

IR Spectroscopy : Vibrational Spectroscopy

Absorption of radiation in this region of infrared by a typical organic molecule results in the excitation of vibrational, rotational and bending modes, while the molecule itself remains in its electronic ground state. Molecules undergo a complex series of vibrations which depend upon:

- symmetry of the molecule
- mass of the bonded atoms
- bond strength

Theory shows that this complexity can be resolved into a limited number of NORMAL MODES OF VIBRATION.

For a non-linear molecule of N atoms there will be: **3N-6 vibrations**

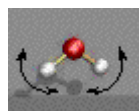
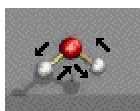
For a linear molecule: **3N-5 vibrations**

Water is nonlinear and N=3, therefore have $(3 \times 3) - 6 = 3$ vibrations shown below

Modes are separated into two types:

- Stretching, ν – changes in bond length
- Bending, δ (def) – changes in bond angles

Stretching modes are at higher frequency (cm^{-1}) [higher energy] than bending modes.



Symmetric Stretch Asymmetric Stretch Symmetric Bend

Molecular asymmetry is a requirement for excitation by infrared radiation and fully symmetric molecules do not display absorbances in this region unless asymmetric stretching or bending transitions are possible.

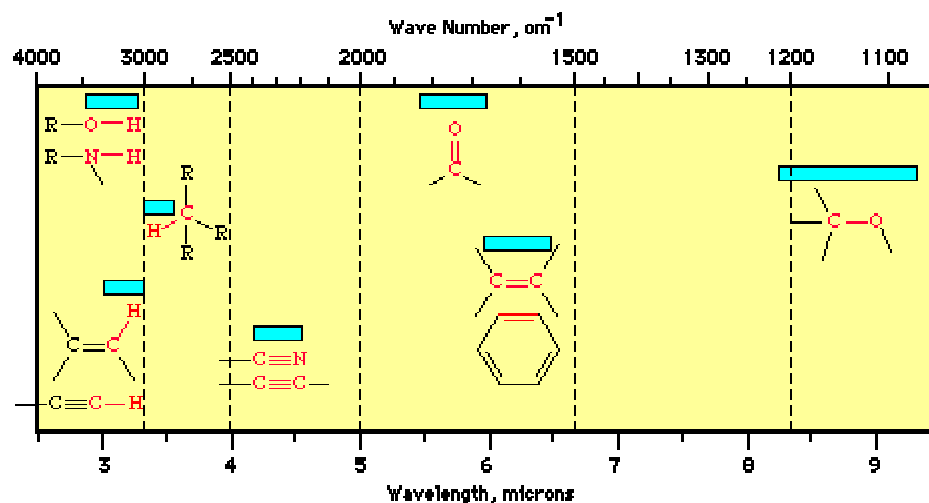
Vibration must produce a change in the dipole moment (magnitude of change determines peak intensity). This is called **Selection rule**. For the purpose of routine organic structure determination, using a battery of spectroscopic methods, the most important absorptions in the infrared region are the simple stretching vibrations. For simple systems, these can be approximated by considering the atoms as point masses, linked by a 'spring' having a force constant k and following **Hooke's Law**. Using this simple approximation, the equation shown below can be utilized to approximate the characteristic stretching frequency (in cm^{-1}) of two atoms of masses m_1 and m_2 , linked by a bond with a force constant k :

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

where $\mu = m_1 m_2 / (m_1 + m_2)$ (termed the 'reduced mass'), and c is the velocity of light. The stretching vibrations of typical organic molecules tend to fall within distinct regions of the infrared spectrum, as shown below:

- Alcohols and amines display strong broad O-H and N-H stretching bands in the region $3400\text{--}3100 \text{ cm}^{-1}$. The bands are broadened due to hydrogen bonding and a sharp 'non-bonded' peak can often be seen at around 3400 cm^{-1} .
- Alkene and alkyne C-H bonds display sharp stretching absorptions in the region $3100\text{--}3000 \text{ cm}^{-1}$. The bands are of medium intensity and are often obscured by other absorbances in the region (i.e., OH).
- Triple bond stretching absorptions occur in the region $2400\text{--}2200 \text{ cm}^{-1}$. Absorptions from nitriles are generally of medium intensity and are clearly defined. Alkynes absorb weakly in this region unless they are highly asymmetric; symmetrical alkynes do not show absorption bands.

- Carbonyl stretching bands occur in the region $1800\text{--}1700\text{ cm}^{-1}$. The bands are generally very strong and broad. Carbonyl compounds which are more reactive in nucleophilic addition reactions (acyl halides, esters) are generally at higher wave number than simple ketones and aldehydes, and amides are the lowest, absorbing in the region $1700\text{--}1650\text{ cm}^{-1}$.
- Carbon-carbon double bond stretching occurs in the region around $1650\text{--}1600\text{ cm}^{-1}$. The bands are generally sharp and of medium intensity. Aromatic compounds will typically display a series of sharp bands in this region.
- Carbon-oxygen single bonds display stretching bands in the region $1200\text{--}1100\text{ cm}^{-1}$. The bands are generally strong and broad. You should note that many other functional groups have bands in this region which appear similar.



Solution IR Spectra for Solid Samples

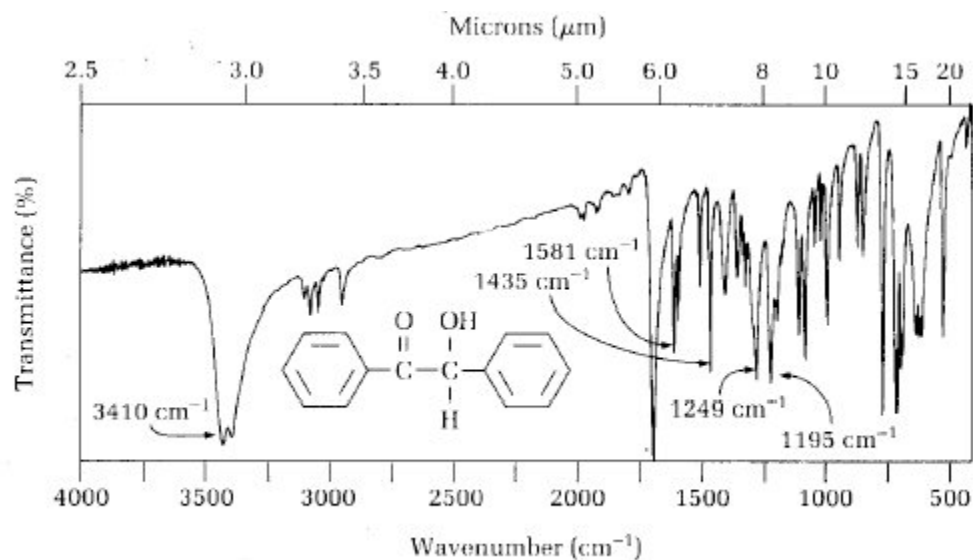
Sometimes neither the KBr pellet nor Nujol Mull method will work well for obtaining the IR of a solid organic compound. In this case, we must finally resort to dissolving the sample in a solvent and recording the spectrum of the solution (both sample and solvent).

- Dissolve as much of the product as possible in 0.1 ml. CCl_4 (carbon tetrachloride).
- Quickly place several drops this solution on the reference solution cell.
- Run reference cell as background. Place the reference cell and take the IR spectrum relatively quickly before the solvent has much chance to evaporate.
- Fill the sample cell with the carbon tetrachloride solution of your sample and run the sample



The drawback to solution IR spectra is that solvent is an organic molecule that will absorb in the infrared region also. CCl_4 is the best choice because it has few absorptions above 900 cm^{-1} . Peaks below 900 cm^{-1} can't be readily observed however. CCl_4 is also carcinogen, so work with it in the hood, wear the blue gloves have lab instructor help you to make samples.

1. [FT-IR procedure for Benzoin](#) you already printed out in benzoin preparation lab
2. Obtain the IR Spectra of cis-Norbornene-5,6-endo-dicarboxylic acid anhydride using solutions cell and solvent methylene chloride.
3. Obtain the IR Spectra of benzil using solutions cell and solvent carbon tetrachloride.
4. Obtain the IR Spectra of benzoic acid using solutions cell and solvent carbon tetrachloride.
5. IR spectrum of Benzoin given below with spectral assignments.
6. Taking benzoin as an example assign the vibration frequencies to specific stretching and bending vibration modes in the IR spectrum and indicate that in the structure of each molecule.



IR spectrum of benzoin (KBr disk).

