2.3: Infrared (IR) Spectroscopy - Looking at Molecular Vibrations
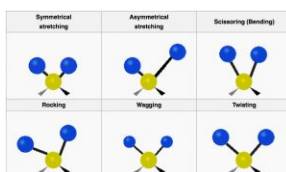
Up to now we have concentrated on the absorption (and emission) of energy associated with transitions of electrons between quantized energy levels. However, as we discussed earlier, electron energies are not the only quantized energies at the atomic/molecular level. In molecules, both vibrations and rotations are quantized, but the energies involved are much lower than those needed to break bonds. Let us begin with the simplest of molecular systems, consisting of two atoms bonded together. In such a system, the atoms can move back and forth relative to each other along the bond axis (vibrations). As they vibrate and change rotational speeds (and directions), the potential energy of the system changes (Why is that? What factors influence these changes?). There are also motions associated with rotations around bonds. But (weirdly, and quantum-mechanically) rather than being able to assume any value, the energies of these vibrations (and rotations) are also quantized. The energy gaps between the vibrational energy states tend to be in the range of infrared radiation. If three or more atoms are bonded together the molecule can also bend, changing the bond angle or the shape of the molecule.[6]

Infrared radiation is of lower energy than visible light (longer wavelength, lower frequency). You are probably familiar with IR heat lamps that are used for warming and night vision goggles that allow the wearer to "see" at night.[7] Recall that objects tend to emit radiation (the phenomenon is called black-body radiation) as the kinetic energy of the atoms and molecules in the object is converted to electromagnetic radiation. Around 300K (room temperature or body temperature) the radiation emitted is in the IR region of the spectrum.[8] Conversely, when IR radiation falls on our skin, we feel that as a warming sensation, mainly because it is causing the molecules in our skin to vibrate and rotate—increasing the kinetic energy and thus the temperature.

When we investigate the light absorbed or emitted as molecules undergo vibrational energy changes it is known as infrared spectroscopy.[9] Why, you might ask, are we interested in the vibrations of molecules? The vibrations, rotations, and bending movements of molecules are influenced by the structure of the molecule as a whole (as well as its environment). The result is that that many molecules and fragments of molecules have very distinctive IR absorption patterns that can be used to identify them. Infrared spectroscopy allows us to identify substances based on patterns in the lab and, for example, in interstellar dust clouds. The presence of quite complex molecules in space (hundreds of millions of light years away from earth) has been detected by the use of IR spectroscopy.

The types of changes that can be detected using IR spectroscopy are associated both with stretching (vibrations of) one particular bond, and with movements associated with three or more atoms such as bending or twisting. Consider methane for example: Each $C-H$ bond can vibrate separately, but we can also imagine that they could vibrate "in phase" (at the same time) so that the $C-H$ bonds lengthen and shorten at the same time. This movement is called the symmetric stretch. Conversely, we can imagine that one might lengthen as the other shortens: this is called the asymmetric stretch. Furthermore, the molecule can bend and twist in a number of ways so that there are quite a number of possible "vibrational modes."[10]
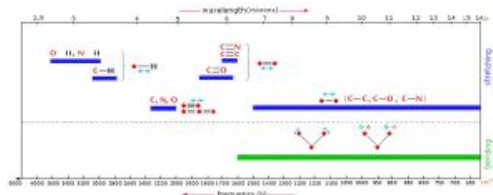
Vibrational Modes of CH$_2$

Here we see the the vibrational modes for part of an organic molecule with a CH_2 group. Not all these modes can be observed through infrared absorption and emission: vibrations that do not change the dipole movement (or charge distribution) for the molecules (for example, the symmetrical stretch) do not result in absorption of IR radiation, but since there are plenty of other vibrational modes[11] we can always detect the presence of symmetrical molecules like methane (and most other molecules) by IR spectroscopy. In addition, the more the charge distribution changes as the bond stretches, the greater the intensity of the peak. Therefore, as we will see, polar molecules tend to have stronger absorptions than non-polar molecules.

For historical reasons, IR spectra are typically plotted as transmittance (that is the amount of light that is allowed through the sample) versus wavenumber (cm^{-1}).[12] That is, the peaks are inverted, so that at the top of the spectrum 100% of the light is transmitted and at the bottom it is all absorbed.
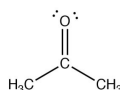
The **position** of the absorption in an IR spectrum depends three main factors:

- **Bondstrength**: it makes sense that the energy needed to stretch a bond (i.e. make it vibrate) depends on the strength of the bond. Therefore, multiple bonds appear at higher frequency (wavenumber) than single bonds.
- Whether the vibrations involved involve bond **stretching or bending**: it is easier to bend a molecule than to stretch a bond.
- The **massesoftheatoms** in a particular bond or group of atoms: bonds to very light atoms (particularly appear at higher frequency).[13]
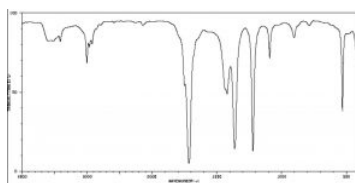
The figure below shows each of the general areas of the IR spectrum and the types of bonds that give rise to absorptions in each area of the spectrum. In general $C-H$, $O-H$, and $N-H$ bond stretches appear above $3000 \mathrm{cm}^{-1}$. Between 2500 and 2000 is typically where triple-bond stretches appear. Between 2000 and $1500 \mathrm{cm}^{-1}$ is the region where double-bond stretches appear, and the region below 1600 is called the fingerprint region. Typically, there are many peaks in this fingerprint region which may correspond to $C-C$, $C-O$ and $C-N$ stretches and many of the bending modes. In fact, this region is usually so complex that it is not possible to assign all the peaks, but rather the pattern of peaks may be compared to a database of compounds for identification purposes.

Vibrational Frequencies for Common Bond Types or Functional Groups

The figure below ($\downarrow$) shows a spectrum of acetone ($\rightarrow$) in which you can see a number of absorptions, the strongest of which appears around $1710 \mathrm{cm}^{-1}$. Note also that there is a discontinuity in scale above and below $2000 \mathrm{cm}^{-1}$. The strong peak around $1710 \mathrm{cm}^{-1}$ can be ascribed to one particular part of the acetone molecule: the $C=O$ (or carbonyl) group. It turns out that carbonyl groups can be identified by the presence of a strong peak in this region although the wavenumber of absorption may change a little depending on the chemical environment of the carbonyl. The presence of a strong peak between around $1700 \mathrm{cm}^{-1}$ almost always signifies the presence of a $C=O$ group within the molecule, while its shift from $1700 \mathrm{cm}^{-1}$ is influenced by the structure of the rest of the molecule.