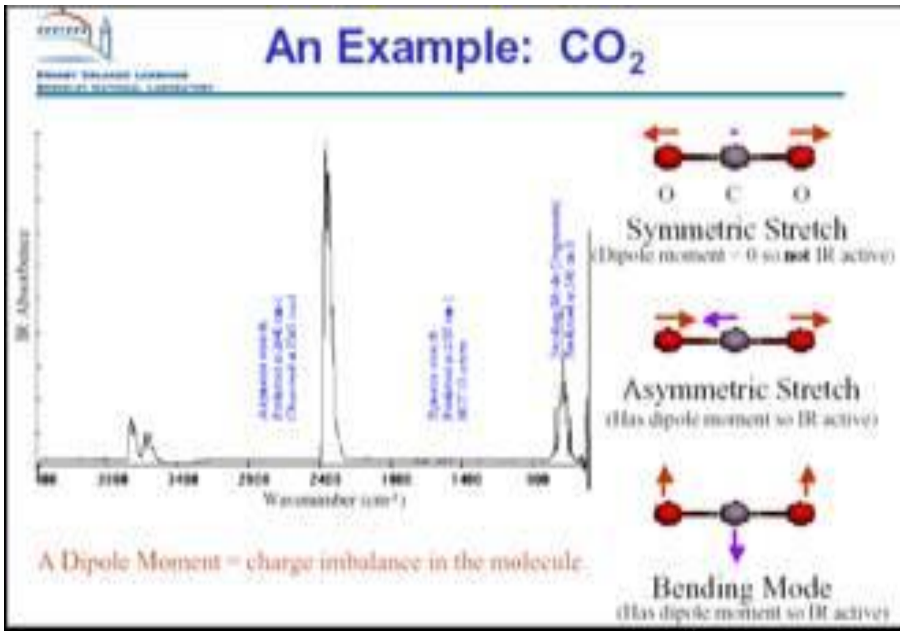
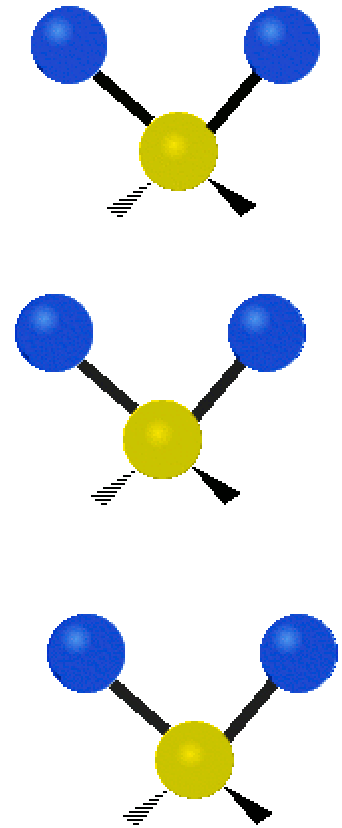
Fourier Transform IR Spectroscopy

- **Absorption peaks in an infrared absorption spectrum arise from molecular vibrations**
- **Absorbed energy causes molecular motions which create a net change in the dipole moment.**

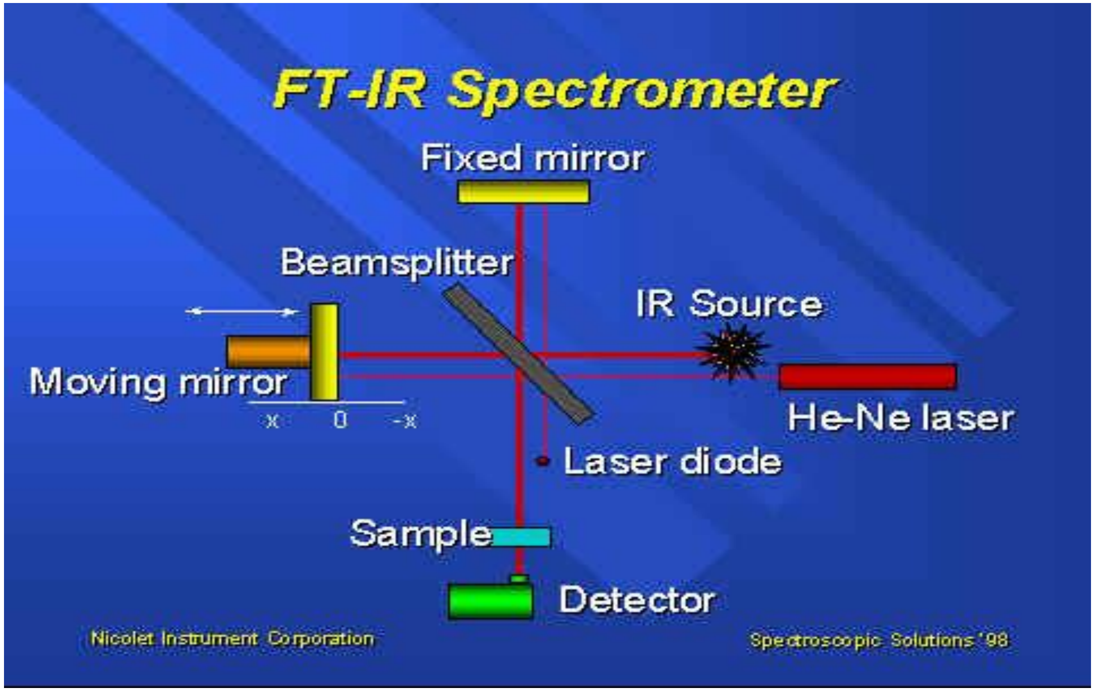




What is FTIR

- **Fourier-transform infrared spectroscopy is a vibrational spectroscopic technique, meaning it takes advantage of asymmetric molecular stretching, vibration, and rotation of chemical bonds as they are exposed to designated wavelengths of light.**
- **Fourier transform is to transform the signal from the time domain to its representation in the frequency domain**

Theory and Instrumentation

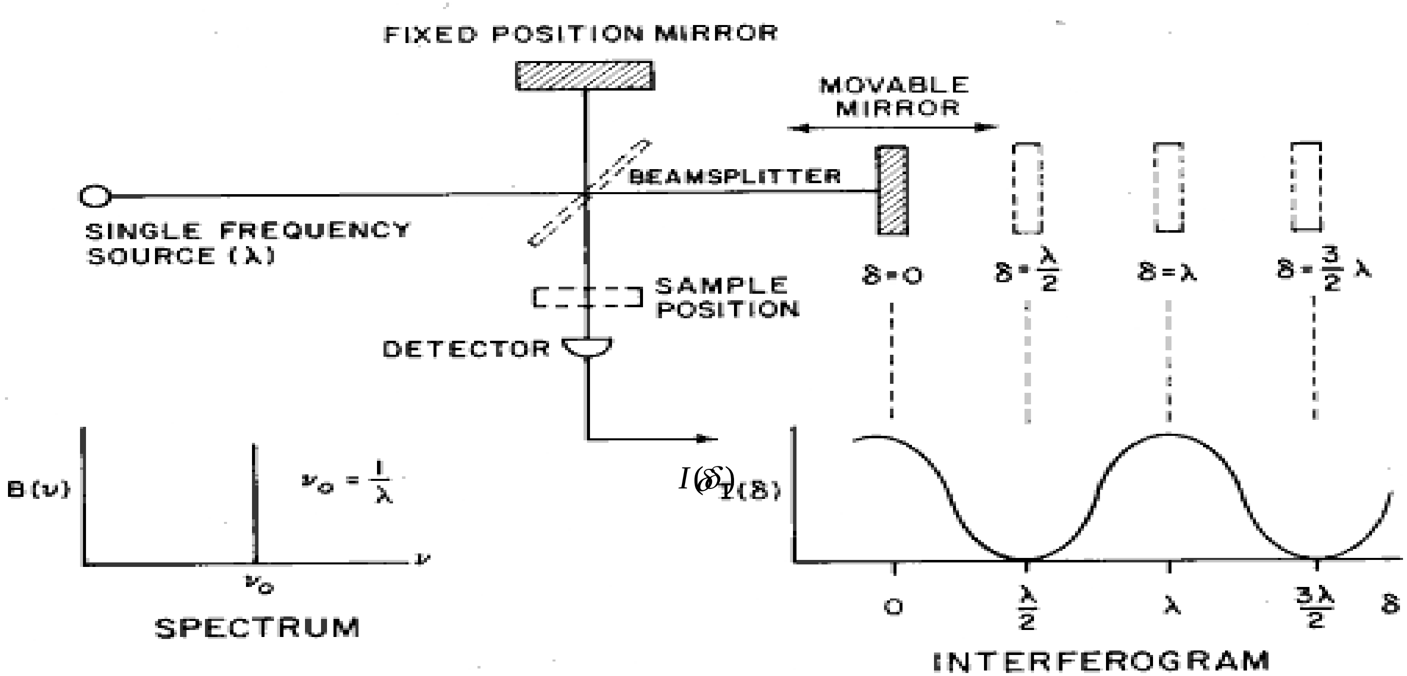


- **Light enters the spectrometer and is split by the beam splitter. The figure above shows what is referred to as the Michelson interferometer**

Theory and Instrumentation(contd.)

- The light originates from the He-Ne laser
- Half of the light is reflected 90 degrees and hits a fixed mirror, while the other half passes through the beam splitter and hits the moving mirror
- The split beams are recombined, but having traveled different distances, they exhibit an interference pattern with each other
- As they pass through the sample, the detector collects the interfering signals and returns a plot of response v. mirror displacement known as an interferogram

Mathematics



- **Optical path difference is** δ
- **Intensity of the detector** $I(\delta)$ **has maxima at** $\delta = n\lambda, n = 0, \pm 1, \pm 2$ **and minima at** $\delta = (n + 1/2)\lambda$

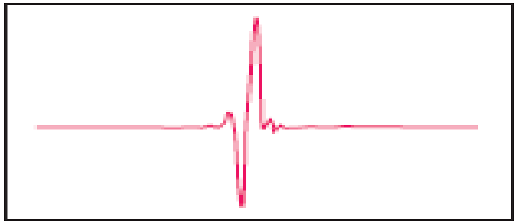
Why Infrared Spectroscopy?

Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory for over seventy years. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive **identification** (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the **amount** of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis.

Why FT-IR?

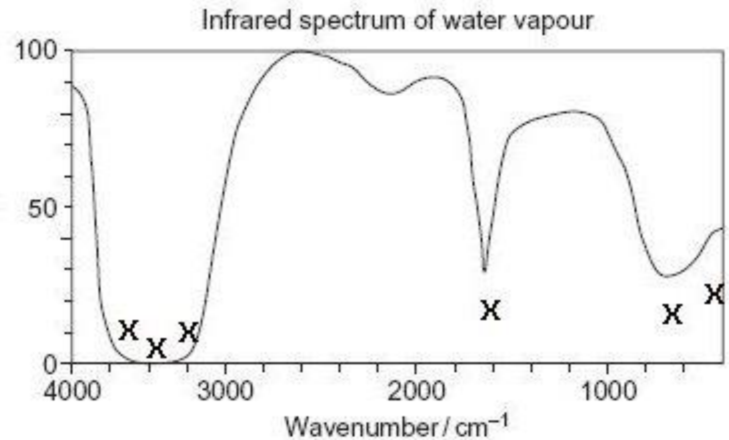
Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies **simultaneously**, rather than individually, was needed. A solution was developed which employed a very simple optical device called an **interferometer**. The interferometer produces a unique type of signal which has all of the infrared frequencies "encoded" into it. The signal can be measured very quickly, usually on the order of **one second** or so. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes.

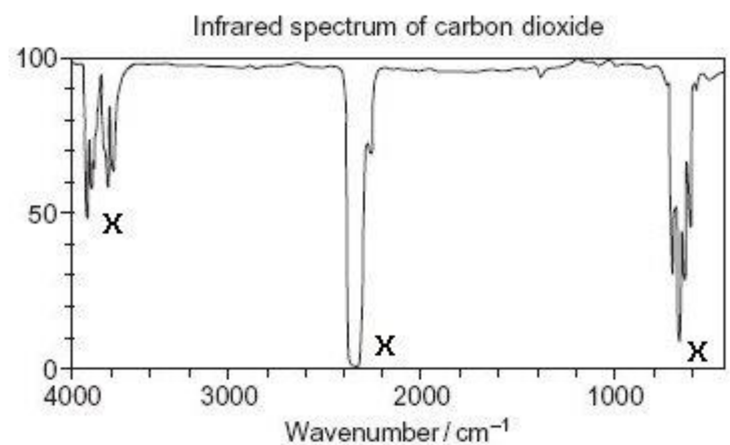
Most interferometers employ a **beamsplitter** which takes the incoming infrared beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place. The other beam reflects off of a flat mirror which is on a mechanism which allows this mirror to move a very short distance (typically a few millimeters) away from the beamsplitter. The two beams reflect off of their respective mirrors and are recombined when they meet back at the beamsplitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams "interfering" with each other. The resulting signal is called an **interferogram** which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source.



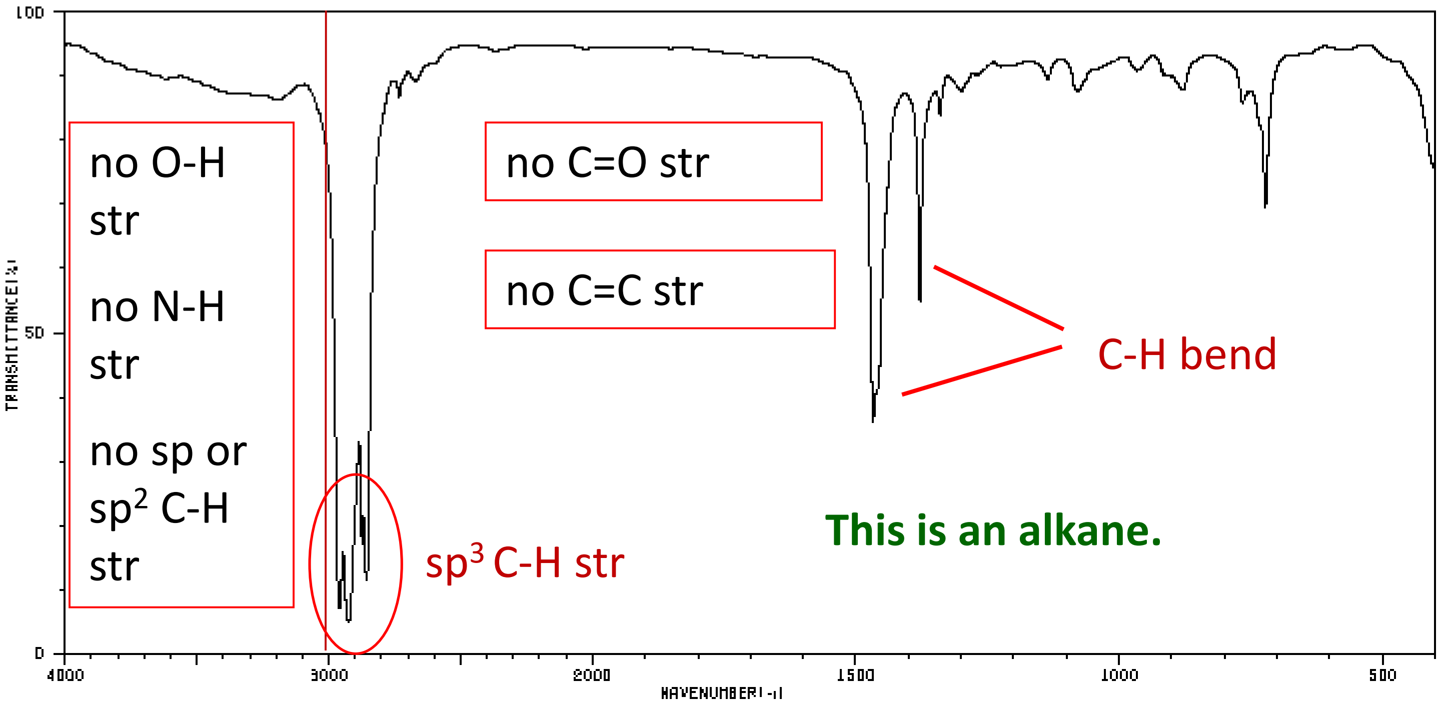
This means that as the interferogram is measured, all frequencies are being measured **simultaneously**. Thus, the use of the interferometer results in extremely fast measurements.

Because the analyst requires a **frequency spectrum** (a plot of the intensity at each individual frequency) in order to make an identification, the measured interferogram signal can not be interpreted directly. A means of "decoding" the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the **Fourier transformation**. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis.


Infrared spectrum of water vapour
100
50
0
4000
3000
2000
1000
Wavenumber / cm⁻¹
X
X
X
X
X
X

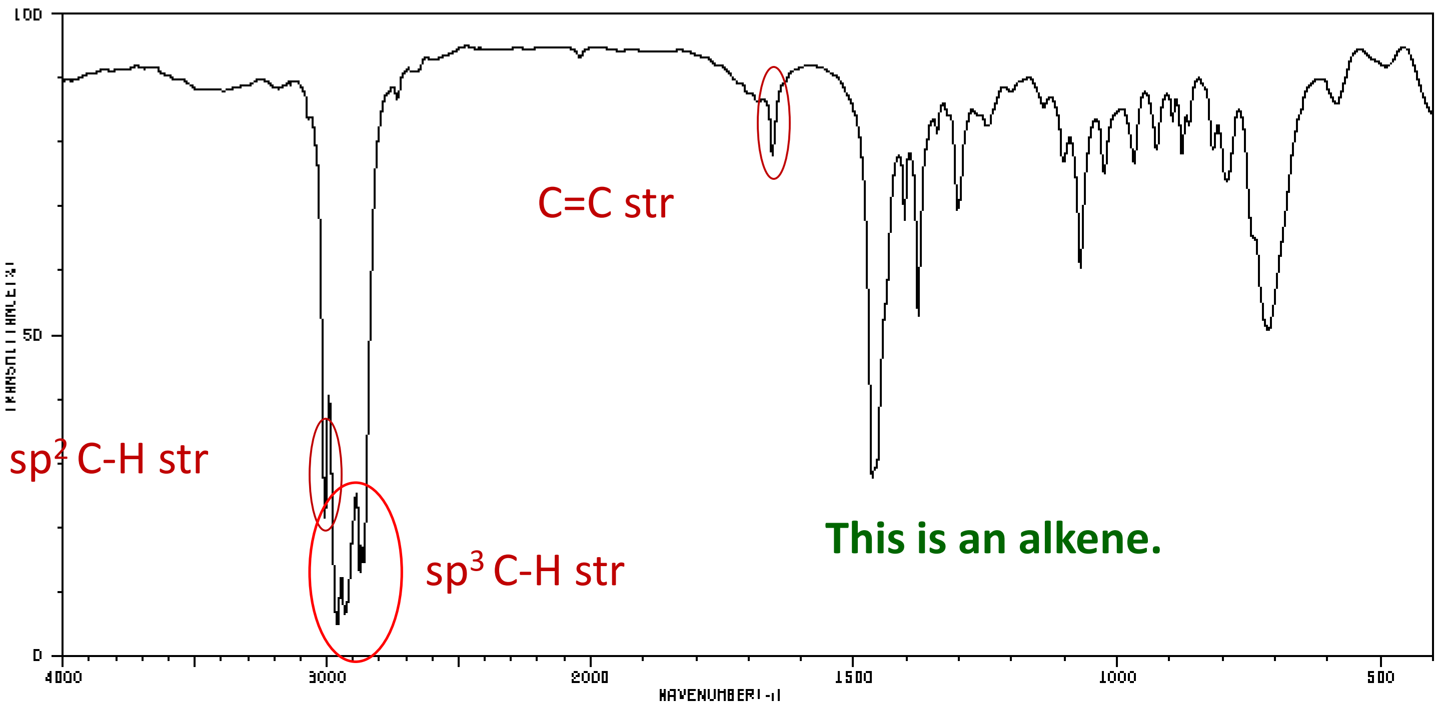

Infrared spectrum of carbon dioxide
100
50
0
4000
3000
2000
1000
Wavenumber / cm⁻¹
X
X
X

IR Spectra - Examples



SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology, 10/15/09)

IR Spectra - Examples



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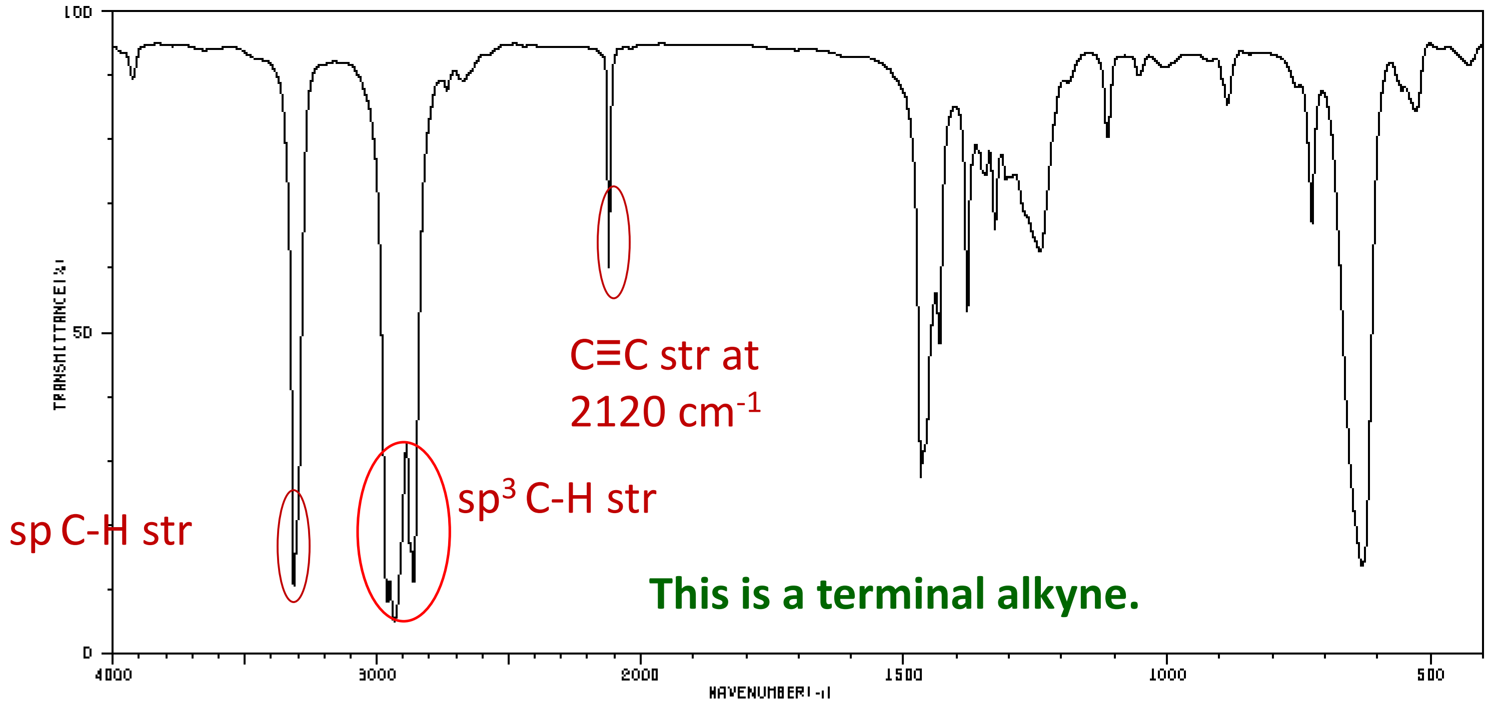

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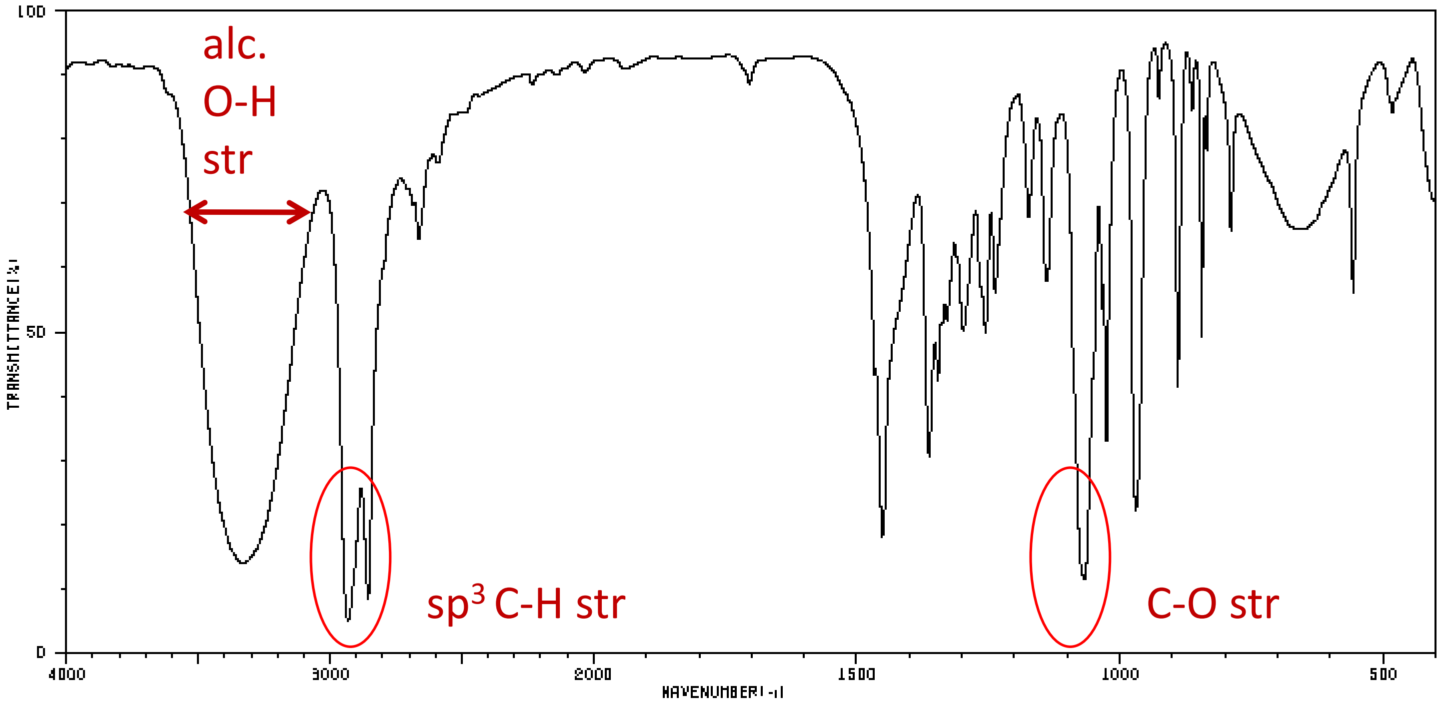
IR Spectra - Examples



This is an alcohol.

SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology, 10/16/09)

Advantages and Disadvantages

- **FT – IR can take wavelength readings across the whole IR region simultaneously and smoothly, making this a very rapid technique.**
- **The technique is non-invasive and non-destructive. Its resolution of .125 cm^{-1} is not spectacular in comparison to other vibrational techniques and it will not give the same detailed structural information that NMR, MS, or X-ray crystallography.**
- **IR spectroscopy is notoriously sensitive to the absorption of water, and it has the tendency to overwhelm all of the other peaks. If there is significant moisture in the sample the penetration distance of the light decreases. It may be advantageous to go with Raman in place of IR in the case of excess moisture.**
- **Spectra in the frequency domain can never be eyeballed conclusively. They are always subject to some sort of manipulation, leading some to believe that the data can say whatever the experimenter wants it to say depending on how it is manipulated.**