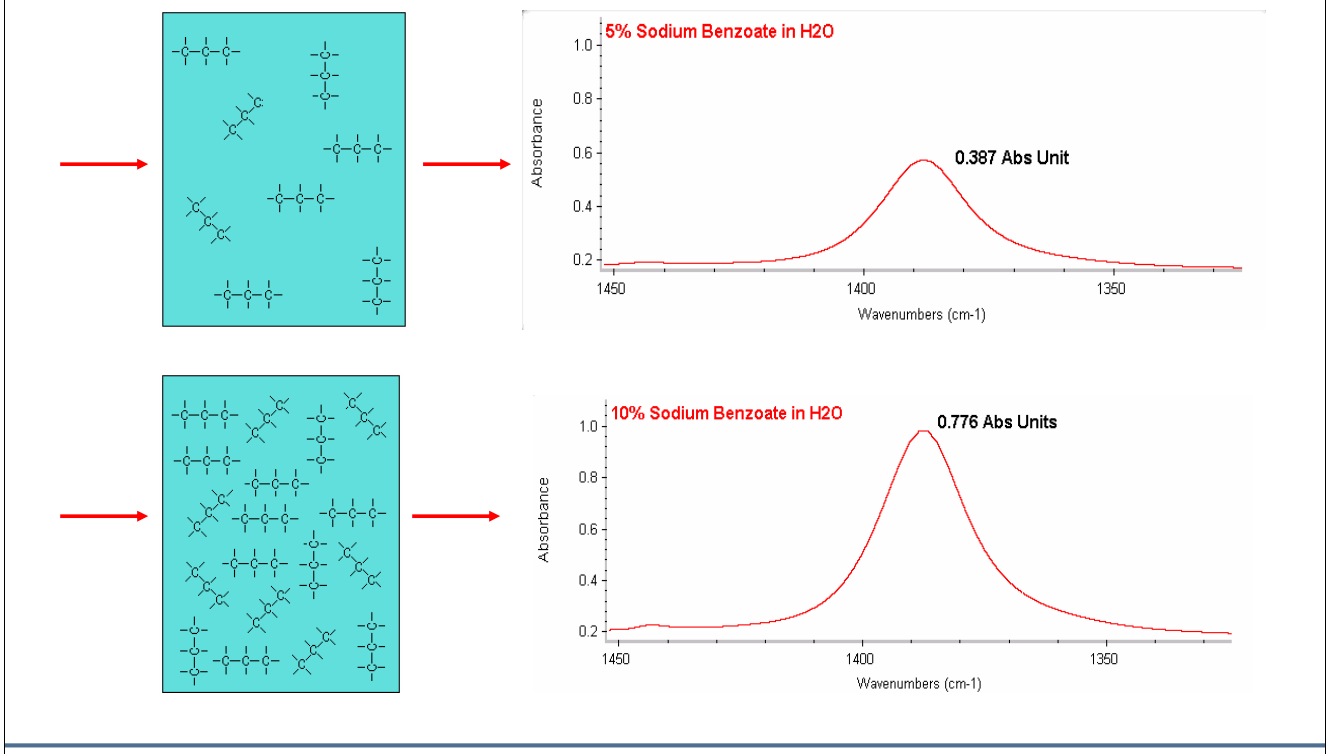
Absorptivity

A property of the material which describes how readily the compound absorbs infrared radiation at a specific wavelength.

Some species are more active in the mid-IR than others.

Constant pathlength: Increased concentration



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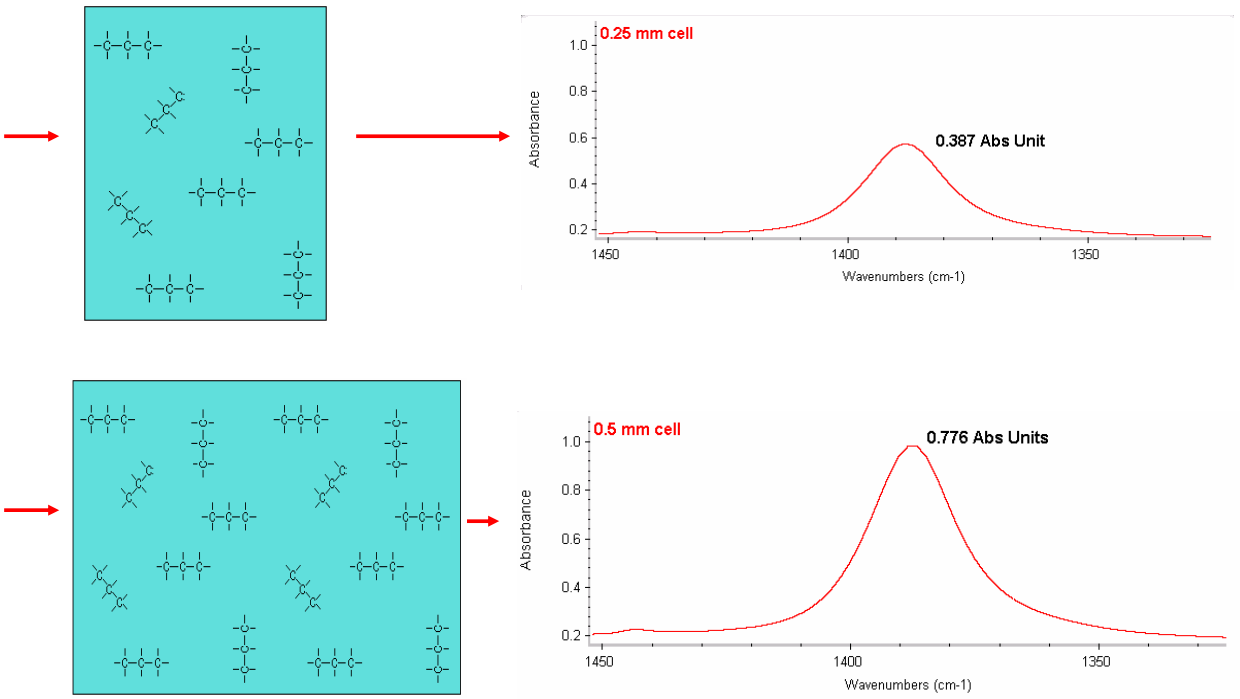
Concentration

In this example, pathlength is held constant and the concentration -- the number of bonds of the analyte of interest -- is increased.

Analyze concentrations that are within the dynamic range of your instrument. Ask what concentrations you need to measure and quantify, model your experiments realistically!

Constant concentration: Increase pathlength



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Pathlength

The longer the pathlength, the greater chance for molecular interactions. Try to select a preparation technique or accessory that provides constant pathlength.

If the pathlength isn't constant, Thermo's TQ analyst offers you alternative treatments to calculate pathlength.

In this case, the analyte of interest, is at a constant concentration. The bottom holder is twice the pathlength and therefore holds more sample. Hence, the absorbance has increased. This graphically illustrates the influence of pathlength on the analysis.

Summary

Using the ***Qualitative*** properties of the infrared data

- **Structural conformation of new materials can be determined**
- **Contaminants can be identified**
- **Competitive products can be determined chemically**

Using the ***Quantitative*** properties of the infrared data

- **Concentration of critical additives can be determined**
- **Consistency of product mixtures can be monitored**
- **Quality of starting materials can be determined**

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Fourier Transform Infrared Spectroscopy - review

- *Introduction*
  - *Electromagnetic radiation*
  - *Vibrational spectroscopy*
- *Instrumentation*
  - *Michelson interferometer*
  - *The Fourier transform*
- *Analysis*
  - *Qualitative – Identification*
  - *Quantitative – Quantification*

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In this section we have provided a brief overview of spectroscopy while detailing the operation of the instrument and introducing you to qualitative and quantitative analysis methods.