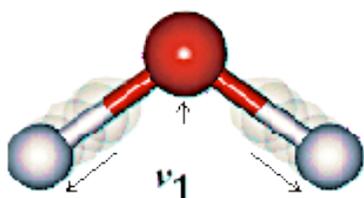


Molecular Vibrations and Infrared Spectroscopy

All bonded atoms molecularly vibrate unless they are at zero degrees Kelvin. Some types of molecular vibrations are shown below.

Molecular

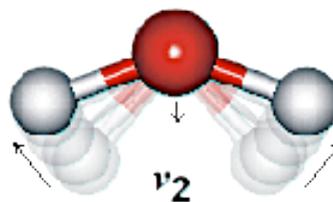


symmetric stretch

The two white atoms are moving along the bond axis in and out, which constitutes stretching. The link below provides an animation of stretching. (The animation titled "Vibrational Motion Of A Heteronuclear Diatomic Molecule").

<http://www.wiredchemist.com/chemistry/instructional/supplemental-material-for-chemistry/chapter-7/animations>

Molecular



bend

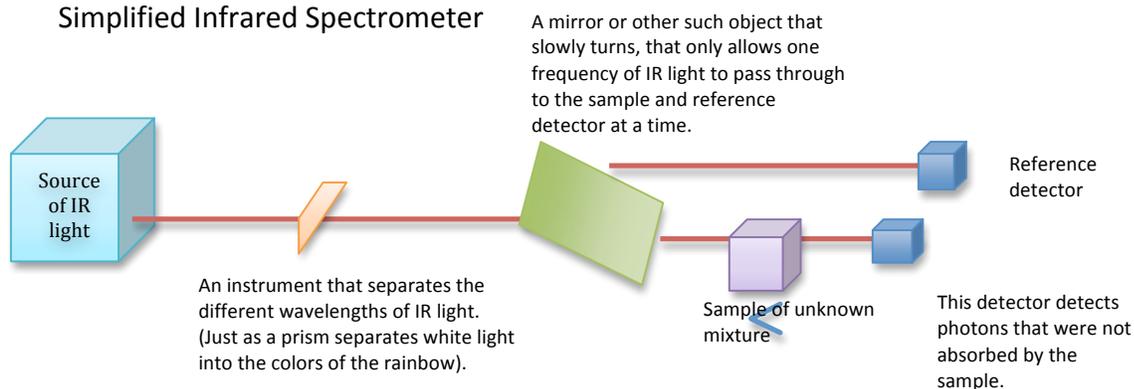
The two white atoms move closer to each other and then away from each other, not along a bond axis, which constitutes bending. The link below provides an animation for bending (look at Mode 4).

<http://www.d.umn.edu/~pkiprof/ChemWebV2/Vibrations/vib3.html>

These types of molecular vibrations happen very fast, one vibration cycle takes typically 10^{-15} seconds.

The primary purpose of infrared spectroscopy is to identify the functional groups present in a molecule. Infrared spectrometry works by analyzing the number of infrared photons and the amount of energy found in infrared photons absorbed by the molecule.

Simplified Infrared Spectrometer

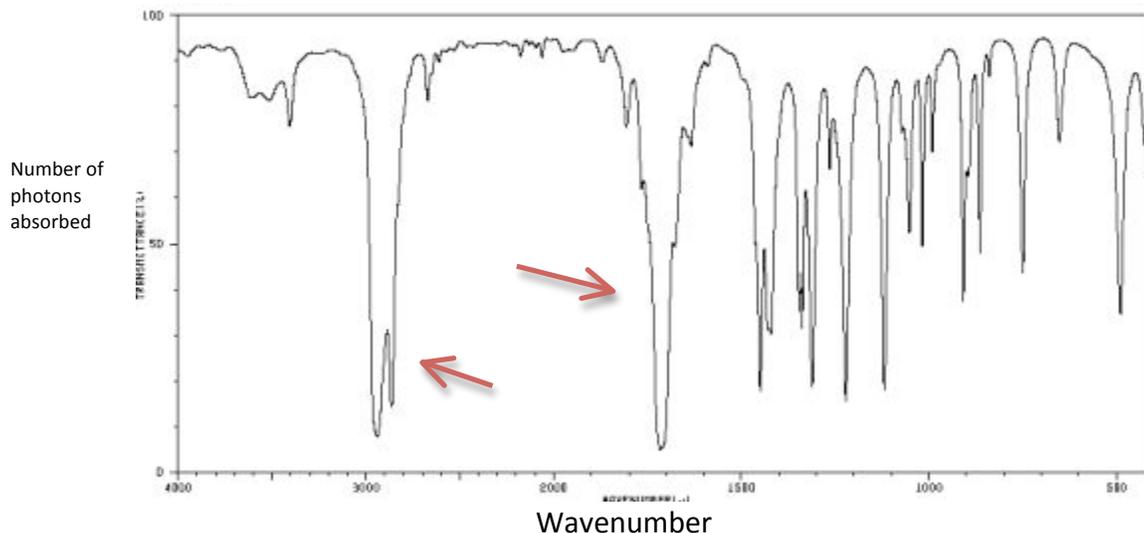


*The red line represents IR radiation

An object produces IR radiation, which is then separated into different wavelengths of IR light. The separated wavelengths of IR light hit a mirror or other such instrument that

allows one particular wavelength of light through at a time. As the mirror slowly turns, it allows a different wavelength of light in at one time. On one side, the IR light directly reaches a detector. This detector acts a reference, so one can know how much IR light there is total. On the other side, the IR light passes through a sample and any IR photons that are not absorbed by unknown sample reach the detector. By comparing the number and energy of the unabsorbed IR photons that reach the detector after passing through the unknown sample, to the amount and energy of the photons that were detected total, one can figure out the quantity and wavenumbers of photons that were absorbed by the unknown sample. This information is then plotted on an **infrared spectrum**.

An Infrared spectrum plots the wavenumber of the photon (which is proportional to the energy of the photon) on the x-axis and the quantity of photons that were absorbed on the y-axis.

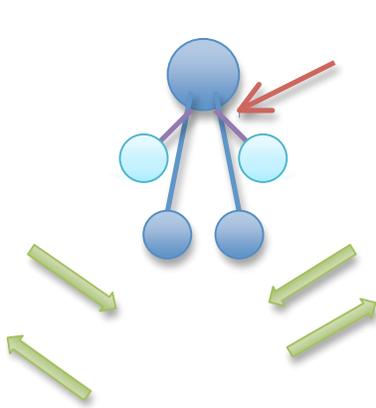


Above is an infrared spectrum of cyclohexanone. The peaks indicated by the red arrows represent areas of high photon absorption. The structure of a molecule controls how many photons of a particular wavenumber are absorbed.

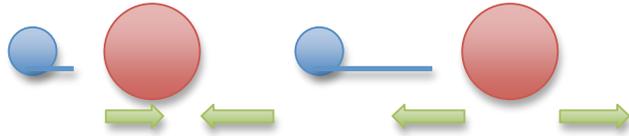
So what happens when the sample of an unknown compound absorbs photons?

When a molecule absorbs a photon, the molecule gains energy and moves from a lower vibrational energy state to a higher vibrational energy state. The lowest vibrational energy state of a molecule is called a **ground vibrational state**. When a molecule is not in the lowest energy state it is called the **excited vibrational state**. The molecule does not physically move from one state to another. When a molecule absorbs vibrational energy in the form of photons, its average bond length increases. Photon absorption

would make atoms in a molecule move farther apart when stretched and would make the bending angle bigger for atoms in a molecule that are bending.



This bond angle becomes bigger when bending occurs. When the molecule is in the excited vibrational state, this angle becomes even bigger as the two atoms stretch closer together increasing the average bond length (shown by the dark blue atoms). The two light blue dots represent atoms in their original state, as they stretch closer together to the position of the two dark blue atoms, the angle indicated by the red arrow increases.



When photons of IR light are absorbed, the atoms stretch farther apart from one another, than they would if they were in the ground vibrational state. This increasing in the stretching distance, constitutes an increase in the average bond length.

An increase in the vibrational energy of a molecule increases the average bond length of a molecule.

Different photons have different energies.

How is the energy in a particular photon calculated?

The E stands for energy of the photon

$$E = h \nu$$

ν gives you the frequency of the photon.

Plank's Constant
 6.626×10^{-34} Hz

Because vibrational state energies are quantized, a molecule can only absorb certain photons with particular amounts of energy in order to change its vibrational energy state. Thus the equation below is used.

The Delta E stands for the change in energy between two vibrational states. This energy is quantized and thus a particular amount of energy is needed for a molecule to move from one vibrational state to another. The energy of the photon must equal the energy difference between two vibrational states.

$$\Delta E = h\nu$$

↑
Plank's

ν gives you the frequency of the photon. In infrared spectrometry it is also referred to as the stretching frequency. This is measured in wavenumbers, which has units cm^{-1} (the number of waves per cm). Be warned: this does not tell you the vibrational stretching frequency of a molecule.

How likely is an IR photon to be absorbed by a molecule (y-axis)?

The chance that a photon will be absorbed is controlled by the change in **dipole moment** that occurs during molecular vibration.

The dipole moment is the vector sum of the **bond dipoles**. Because calculating the dipoles moment of a molecule with many atoms can be very difficult, the dipole moment is often estimated by looking at the individual bond and its changing bond dipoles instead.

Bond dipoles depend on the magnitude of the electronegativity difference between the atoms multiplied by the bond length.

- The higher the electronegativity differences between the atoms, the stronger the bond dipole.
- The longer the length of the bond, the stronger the bond dipole.

The stronger the bond dipole, the more photons are absorbed. The more photons that are absorbed, the more intense the peak.

Bonds that are very polar will display intense peaks in the infrared spectrum. Nearly symmetric and symmetric molecules, which are often nonpolar, will have weak or no peaks in the spectrum.

What controls the IR stretching frequencies (x-axis)?

IR stretching frequencies are controlled by the functional group, which is why IR spectrometry is used to determine which functional groups are present/absent in a molecule. The stretching frequency, plotted on the x-axis, is explained through Hooke's Law.

$$\text{Stretching Frequency} = \frac{1}{2\pi c} \left[\frac{f(m_a + m_b)}{m_a m_b} \right]^{1/2}$$

*The m_a and m_b are the masses of the two atoms that are bonded.

*F is the spring stiffness, which is how much the molecule is resistant to stretching.

Hooke's Law relates how two masses on a spring behave. For simplification purposes the masses can be represented as atoms and the spring is represented by the bond between the atoms. The more electrons shared between atoms, the more resistant the atoms are to being stretched apart. The higher the bond order, the higher the spring stiffness, and thus the higher the stretching frequency.

The energy change between molecular vibrational states is based on the bond order and the masses of the atoms that are bonded. Functional groups are described by the bond order and the masses of the atoms that are bonded. By recognizing common patterns of IR photon absorption (the amount and wavenumber of the photons absorbed) one can predict the functional groups present in a molecule.

Sources

Thinkbook

Professor Lavelle's Course Reader

Images from

<http://www.lsbu.ac.uk/water/vibrat.html>

<http://www.gravitywaves.com/chemistry/CHE303L/OxidationofCyclohexanol.htm>