

The Fundamentals of Infrared Spectroscopy

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The Principles of Infrared Spectroscopy

Spectroscopy is the study of the interaction of electromagnetic radiation with matter. The electromagnetic radiation may be anywhere from very high energy gamma rays to low-frequency radio waves. The nature of the interaction depends upon the frequency or energy of the electromagnetic radiation and also on the properties of the matter. The interactions may be ionizing (gamma- and x-rays), chemical-electronic (UV-visible), vibrational / rotational (infrared), or magnetic (microwave or lower). There are many aspects to spectroscopy and it is not in the scope of this note to consider all of these.

The electromagnetic spectrum covers a wide range of wavelengths. The infrared regions are classified as follows:

Near Infrared	12,500 to 4,000 cm^{-1} (0.8 to 2.5 μm)
Mid Infrared	4,500 to 400 cm^{-1} (2.5 to 50 μm)
Far Infrared	400 to 12.5 cm^{-1} (50 to 800 μm)

Using these units, visible light is from 0.36 to 0.75 μm , or 27,778 to 13,333 cm^{-1} . There is a discussion of these units below.

In the case of infrared spectroscopy, infrared light passes through a sample and certain frequencies of the light are absorbed by the chemical bonds of the substance, leading to molecular vibrations. The infrared region considered in this note is the mid-infrared, from 4500 cm^{-1} to 400 cm^{-1} . The frequencies and intensities of absorbed infrared light depend on the specific bond strengths and atoms of that molecule, and the absorption pattern (called a spectrum) is unique for each material. The condition of the material, such as the temperature, the state (solid, liquid, or gas), concentration, pressure, and other materials in a mixture also affect the spectrum. It is this spectrum that makes infrared spectroscopy a very powerful tool for both qualitative and quantitative analysis.

Spectroscopy instrumentation, in simplest terms, involves a light or emission source, optics, a sample holder, and a detector. The optics are used to direct the light from the source through the sample and on to the detector. The optics are also used to condition the light in such a way that the light collected from the detector can be interpreted. In

some cases this involves breaking the light up into component wavelengths so that the sample is exposed to only a narrow region of the spectrum at any one time. In this form of infrared spectroscopy the wavelength of light incident on the detector at a given time is known. This is called DISPERSIVE spectroscopy because the light is dispersed into its component wavelengths. In many cases, however, the optics are more complex. In the case of Fourier Transform infrared spectroscopy (FTIR), the optics include an INTERFEROMETER, which modulates the infrared light such that the sample is exposed to the entire spectrum simultaneously. The individual wavelengths are then determined using mathematical operations (specifically the Fast Fourier Transform) to interpret the modulated light. This arrangement, while more complicated, leads to great advantages in terms of collection time, resolution, and signal-to-noise ratio. The mechanical and operational details of the interferometer are discussed in another applications note.

The infrared spectrum is measured by either absorbance or percent transmittance on the y-axis and by either the wavelength (μm) or wavenumber (cm^{-1}) to measure the position of an infrared absorption on the x-axis. Most compounds have characteristic absorptions in the infrared region. Tables of characteristic IR absorptions of functional groups can be found in most organic chemistry text books. A simple spectrum showing an idealized band is shown in Figure 1.

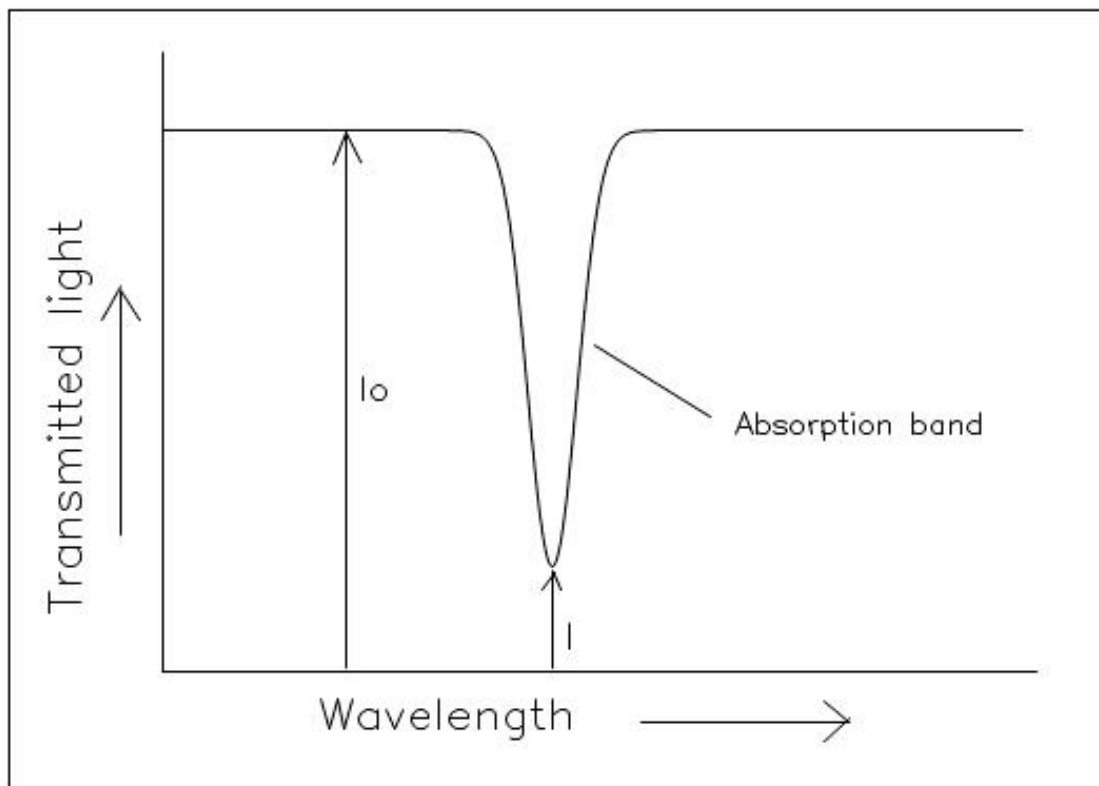


Figure 1. An idealized absorbance band in transmittance on the y-axis.

In this case, the y-axis shows transmittance, in which case the line at the top indicates all of the light at that wavelength is making it to the detector. The absorption band points downward. The strength of the absorption band is often reported as a value from 0 to 100 in percent transmittance. The light at that frequency or wavelength is being absorbed, or soaked up, by the chemical bond, causing it to vibrate more. The light that is absorbed by the chemical bond does not make its way to the detector, and so the transmitted light is reduced at that frequency. The intensity of the absorption is described in Equation 1:

$$\text{Transmittance} \quad T = I/I_0 \quad \text{Equation 1}$$

I_0 = Intensity of incident radiation from the infrared source at that frequency

I = Intensity of transmitted radiation that reaches the detector at that frequency

An infrared spectrum is often viewed in absorbance, with the peaks pointing up from the baseline instead of downward. The relationship between transmittance and absorbance is logarithmic, as described in Equation 2. That is, 100% transmittance is 0 absorbance units, 10% transmittance is 1 absorbance units, 1% transmittance is 2 absorbance units, etc.

$$\text{Absorbance} \quad A = \log(1/T) = \log(I_0/I) = \epsilon cL \quad \text{Equation 2}$$

ϵ = molar extinction coefficient (or molar absorptivity)

c = concentration

L = sample pathlength

An absorption band can be characterized by two parameters; the wavelength at which maximum absorption occurs, and the intensity of absorption at this wavelength. In an absorption spectrum, the intensity of the band is proportional to the number of molecules (i.e. the concentration) of the material being sampled. Similarly, the sample pathlength term means that a longer (or thicker) sample will absorb more strongly. Both of these factors make infrared spectroscopy a very powerful tool for quantitative analysis.

The units commonly used on the x-axis in infrared spectroscopy are either the wavelength in micrometers or microns, using the Greek letter mu (μ), or wavenumbers, also referred to as reciprocal centimeters (cm^{-1}). Consider the wave properties of light. The wavelength is simply the distance between one wave maximum and the next. See Figure 2.

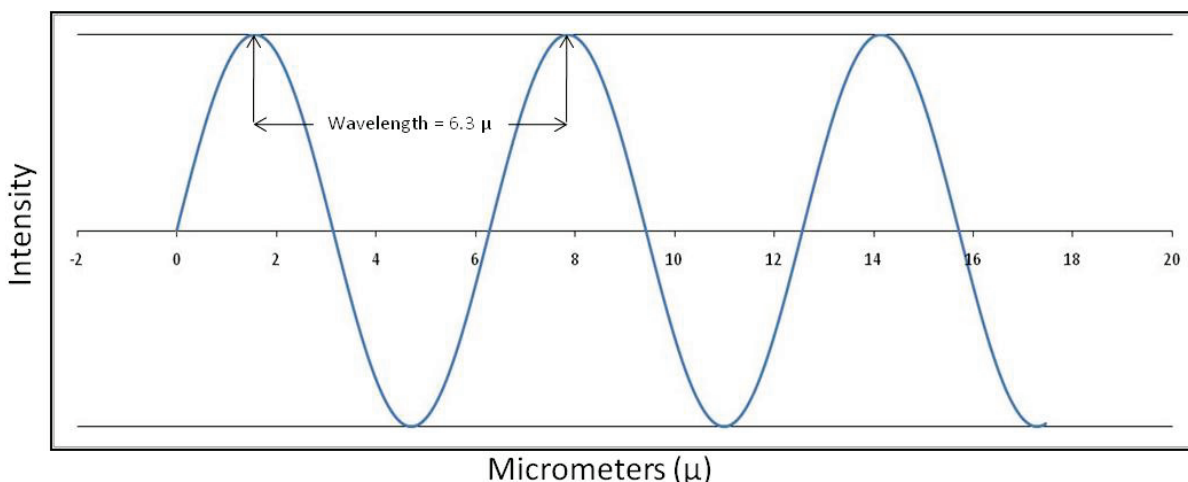


Figure 2. Wavelengths and wavenumbers.

In this case, the sine wave has maxima at 1.4, 7.7, and 14.0 micrometers, so the wavelength is 6.3 micrometers. If this drawing were extended out to fill one entire centimeter (10,000 micrometers per cm), then there would be a total of $10,000/6.3 = 1587.3$ of these maxima. This is the wavelength as measured in reciprocal centimeters; $6.3\mu = 1587.3 \text{ cm}^{-1}$. Spectroscopists use both wavelength and wavenumbers, but wavenumbers are preferred because the energy of light varies directly with wavenumber. In other words, the energy of light increases (red to blue) as the wavenumber value increases. Wavelengths were used extensively in the early days of infrared spectroscopy, but wavenumbers are used almost exclusively today. Wavenumbers will be used exclusively in the remainder of this note.

Fundamental Vibrations of Molecules

As mentioned, infrared light matches the vibrational frequencies of the molecular bonds. When infrared light is incident on the molecule, the frequency which corresponds with the natural vibrational frequency may be absorbed by the molecule, increasing the magnitude of the natural molecular vibrations. Some bonds absorb more strongly than others, and some compounds give very complex spectra. The details governing the specifics of an absorption band can be described mathematically and are couched in quantum mechanical terms. In order for a vibration to be "infrared active", it is necessary for a change in the dipole moment to occur during the absorption of the infrared light. In other words, the electronic charge distribution from one side of the bond to the other must occur. Consider hydrogen chloride, HCl. When HCl vibrates along the bond, the chlorine takes on a slightly more negative charge, and the hydrogen takes on a slightly more positive charge. Consequently, a change in dipole moment of the HCl molecule occurs. In some molecules, such as homonuclear diatomics (O_2 , N_2 , H_2 , F_2 , Cl_2 , Br_2 , I_2) there is no induced dipole moment, and these compounds are considered IR-inactive. Similarly, the noble gases (He, Ne, Ar, Kr) and most vaporized elements (e.g. Hg) are monatomic and have no bonds at all. These compounds are few and there are other techniques for measuring them.

The actual frequency of the vibrational modes for simple molecules can be calculated using the harmonic oscillator or “weight on a spring” model, which considers the atomic mass of both atoms as well as the strength of the bond. The traditional “weight on a spring” involves an object of some mass m hanging from spring attached to a fixed ceiling or support. Since molecules are not fixed in space, the reduced mass is used instead, Equation 3. For diatomic molecules, the absorption frequency can be calculated.

$$\nu = \frac{1}{2 \pi c} \sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}}$$

Equation 3

m_1, m_2 = masses of vibrating atoms, g

c = velocity of light, 3×10^{10} cm/sec

ν = wavenumber, cm^{-1}

k = force constant (bond strength), dynes/cm

Bond Strength

For a single bond $k = 5 \times 10^5$ dynes/cm

double bond $k = 10 \times 10^5$ dynes/cm

triple bond $k = 15 \times 10^5$ dynes/cm

Example: Calculate the fundamental frequency expected in the infrared absorption spectrum for the C-O stretching frequency using Equation 3.

$$\nu = \frac{\sqrt{\frac{5 \times 10^5 (12 + 16) (6.02 \times 10^{23})}{12 \times 16}}}{2 \times 3.14 \times (3 \times 10^{10})}$$

$$= 1111.5 \text{ cm}^{-1}$$

Avogadro's number = 6.023×10^{23} atoms/mole

Carbon-oxygen single bonds span a range from 1000 cm^{-1} to 1250 cm^{-1} depending on the rest of the molecule. Using this calculation for carbon-oxygen double bonds, we obtain 1571 cm^{-1} (typical carbonyls are from about 1675 cm^{-1} to 1800 cm^{-1}) and for the carbon-oxygen triple bond at 1925 cm^{-1} (carbon monoxide is centered at about 2145 cm^{-1}). The variation depends on many factors, not the least of which is that the C-O and C=O bonds are not diatomic, but the fundamental idea of a weight-on-a-spring is still valid for calculation of bond frequencies.

Some modes of vibration:

Stretching - distance between 2 atoms increases or decreases.

Bending - position of the atom changes relative to the original bond axis.

Scissoring – a bent molecule (e.g. H₂O) bends inward and outward.

Rocking – a twist of a bond with several other adjacent atoms

As molecules get more complex, the number of possible modes increases as $3n-6$, where n is the number of bonds. Bear in mind that these are primary motions; there are also combination bands, overtones, and rotational bands (gas phase). In addition, some transitions are considered “forbidden” for quantum mechanical reasons.

The CO₂ molecule is a typical example that illustrates the stretching and bending vibration modes, as shown in Figure 3. A symmetrical vibration along the axis produces no change in the dipole moment and therefore is infrared inactive. The unsymmetrical stretching gives a charge separation (change in the dipole moment) and thus is capable of interacting with light of the same frequency; absorption is observed. Bending motions can also occur as shown. The bending motions are at a lower frequency.

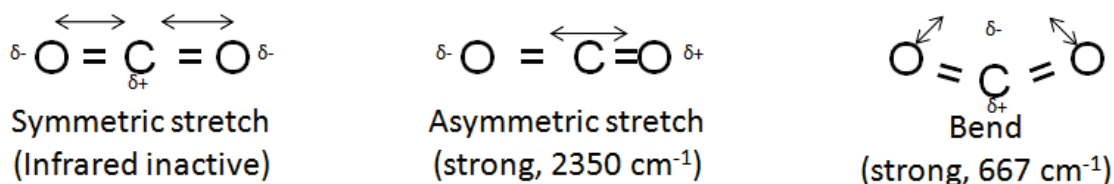


Figure 3: Vibrational modes of CO₂.

As a consequence of the multiplicity of bending and stretching modes, the infrared spectra get very complicated. Most organic chemistry and spectroscopy books have tables of common infrared absorbance bands. In addition, there are many excellent books on infrared spectral interpretation that can be used as guides for analyzing infrared spectra.

The Infrared Spectrum

As mentioned earlier, the primary optical component of an FTIR spectrometer is the interferometer. The interferometer has a moving mirror, a fixed mirror, and a beamsplitter. A further discussion of these components is presented in an Applications Note called FTIR Hardware: Interferometers. This note discusses both the modulated light seen by the detector, called the *interferogram*, and how it is changed to the *single beam spectrum*, and then on to the transmittance spectrum.

The interferogram looks like a cross (double-sided interferogram), or a sideways letter T (single-sided interferogram) with an intense signal at one point and much smaller signals for the rest of the spectrum. In the interferogram, all of the wavelengths of light are combined in such a way that the Fourier Transform can convert them into an infrared

spectrum. A background interferogram (without sample) will be taken first. The background interferogram will show the spectral response of the FTIR; source emissions, reflection and transmission efficiencies of the interferometer, the response of the detector, and the effects of the electronics. The sample is then placed in the path of the light, and a second interferogram is collected. This interferogram will be more complex. It will have the actual spectrum of the sample compound superimposed onto the background interferogram. See Figure 4.

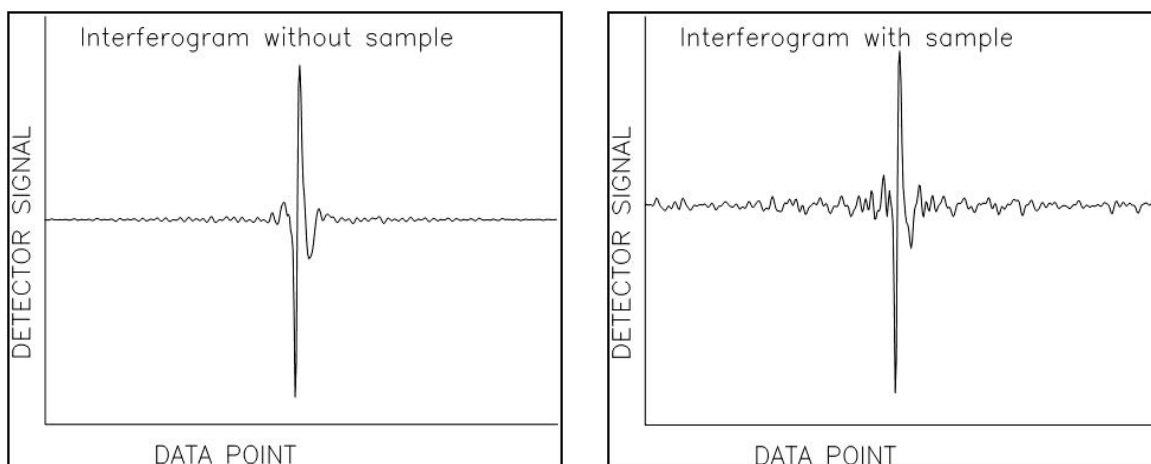


Figure 4. Background and sample interferograms.

Both of the interferograms are converted to single-beam spectra using the Fourier Transform, a mathematical operation that “decodes” the interferogram into individual wavelengths called single beams, Figure 5. This name was originally employed to distinguish from early dispersive “double-beam” spectrometers, where the optical path was duplicated and the reference and sample spectra were collected simultaneously (and slowly). In the case of FTIR, the background and sample are collected separately and mathematically combined later.

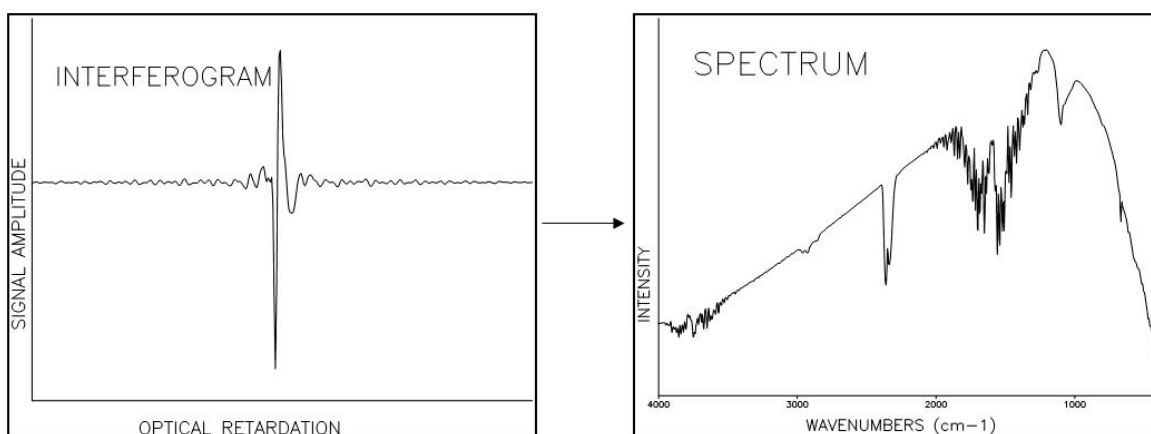


Figure 5. Interferogram and single beam.

The single beam spectra reflect the spectral response of the optics and electronics of the FTIR spectrometer, such as the emission of the source, the detector response, the efficiencies of the mirrors and beamsplitters, and effects of electronics (such as band-pass filters). See Figure 6. The background single beam is relatively featureless except for sharp bands from water vapor and CO₂. These are also present in the sample single beam, so they will effectively cancel out in the final spectrum.

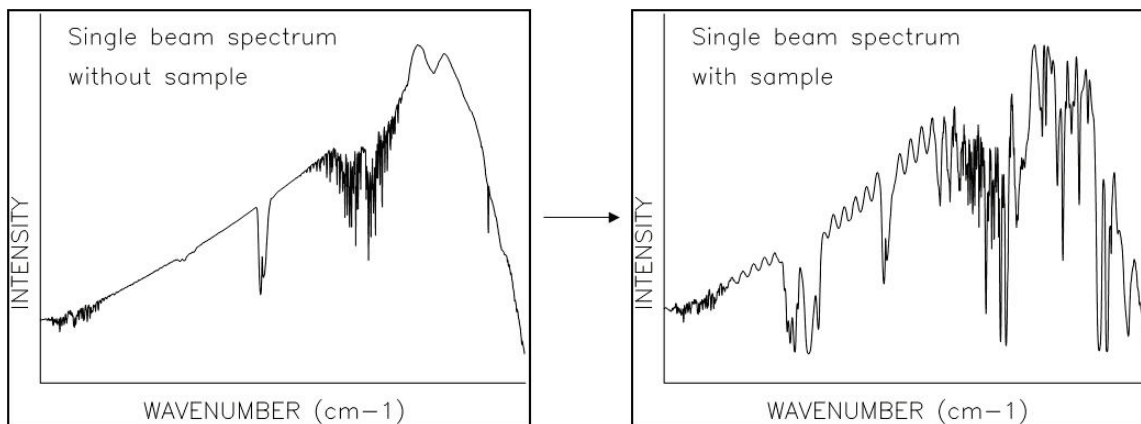


Figure 6. Background and sample single beams.

The single beams are then ratioed, or divided. Specifically, the sample spectrum is divided by the background spectrum (I/I_0 , Equation 1) at every wavelength, data point by data point. The resultant transmittance spectrum will show relative intensities of the different bands dropping from a baseline at the top of the spectrum, Figure 7. In this case, a point on the spectrum that is close to the top means that very little light is being absorbed by the sample at that wavelength (or wavenumber), whereas the bands that approach the bottom of the transmittance spectrum are very strong and nearly all of the light is being absorbed. While this class of infrared spectrum is qualitatively useful, the final step is typically conversion from % Transmittance to Absorbance according to Equation 2, as absorbance is linear with concentration.

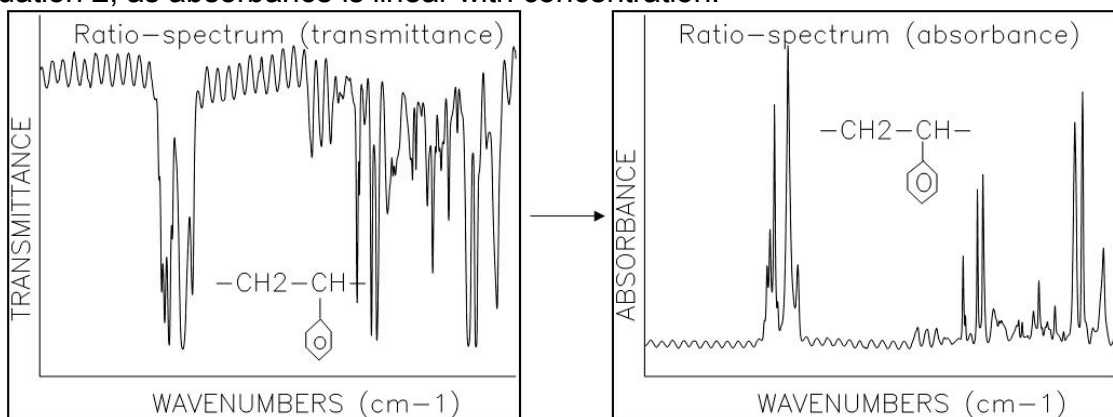


Figure 7. Transmittance and absorbance spectrum of polystyrene.

An example of an absorption being linear with concentration is seen with carbon monoxide in Figure 8.

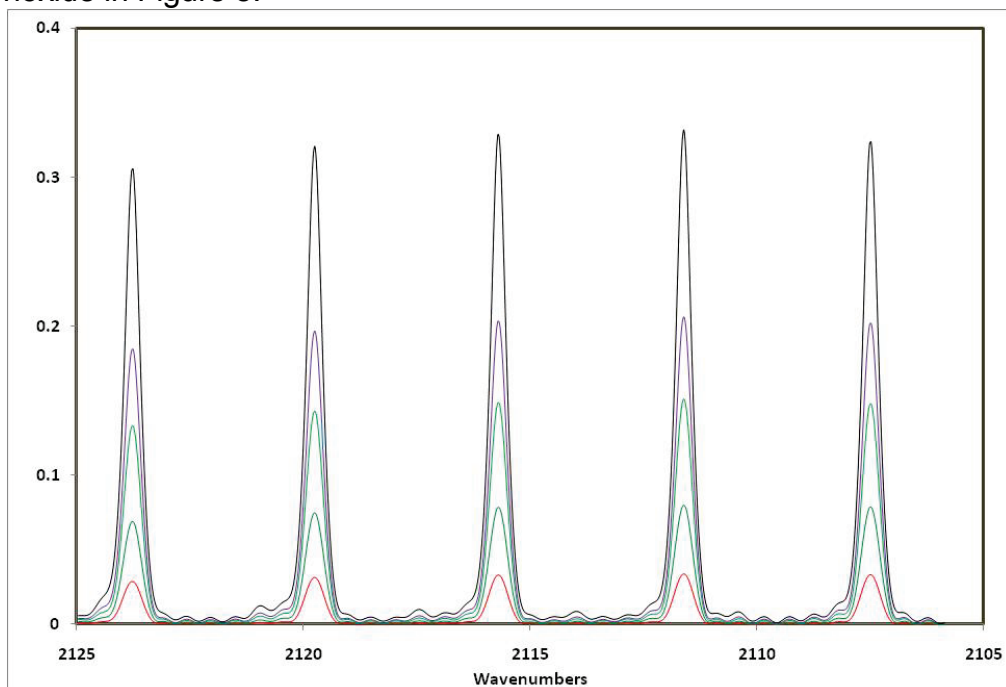


Figure 8. Carbon monoxide at 20, 50, 100, 150, and 300 ppm.

Some common spectra

An infrared spectrum can be collected of nearly any compound or sample.

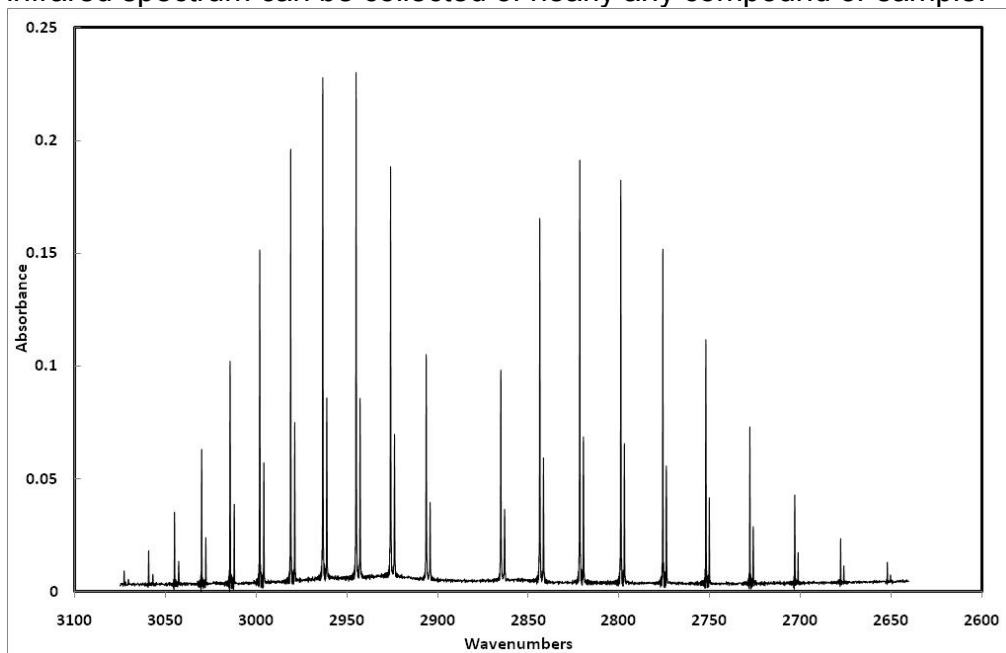


Figure 9. Hydrogen chloride, high resolution.

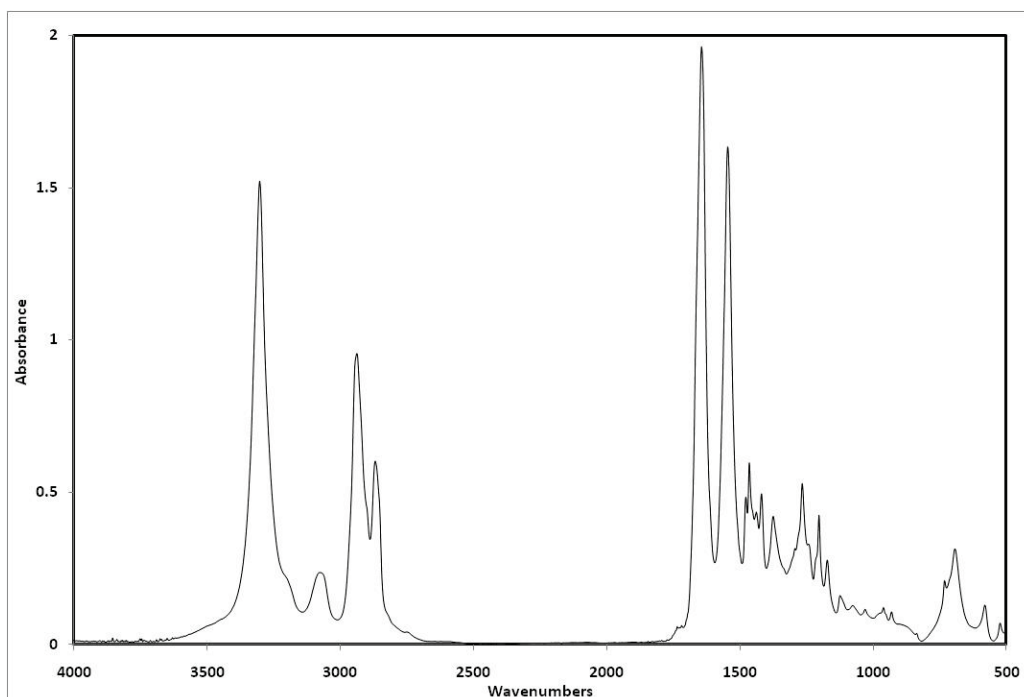


Figure 10. Nylon-6

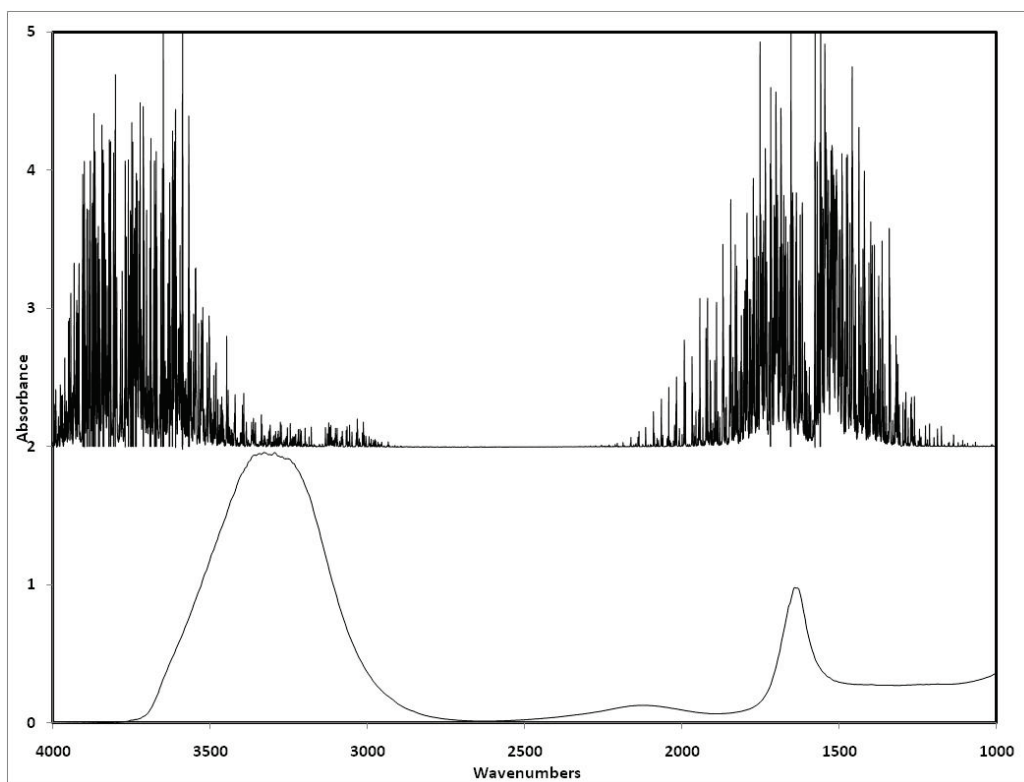


Figure 11, Water vapor (top), liquid water (bottom).

Summary

Infrared spectroscopy is a technique which measures the infrared absorbances of various materials in gas, liquid, or solid phases using suitable sampling techniques. The infrared spectrum is qualitatively useful in determining the identity of a compound, as all materials have different infrared signatures. The infrared spectrum is also quantitatively useful as the strength of the infrared absorbances vary with concentration. Gas phase measurements using infrared spectroscopy are especially powerful as sample concentrations can be analyzed over 12 orders of magnitude, from parts-per-billion levels up to pure materials where trace impurities are of interest. The technology of infrared gas analysis is very mature and well-established in both industrial and research applications.