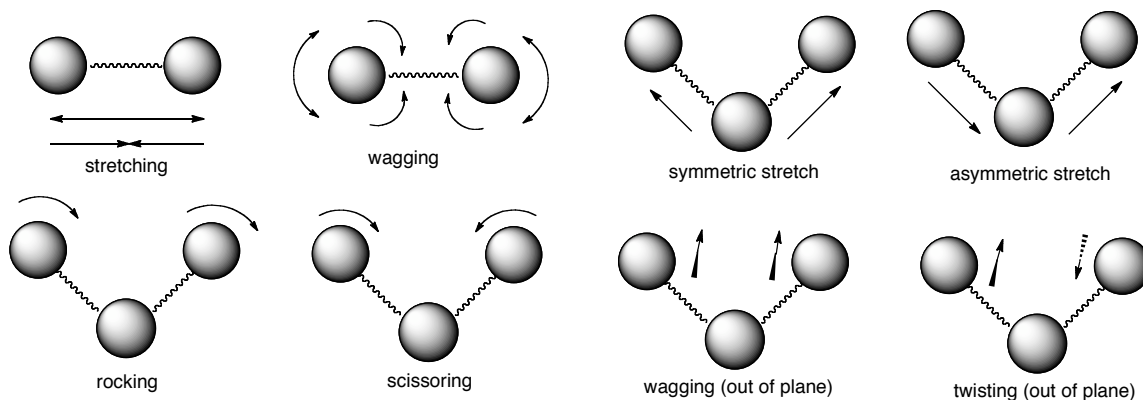


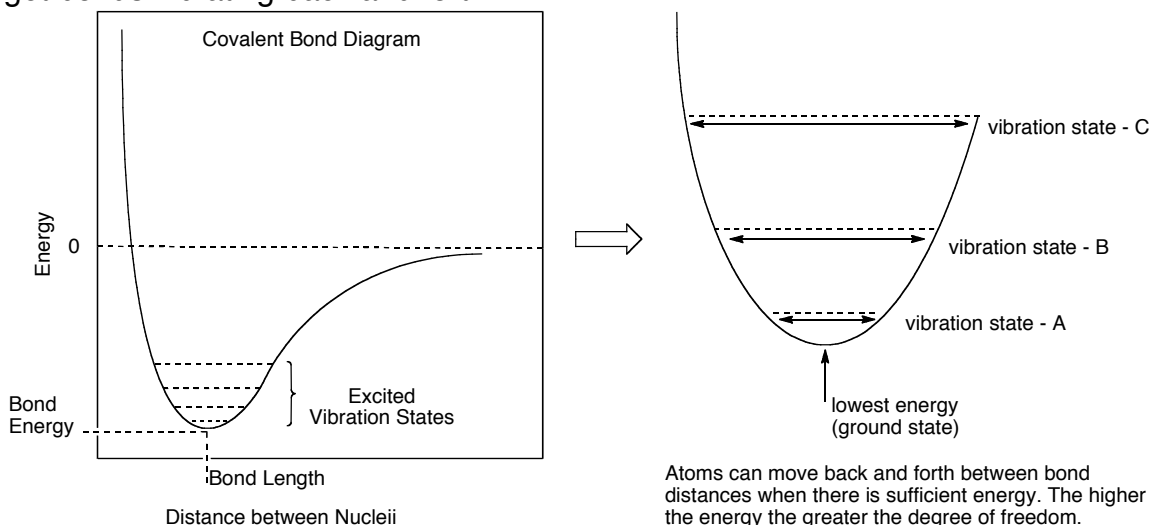
# Introduction to Spectroscopy I: Infrared Spectroscopy

## Basic Theory:

Covalent bonds exist as sharing of electrons between non-metal atoms. These bonds act in many ways like springs with the atoms as weights that can vibrate back and forth along the bond length or even wag off the bond axis. These vibrations can be symmetrical, asymmetrical, they can stay in a plane or twist out of a plane, and they can be between two bonded atoms or multiple bonded atoms to give more complex harmonic oscillations.



At ground state the atoms are at the lowest possible energy (with the spring in a neutral state) and are at a particular distance aka bond length apart (the length of the spring). If the bond absorbs energy the atoms can move a small distance closer together or further apart as the bond (spring) compresses or expands. The more energy that is absorbed the larger the compression and expansion. If sufficient energy is absorbed the bond will break. Breaking bonds generally requires absorption of ultraviolet light, but infrared is sufficient energy to get bonds vibrating back and forth.



In order to be visible by IR spectroscopy a vibration must show a change in dipole, an N<sub>2</sub> stretch will not show up in the IR as the electrons are evenly distributed, but a CO stretch will show up as there is an overall dipole and the distance between the areas of positive and negative charge changes as the bond compresses/expands.

The frequency of light absorbed will be the natural oscillation frequency of the bond as it expands and contracts. The frequencies associated with IR spectroscopy are the mid-range infrared (~2.5-25 μm). IR absorptions are usually measured in wavenumbers or inverse wavelength ( $\nu = 1/\lambda$ ), which have the units of cm<sup>-1</sup> and the range of wavenumbers we observe for IR spectroscopy is 4000 to 400 cm<sup>-1</sup>. Since the wavenumber of a vibration is the resonance frequency of the oscillation of the bond, it follows Hooke's Law of elasticity: where c = speed of light, k = spring constant/bond strength, m<sub>1</sub> = mass of atom 1, m<sub>2</sub> = mass of atom 2, and  $\nu$  = the wavenumber of the associated frequency.

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

Hooke's Law shows that the stronger the bond (large k), the larger the frequency, the shorter the wavelength and the larger the wavenumber associated with that resonance frequency. Decreasing the mass of the atoms (small m) will also give a larger resonance frequency, a shorter wavelength and a larger associated wavenumber.

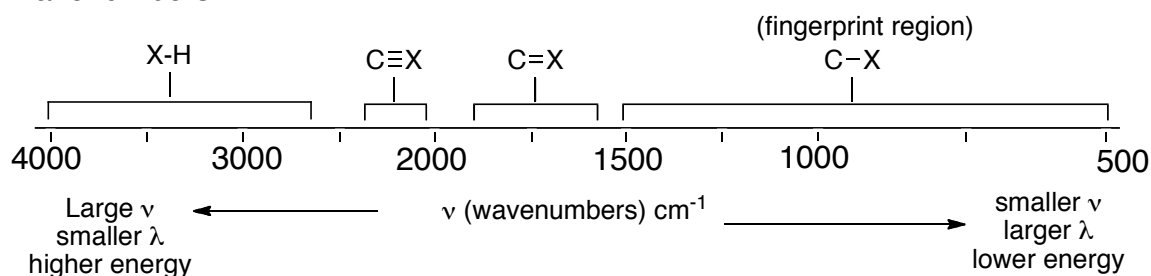
### Key Points:

- IR spectroscopy measures the vibration of covalent bonds.
- IR spectroscopy is typically measured as percent transmittance with a scale of wavenumbers decreasing from left to right.
- Frequencies of light that are associated with a particular molecular vibration are absorbed and show a low percent transmittance.
- Frequencies of light that are not absorbed pass through the sample and show 100% transmittance of the light.
- Resonance frequencies are associated with bond strength and atomic mass therefore each particular kind of bond will have its own resonance frequencies. O-H is different from C-H which is different from C-C or C=C.
- IR spectroscopy allows identification of bond type (functional groups), but not number of bonds or relative positioning of functional groups.

## Interpreting IR:

Each absorption peak (peak of minimum transmittance) in the IR corresponds to a particular bond type. Knowledge of the bond type(s) in a molecule can lead identification of what functional groups are present, but NOT the exact identity of the molecule unless a comparison is made to a known compound.

### Wavenumbers:



There are 4 major regions of wavenumbers in an IR spectrum:

- 4000 to 2700 cm<sup>-1</sup>: *The X-H region*. H atoms are much lighter than other atoms in organic molecules so have higher wavenumber oscillating frequencies.
  - C-H, C=C-H, C-C-H, O-H, N-H, and O=C-H
- 2300 to 2150 cm<sup>-1</sup>: *The triple bond region*. Triple bonds are stronger so have a larger k and thus higher wavenumbers than other bond types between the same atoms.
  - C≡C and C≡N
- 1820 to 1550 cm<sup>-1</sup>: *The double bond region*. Double bonds are stronger than single bonds, but weaker than triple bonds so are their oscillation frequency is in between the ranges of triple and single bonds.
  - C=O, C=N, and C=C
- 1500 to 500 cm<sup>-1</sup>: *The single bond region a.k.a. the fingerprint region*. Single bonds are much weaker than multiple bonds so have smaller wavenumber oscillating frequencies. Since most organic molecules have many C-C bonds this region is generally not easily interpreted, but can be used to 'match' a known compound as a fingerprint.
  - C-C, C-N, C-O, and C-X

NOTE: Know the peaks in Table 11.5 of Vollhardt + Schore for basic IR peaks. Additional peak ranges will be added as we learn new functional groups!

### Peak Shape and intensity:

Intensity is also a factor in interpreting IR spectra. Peaks may be strong (low %T) or weak (high %T). A C=O is typically a strong absorption (low %T) while C-H is weak to medium. If the C=O peak is weaker than the C-H peak it may imply there are many C-H, while if the C-H peak is weak compared to other peaks, it may imply that there are relatively few C-H bonds in the molecule. This will not allow assignment of the exact structure, but can along with other information help narrow the possibilities.

Peak shape can also be relevant to assignment of functional groups. Peaks may be sharp (narrow) or broad. Some peaks (NH<sub>2</sub> groups) are doubled. The exact peak shape can help differentiate between an alkyne C-H (a short, sharp peak at 3300 cm<sup>-1</sup>) and an alcohol O-H (a broad deep peak at 3300 cm<sup>-1</sup>) or a carboxylic acid O-H (a very broad, shallower peak, at 3150 cm<sup>-1</sup>). Alcohols tend to be distinct from the alkyl C-H, while acids tend to blur into the alkyl C-H.

