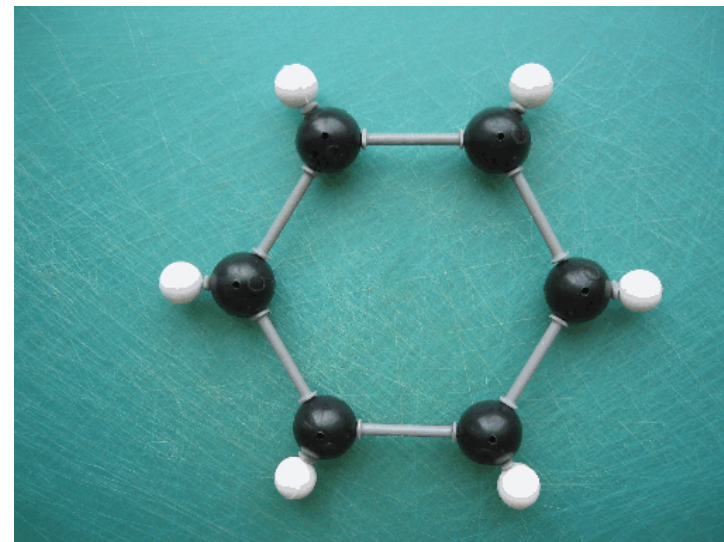
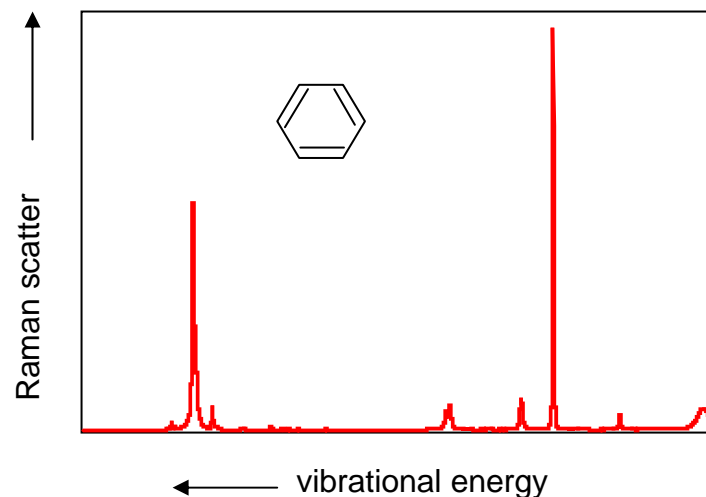


Chemists most often work with representations of molecules where the position of each atom is fixed with respect to the others. This is demonstrated by the ball and stick model of benzene shown in the figure. In contrast to such static descriptions, the atoms in a molecule are constantly moving with respect to each other. These motions are called vibrations. Each vibration has a characteristic energy, which depends upon the mass of the moving atoms and the strength of the bonds holding the atoms together. Vibrational energy corresponds to that obtained from one quantum of radiation in the infrared region of the electromagnetic spectrum. A graph depicting the energy of all molecular vibrations is called a vibrational spectrum. This spectrum can be used to determine the structure of a molecule or obtain the concentration of a molecule with a known structure.



This tutorial will cover the following topics:

- how many unique vibrations can a molecule have?
- different classes of vibrational motion
- the mathematical relationship between molecular mass, bond strength, and vibrational energy
- functional groups and their characteristic vibrational energies
- obtaining a vibrational spectrum by measuring infrared absorption
- obtaining a vibrational spectrum by measuring Raman scattering
- similarities and differences between infrared and Raman spectra



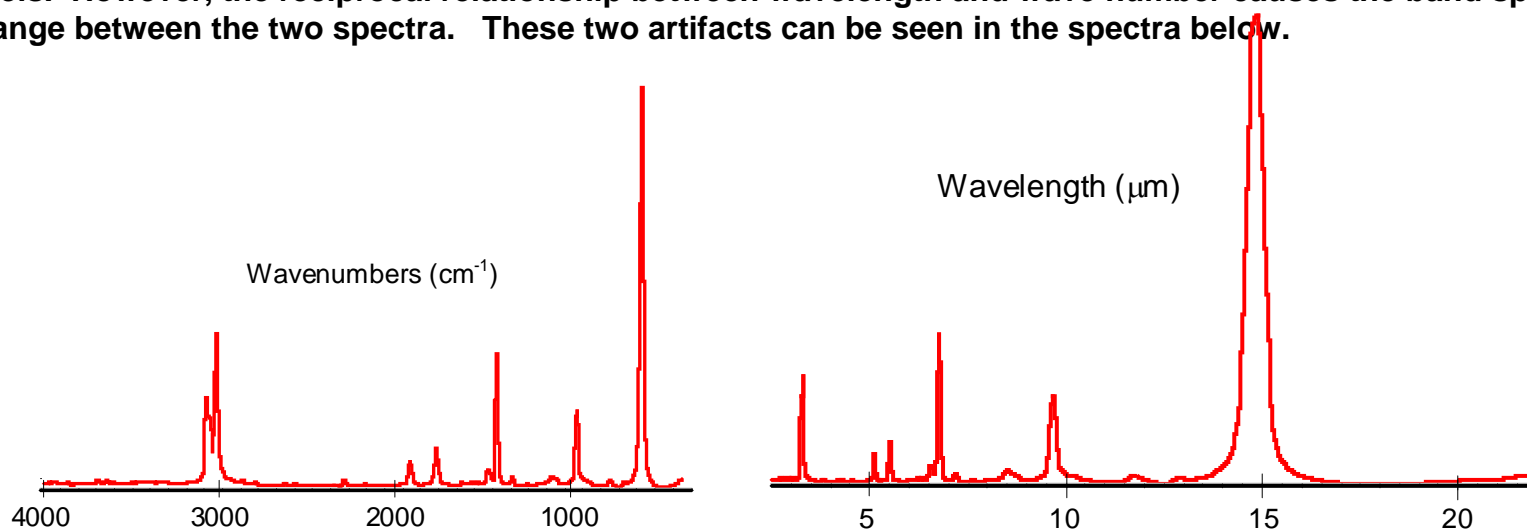
Graphing Vibrational Spectra

The molecular vibrations of most interest fall in the region of the electromagnetic spectrum called the mid-infrared. Historically wavelength was known to a higher precision than frequency (this is no longer true!). For this reason infrared spectra were displayed using wavelength. The most common units in the infrared were microns (micrometers, μm). Using these units the mid-infrared extends from 2.5 to 50 μm .

Because wavelength is not proportional to energy, a more modern convention plots infrared spectra using reciprocal wavelength, which is called wave number. The most common unit for wave number is cm^{-1} . The proportionality of wave number to energy can be seen by rewriting Planck's Law, $E = h\nu = hc(1/\lambda)$.

Converting the above infrared wavelength limits into centimeters gives 2.5×10^{-4} to 5×10^{-3} cm. Taking the reciprocal gives the infrared limits as 4,000 to 200 cm^{-1} . When speaking, wave numbers are often called frequency or energy, thus one might refer to a "vibrational band at a frequency of 1,060 reciprocal centimeters."

By convention an infrared spectrum is plotted with wave number decreasing toward the right – which seems backwards. This convention was chosen to preserve the order of the vibrational bands with either set of x-axis labels. However, the reciprocal relationship between wavelength and wave number causes the band spacings to change between the two spectra. These two artifacts can be seen in the spectra below.



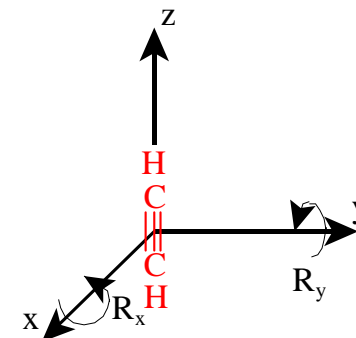
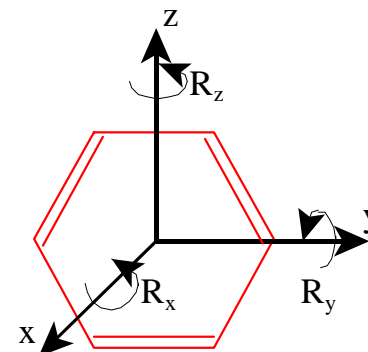
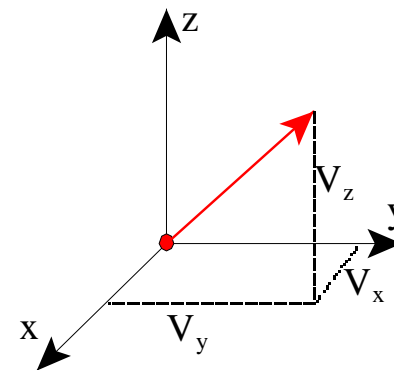
Degrees of Freedom for Molecular Motion

Since three axes are required to fully describe any direction in space, an atom is said to have three degrees of freedom for molecular motion. For a collection of N un-bonded atoms $3N$ degrees of freedom would be required to describe the molecular motion of all atoms.

When N atoms are bonded together, the degrees of freedom describe motion of the atoms with respect to each other. Degrees of freedom are not lost upon bonding, so an N -atom molecule has $3N$ degrees of freedom. One coordinated motion of the bonded atoms would be the movement (or translation) of the whole molecule. This description requires three degrees of freedom, leaving $3N - 3$ degrees of freedom to describe other coordinated atomic motion.

A second coordinated motion of the bonded atoms involves rotation of the molecule about its center of gravity. Three possible rotations of benzene are shown at the right, where the molecule is laying in the y,z -plane. Rotation about the x -axis keeps the molecule within the y,z -plane. Rotation about the y and z -axes rotates the plane of the molecule. For benzene and other non-linear molecules there are three independent ways to rotate a molecule, leaving $3N - 6$ degrees of freedom to describe vibrations. Thus for benzene there would be $3 \times 12 - 6 = 30$ vibrational degrees of freedom.

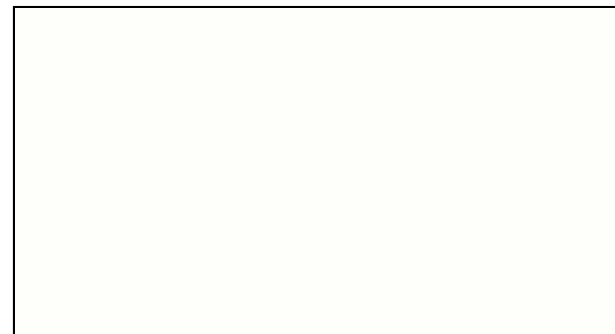
Linear molecules only have two independent rotations. Rotation about the bonding axis does not involve the movement through space of any atoms, thus does not exist. For linear molecules this leaves $3N - 5$ degrees of freedom to describe vibrations. Thus for acetylene there would be $3 \times 4 - 5 = 7$ vibrational degrees of freedom.



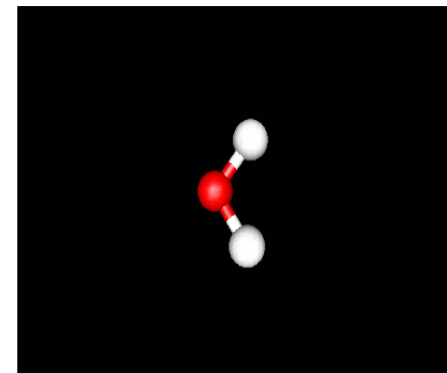
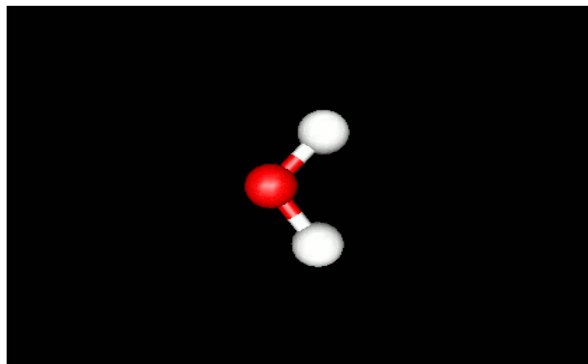
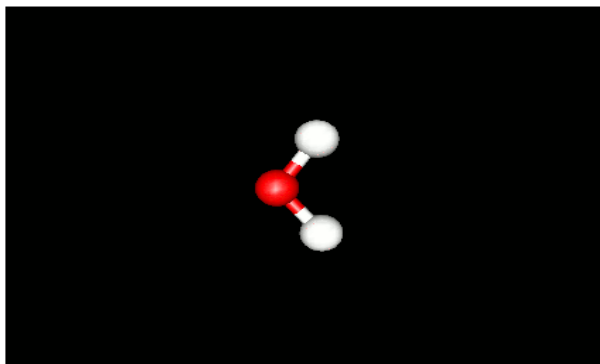
Two Simple Vibrational Motions

A stretching vibration expands and contracts bond lengths while keeping the bond angles constant. Bending vibrations change bond angles.

The top image represents carbon monoxide. CO has $3 \times 2 - 5 = 1$ vibrational mode. The stretching motion shown is the simplest possible since there are only two atoms involved. This vibration appears at a frequency of 2143 cm^{-1} (click on the image to observe the vibration).



The bottom images represent sulfur dioxide. SO_2 has $3 \times 3 - 6 = 3$ vibrational modes. Two of the modes are stretching and one is bending. The left panel shows a symmetric stretch which appears at 1151 cm^{-1} , the center shows an asymmetric stretch which appears at 1361 cm^{-1} . The right panel shows a bend which appears at 519 cm^{-1} .



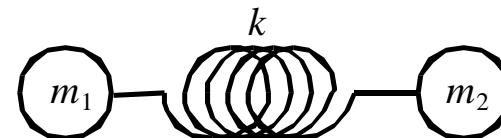
Thanks to Ronald Wampler from the Purdue Chemistry Department for creating the animations!

Harmonic Oscillator Equation

The stretching vibration of a diatomic molecule is described by the harmonic oscillator equation,

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

where $(1/\lambda)$ is the wave number (cm^{-1}), ν is the vibrational frequency (s^{-1}), c is the speed of light (cm s^{-1}), k is the bond force constant (kg s^{-2}), and μ is the reduced mass (kg) where $\mu = m_1 m_2 / (m_1 + m_2)$ and m_1 and m_2 are the atomic masses in kilograms.



Mechanical harmonic oscillator consisting of two spherical masses connected by a spring.

The harmonic oscillator equation predicts that the vibration wave number is proportional to the root of the bond force constant and inversely proportional to the root of the reduced mass. As a result large vibrational frequencies will be associated with light atoms and/or strong bonds. Thus the H_2 vibration is $4,159 \text{ cm}^{-1}$ (light atoms) and HF is $3,960 \text{ cm}^{-1}$ (strong bond). In contrast the I_2 vibration is 213 cm^{-1} (heavy atoms) and NaCl is 378 cm^{-1} (weak bond).

When hydrogen is bonded to a heavier atom the reduced mass of the pair is ~ 1 . For this case the bond force constant determines the relative vibrational frequencies. For example, the bond force constants are $\text{BH} < \text{CH} < \text{NH} < \text{OH} < \text{FH}$. This ordering is consistent with the fact that NH and OH vibrations appear at higher frequencies ($3,700 - 3,100 \text{ cm}^{-1}$) than CH vibrations ($3,000 - 2,700 \text{ cm}^{-1}$).

Since the bond force constant is roughly proportional to bond order, the harmonic oscillator equation can also be used to predict that triple bonded atoms will appear at higher frequencies than double bonded atoms, e.g. N_2 is 2331 cm^{-1} , O_2 is 1556 cm^{-1} and F_2 is 892 cm^{-1} . This same trend can be seen in hydrocarbons where carbon-carbon triple bond stretches appear in the range $2,300 - 1,900 \text{ cm}^{-1}$, while the double bond stretches appear in the range $1,700 - 1,550 \text{ cm}^{-1}$.

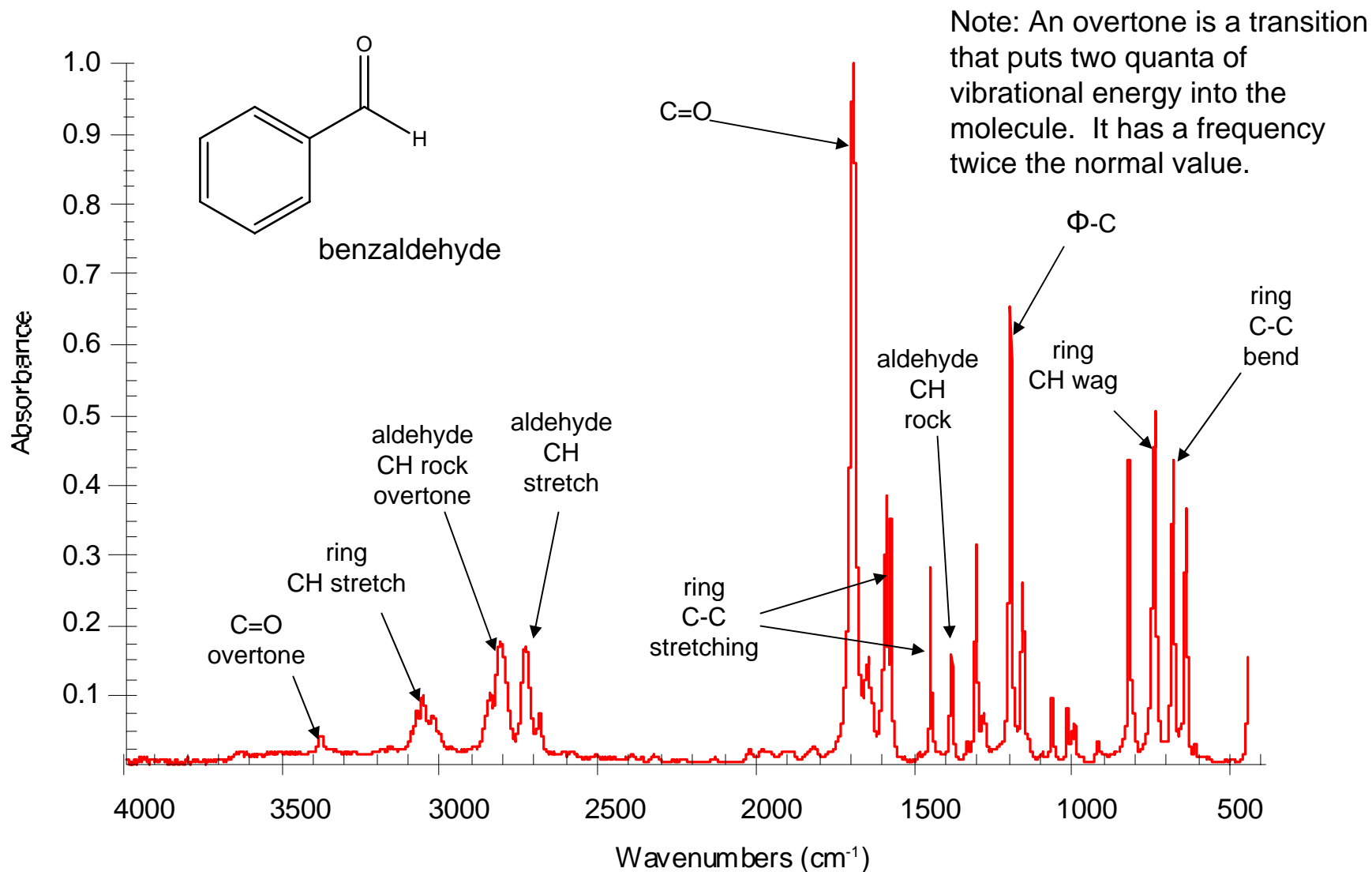
The mathematical description of polyatomic molecular vibrations is quite complex. Because of this the identification of normal modes and prediction of corresponding frequencies requires sophisticated computer programs. Fortunately certain sub-groupings of atoms have characteristic vibrations that fall within well-defined ranges of frequencies. These *group frequencies* are to a first approximation independent of the remaining structure of the molecule. This often makes it possible to identify the structure of a molecule by visually examining its vibrational spectrum.

The following is a list of frequency regions (in cm^{-1}) and associated functional groups for organic compounds.*

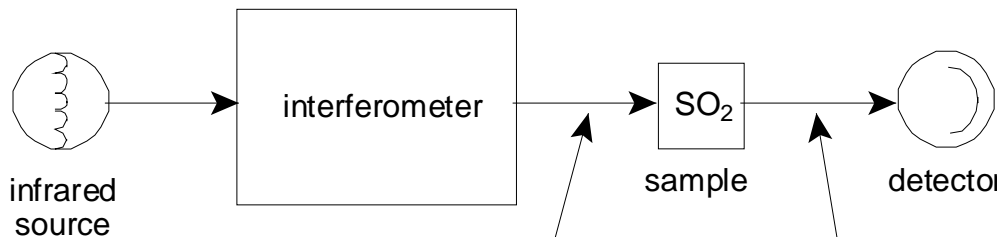
- 3,700 - 3,100: OH, NH and $\equiv\text{CH}$
- 3,180 - 2,980: aryl, olefinic, and three-membered ring CH
- 3,000 - 2,700: aliphatic CH
- 3,100 - 2,400: acidic and strongly bonded hydrogens
- 2,300 - 1,900: $\text{C}\equiv\text{C}$ and $\text{C}=\text{C}=\text{C}$
- 2,000 - 1,700: aryl and olefinic overtones
- 1,900 - 1,550: $\text{C}=\text{O}$
- 1,700 - 1,550: $\text{C}=\text{C}$ and $\text{C}=\text{N}$
- 1,660 - 1,450: $\text{N}=\text{O}$
- 1,660 - 1,500: NH_2 , CNH
- 1,620 - 1,420: aromatic and heteroaromatic rings
- 1,500 - 1,250: CH_3 and CH_2
- 1,350 - 1,150: CH_2 and CH wag
- 1,300 - 1,000: $\text{C}-\text{O}$
- 1,000 - 600: olefinic and acetylenic wag
- 900 - 700: aromatic wag
- 900 - 500: OH, NH and NH_2 wag
- 830 - 500: CCl , CBr and Cl

*Colthup, N. B.; Daly, L. H.; Wiberley, S. E., *Introduction to Infrared and Raman Spectroscopy*, 3rd edition, Academic Press, Boston, 1990, Chapter 13.

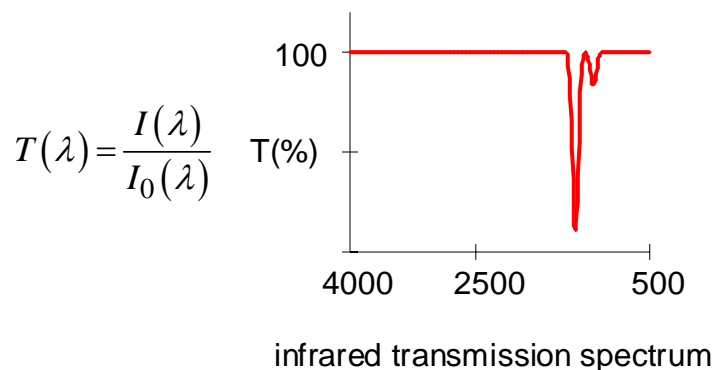
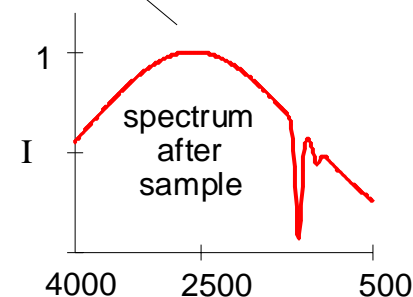
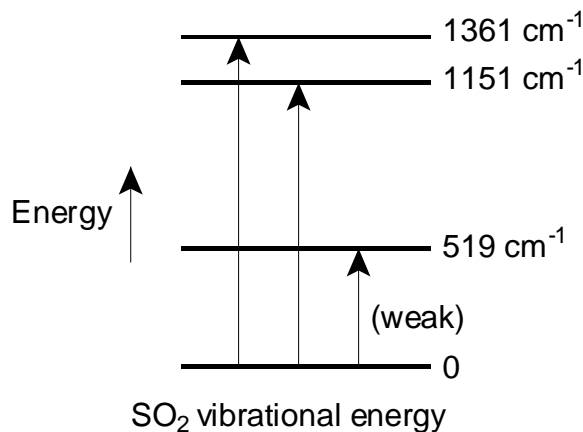
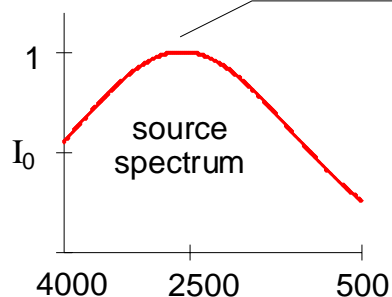
Example of Infrared Group Frequencies



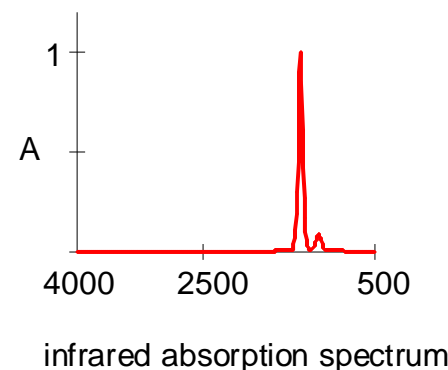
Obtaining an Infrared Absorption Spectrum



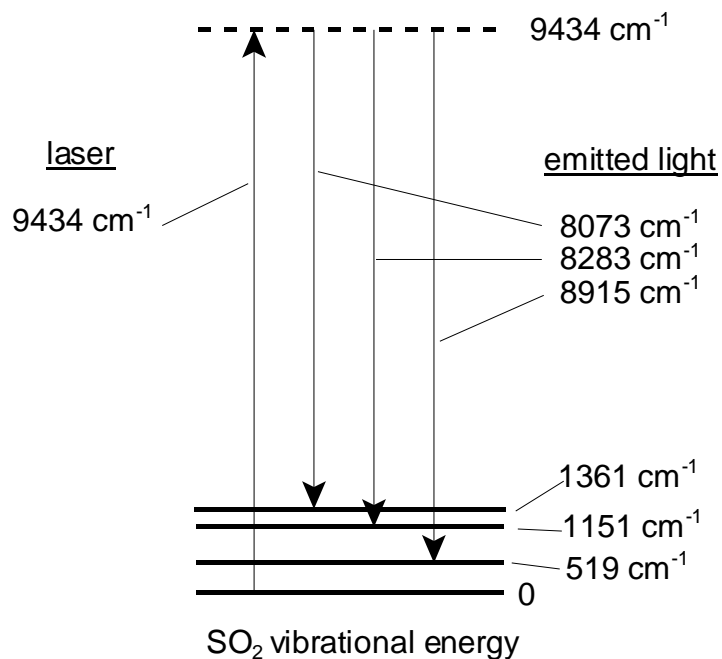
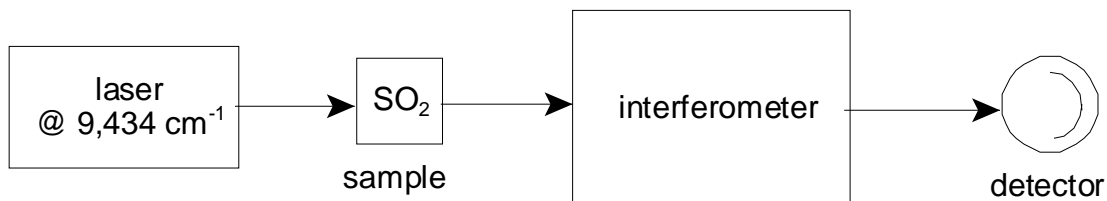
Note: The sample is removed to obtain the source spectrum.



$$A(\lambda) = \log\left(\frac{1}{T(\lambda)}\right)$$

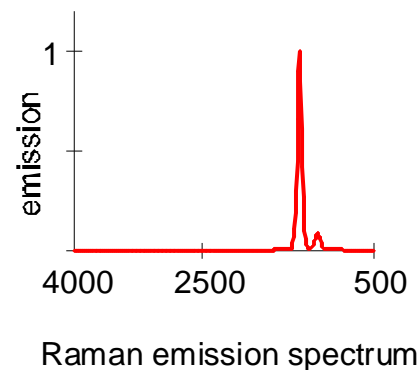


Obtaining a Raman Emission Spectrum



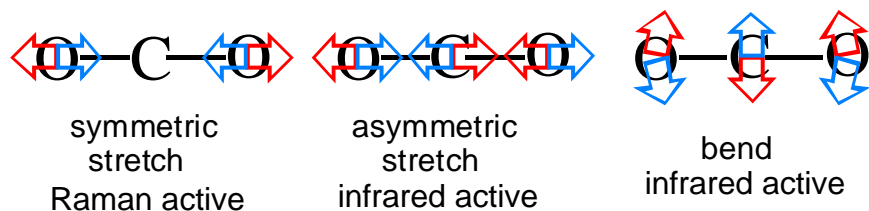
In a Raman instrument a near-infrared laser excites the sample. During this process new frequencies are emitted when the molecule acquires vibrational energy from the laser beam.

A Raman spectrometer differs from an infrared instrument in that the emitting sample is the "source." The emission spectrum is converted to a vibrational spectrum by computing the difference between the laser and emitted frequencies.



Strength of Infrared and Raman Vibrations

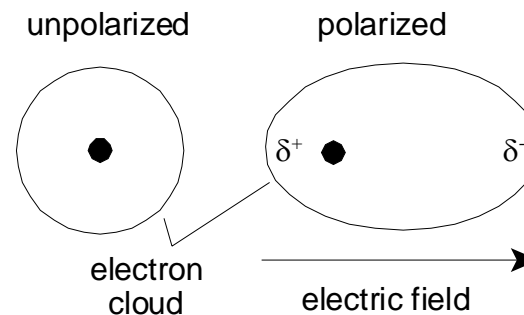
In order to appear in an infrared spectrum (be IR active) the vibration must cause a change in dipole moment. The three vibrations of CO₂ (linear) are shown below.



CO₂ does not have a permanent dipole since the "center of gravity" for the positive charge overlays that for the negative charge. The symmetric stretch does not change the centers of charge, thus this vibration is not infrared active. The asymmetric stretch moves the center of negative charge away from the carbon atom. This induces a dipole along the molecular axis making the vibration infrared active. The bending mode creates a dipole perpendicular to the molecular axis thus is also infrared active.

When a molecule has a center of symmetry, as CO₂ does, infrared active vibrations are those that destroy the center of symmetry. If the vibrational motion maintains the center of symmetry (the symmetric stretch) it is not infrared active.

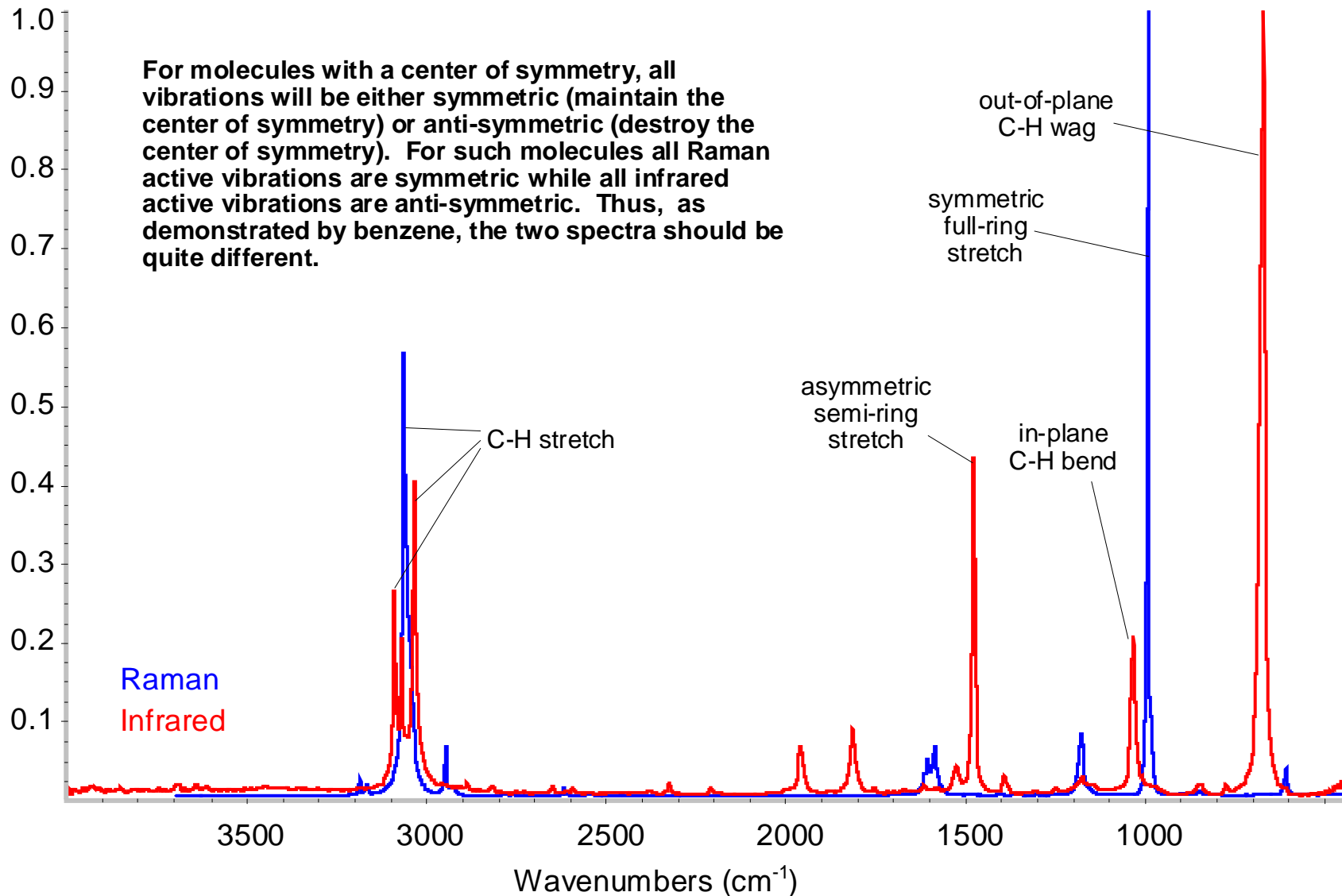
Molecular polarizability is the ability of an applied electric field to separate positive and negative charges. This is shown diagrammatically below. Tightly bound electrons are less polarizable than loosely bound electrons. Thus bond lengths and angles can affect polarizability.



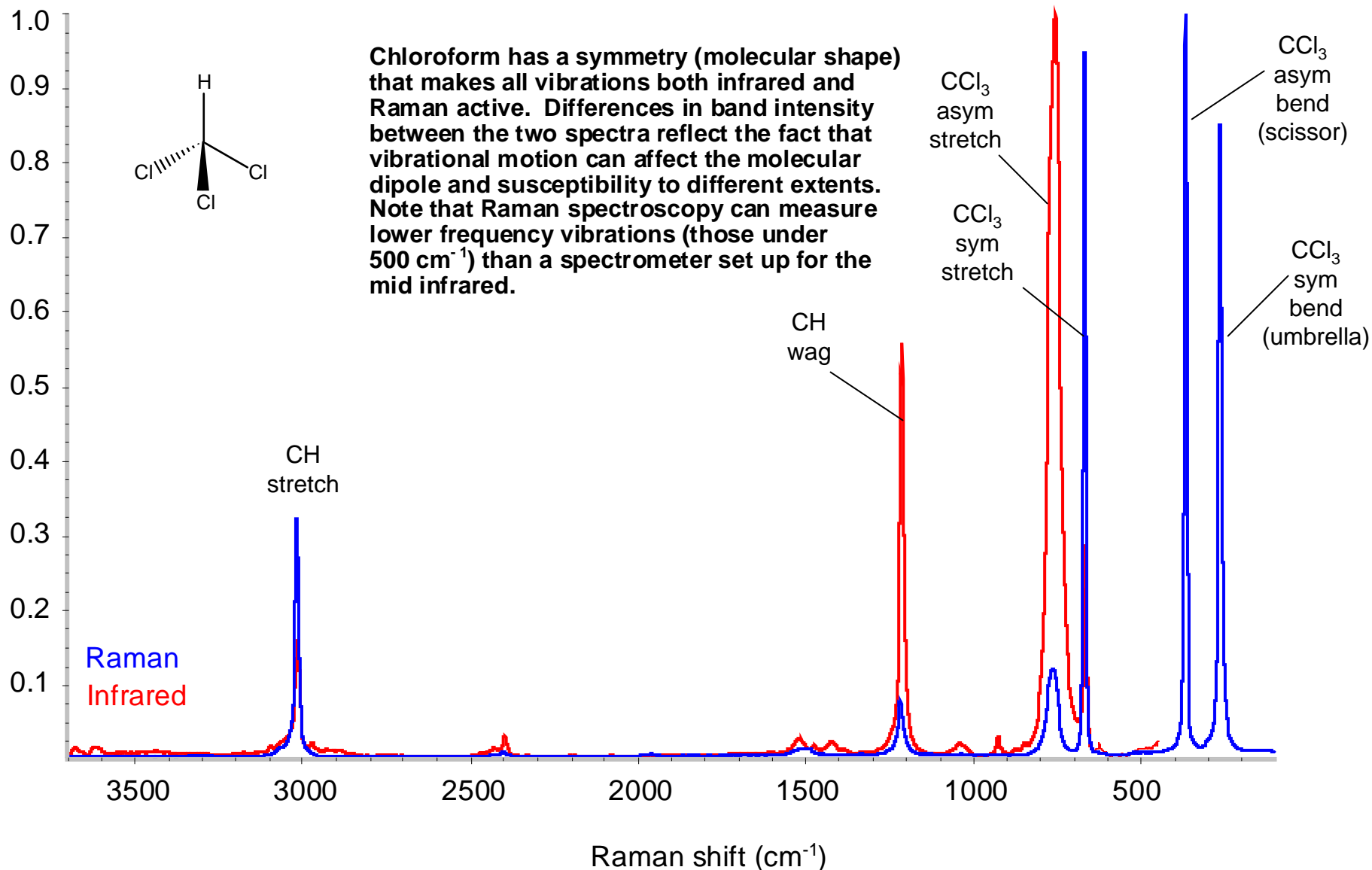
In order to appear in a Raman spectrum (be Raman active) the vibration must cause a change in the molecular polarizability. Since polarizability exists in all three dimensions it is more difficult to visualize than molecular dipoles. As a result it is difficult to make qualitative estimates of Raman activity.

When a molecule has a center of symmetry Raman active vibrations are those that maintain the center of symmetry. If the vibrational motion destroys the center of symmetry (like the CO₂ asymmetric stretch or bend) it is not Raman active.

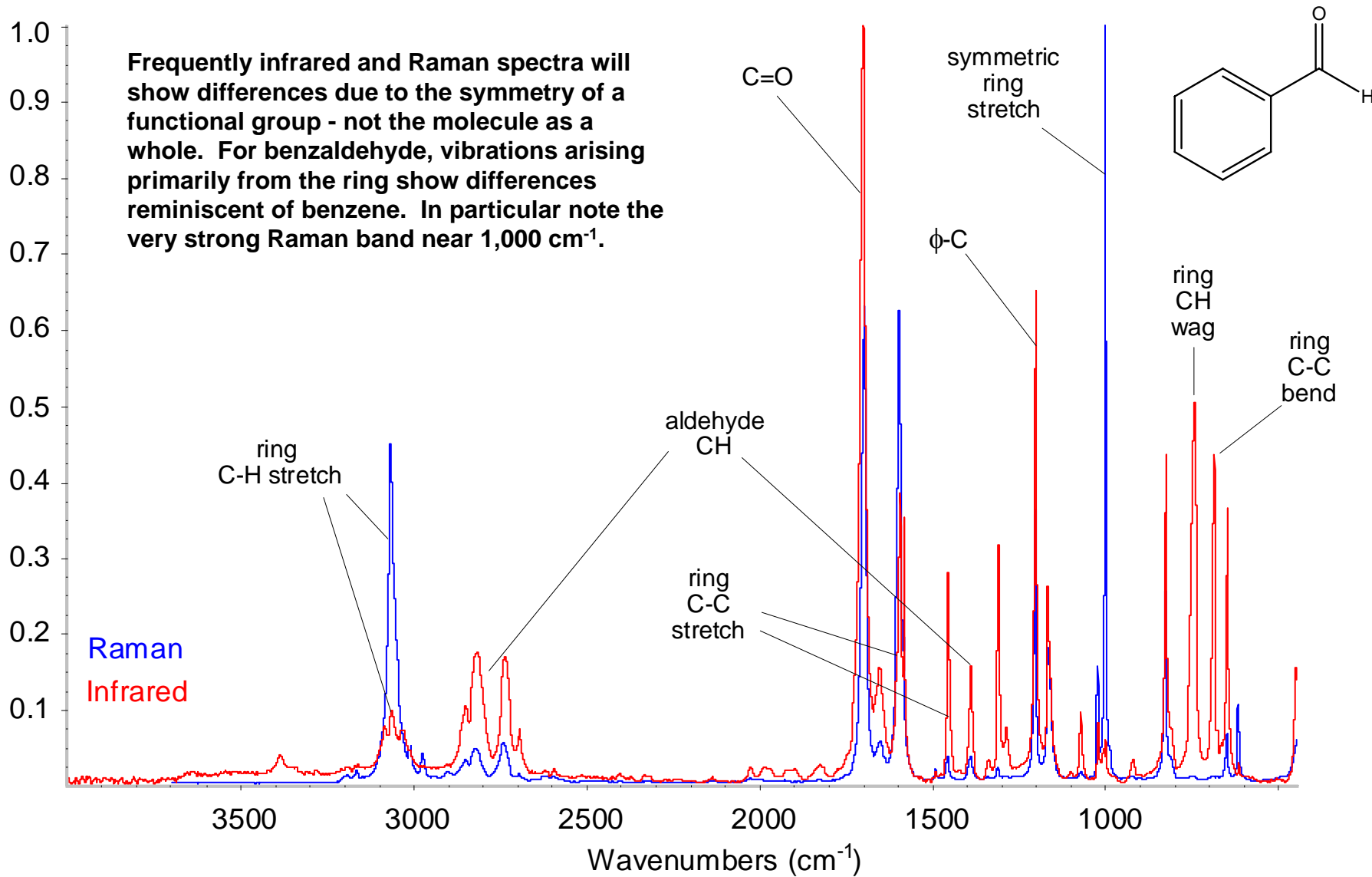
Benzene Infrared and Raman Spectra



Chloroform Infrared and Raman Spectra



Benzaldehyde Infrared and Raman Spectra



Fourier transform infrared absorption spectroscopy is a well-established technique that has been honed to perfection over many decades. In contrast Fourier transform Raman scattering is relatively new, with sensitive and reliable instrumentation only being available for the last 5-10 years. Because of this discrepancy in "age", most vibrational spectral interpretation has been taught using infrared data. The same interpretation can be obtained from Raman data, but often new functional group/frequency correlations have to be learned. As the previous examples have shown, having both types of spectra enhances the ability to predict molecular structure.

The main strength of Raman spectroscopy is its ability to handle liquid and solid samples with little to no preparation. To obtain an infrared spectrum the solid samples have to be ground into a Nujol mull or a KBr pellet, and liquid samples require cells with infrared transparent windows. In the CASPIE lab we use ordinary glass NMR tubes to hold either type of sample for collecting Raman spectra.

There are several advantages of Raman instrumentation over infrared

- infrared spectrometers have to be purged with nitrogen to eliminate water and CO₂ absorption, whereas these gases do not interfere with the measurement of Raman spectra
- with near infrared laser excitation, spectra are typically characterized by a flat baseline
- Raman autosamplers are much simpler and less expensive than infrared autosamplers
- although the CASPIE lab does not yet do microscopy, the spatial resolution of Raman is much better than infrared

Most of the disadvantages of Raman instrumentation are due to the laser

- the laser has a finite lifetime and is expensive, thus over time it costs more to run a Raman spectrometer
- the laser can burn samples that strongly absorb near infrared radiation
- because of the optical hazard created by the laser, the autosampler must be covered when in use (which means that you can't visually verify that it is working)