

INFRARED SPECTROSCOPY

For some recapitulation, the bond between two atoms in a molecule is not rigid. It has elasticity and as a consequence the atoms in the molecule do not remain fixed in their positions. They are in a constant state of motion around their mean position. The molecule is said to be undergoing vibrational motion. The quantum mechanical treatment of the molecular vibrational motion shows that it is quantised. As the transitions between these quantised energy levels can be brought out by using EM radiation in the infrared range it gives rise to an IR spectrum. As the excitation among the quantised vibrational energy levels of the molecules is involved, the IR spectroscopy is also known as vibrational spectroscopy.

****Note:** electronic transitions involve energies in the range 100-400 kJ/mol and correspond to the UV-Vis region whereas vibrational transitions involve energies in the region 20 kJ/mol and correspond to infrared radiation.

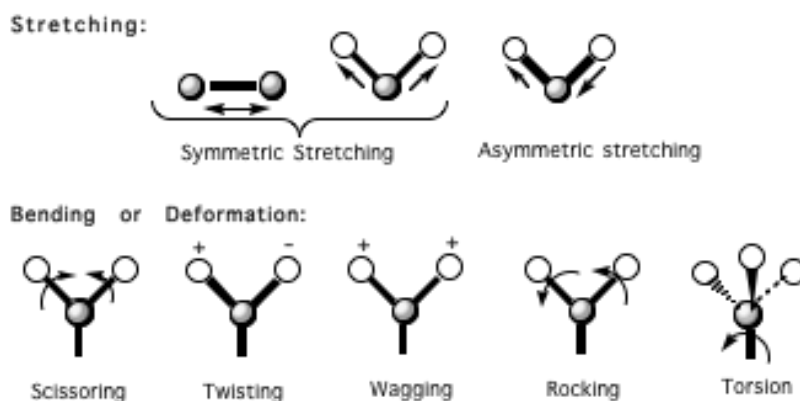
Absorption of infrared wavelengths causes changes in the modes of vibration (the various ways in which the molecules vibrates). The wavelengths absorbed correspond to transitions between quantised energy levels. The wavelength of absorption is characteristic of the type of bond present, so infrared absorption spectra gives two sorts of structural information:

- Certain groups of atoms give rise to characteristic absorptions which can be used to identify specific functional groups
- Molecules with different structures have different vibrational energy levels and so the infrared spectrum of a compound is not shared by any other compound

The presence of quantised energy levels does not ensure transitions amongst them when the radiation of appropriate wavelength is made to fall on it. For the oscillating electrical field of the EM radiation to interact with the vibrating molecule, it is essential that the molecule has a fluctuating or oscillating dipole moment. In the absence of such a dipole moment the radiation cannot interact with the molecule and we say that the vibration in the molecule is IR inactive. For example, a homonuclear diatomic molecule like H₂, O₂ or N₂ would not give an IR spectrum because it does not have a dipole moment and also it does not generate a fluctuating dipole moment. On the other hand, HBr gas has a dipole moment and it does absorb in the IR region.

A molecule can vibrate only in certain modes, known as normal modes. Each normal mode corresponds to a vibrational degree of freedom. There are two types of the normal modes of vibration for polyatomic molecules: stretching vibrations and bending vibrations.

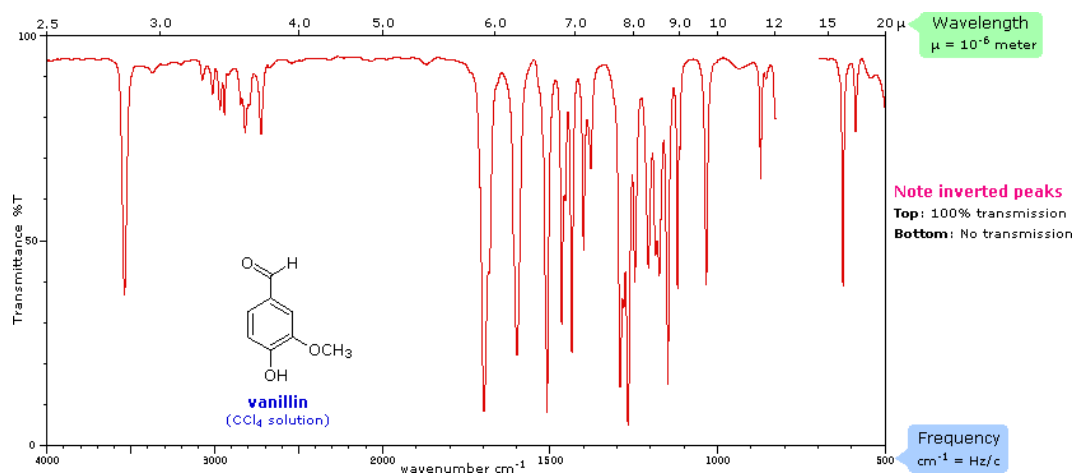
- **Stretching vibrations:** In stretching vibrations, the atoms move along the bond axis so that the bond length increases or decreases at regular intervals. The stretching vibrations again are of two types – symmetric and anti-symmetric stretching. In symmetric stretching of a triatomic molecule, both the bonds connected to a common atom either elongate or contract simultaneously. In case of anti-symmetric stretching, if one bond is lengthened, the other bond is shortened or vice-versa.
- **Bending vibrations:** The bending vibrations are said to occur when there is a change in the bond angle between bonds connected to a common atom. In some cases, the movement of a group of atoms with respect to the remaining atoms in the molecule also causes bending vibrations for a polyatomic molecule. A linear triatomic molecule has two bending vibrations. The bending modes also are of different types. These are called scissoring, rocking, wagging and twisting.



The sample is typically a pure liquid or a solid mixed with an inorganic salt like KBr, though gases can also be analysed. Solids can be compressed with anhydrous KBr into a disc that is placed in the light beam. Alternatively, the solid can be ground and mixed with a mineral oil to produce a mull which can be examined. In the case of liquid samples, a spectrum can be obtained of the undiluted liquid by placing a few drops of it between optically polished plates of NaCl that are placed in the light beam. Alternatively, a small contained (called a cell) with optically polished NaCl windows is used to hold samples dissolved in solvents. Ionic substances without covalent bonds are used for discs, plates and cells because they don't absorb IR radiation (glass, quartz and polymers have absorbing covalent bonds). When solutions are used, they must be in solvents that have a few absorption bands in the region of interest. Commonly used solvents are CH_2Cl_2 and CHCl_3 . In a double beam spectrophotometer, the IR radiation is split into two beams – one that passes through the sample cell and the other that passes through a cell (of the same composition) containing only the solvent. Any absorptions of the solvent are thus cancelled out so that the absorption spectrum is that of the solute alone. In addition, by using a reference cell any interference from water and carbon dioxide in the atmosphere and from the background temperature of the room can be discounted. The IR source is usually a glower filament lamp or a globar.

The sample absorbs certain wavelengths of the IR radiation more than others and an IR spectrum is produced. A detector generates a plot of per cent transmission of radiation versus the wavenumber (or wavelength) of the radiation transmitted. The ordinate (y-axis) represents per cent transmittance whereas the abscissa (x-axis) is wavenumber or wavelength. This means that the positions of IR absorption signals are presented as either wavenumbers (ν) or wavelengths (λ). The wavenumber unit (in cm^{-1} , reciprocal centimetre or centimetre inverse) however is preferred over wavelength because an increase in it corresponds to an increase in energy (and frequency) whereas the wavelength is related inversely to the energy. Also, though abscissa is marked in cm^{-1} , it is commonly (though incorrectly) referred to as the frequency.

The spectrum appears as a series of downward pointing peaks of varying depth and sharpness. Each downward spike in the IR spectrum represents absorption of energy. The spikes are called absorption bands. The interpretation of infrared spectra involves the correlation of absorption bands in the spectrum of an unknown compound with the known absorption frequencies for types of bonds. Significant for the identification of the source of an absorption band are intensity (weak, medium or strong), shape (broad or sharp) and position (cm^{-1}) in the spectrum. Broad peaks are often combinations of peaks corresponding to a number of vibrational changes that have overlapping energies. An example of an IR spectrum is that of the flavouring agent vanillin.



An IR spectrum can be divided into two areas. The left hand two-thirds of an IR spectrum ($4000\text{--}1400\text{ cm}^{-1}$) is where most of the functional groups show absorption bands. This region is called the functional group region. Because it takes more energy to stretch a bond than to bend it, absorption bands for stretching vibrations are found in the functional group region. The right-hand third ($1400\text{--}600\text{ cm}^{-1}$) of the IR spectrum is called the fingerprint region because it is characteristic of the compound as a whole. For example, pentan-2-ol and pentan-3-ol have the same functional groups and so they show similar absorption bands in the functional groups but will have different fingerprint regions. A compound can be positively identified by comparing its fingerprint region with the fingerprint region of the spectrum of a known sample. No two molecular compounds are identical in bonds and bonding environment. Absorption bands for bending vibrations are typically found in the fingerprint region. Therefore, stretching vibrations are the most useful vibrations in determining what kinds of bonds a molecular contains.

For a molecule to absorb infrared radiation, the bond undergoing vibration must be polar (even if the molecule is non-polar overall) and its vibration must cause a periodic change in the bond dipole. The greater the polarity of the bond, the more intense the absorption. Any vibration that meets this criterion is said to be infrared active. For example, the symmetrical stretch of CO_2 will be infrared inactive whereas the asymmetric stretch of CO_2 results in a dipole change and so is infrared active.

The intensity of an absorption band also depends on the number of bonds responsible for the absorption. For example, the absorption band for the C-H stretch will be more intense for a compound such as iodooctane, which has 17 C-H bonds, than for iodomethane, which has only three C-H bonds.

Each vibrational motion (both stretching and bending) has its own natural frequency, which is based on the type of motion, the masses of the atoms and the strength of the bond between them. The energy required to stretch a bond depends on the strength of the bond and the masses of the bonded atoms. The stronger the bond, the greater energy required to stretch it. The frequency of the vibration is inversely related to the mass of the atoms 'attached' to the bond, so heavier atoms vibrate at lower frequencies. Bonds to hydrogen atoms have higher stretching frequencies than those to heavier atoms, e.g. C-H around 3000 cm^{-1} compared to C-O around 1100 cm^{-1} .

Once again, the energy of vibrations is quantised. Just as an atom can absorb a photon whose energy corresponds to the difference between two quantised electron energy levels, a molecule can absorb an IR photon whose energy corresponds to the difference between two of its quantised vibrational energy levels. So when a compound is bombarded with radiation of a frequency (and energy) that exactly matches the energy difference between one of its original vibrational energy levels and one of its allowed higher vibrational energy levels the molecule will absorb energy. This allows the bonds to stretch and bend a bit more but only in a quantised fashion.

The IR spectrum is particularly useful for compound identification because of two related factors. First, each kind of bond has a characteristic range of IR wavelengths it can absorb. For example, a C-C bond absorbs IR photons in a different wavelength range from those absorbed by a C=C bond, a C-H bond, a C=O bond and so forth. Furthermore groups of atoms that characterise particular types of organic compounds – alcohol, carboxylic acid, ether etc. – absorb in slightly different wavelength regions. Second, the exact wavelengths and quantity of IR radiation that a molecule absorbs depends on the overall structure of the molecule. Combinations of absorptions overlap to create a very characteristic pattern for a given type of compound. This means that each compound has a characteristic IR spectrum that can be used to identify it.

A non-linear molecule containing n atoms has $3n$ degrees of freedom, six of which are translations and rotations, leaving $3n-6$ allowed fundamental vibrations. Consider the four-atom molecule of methanal. We would expect six fundamental vibrations ($12-6=6$) and these have been assigned to the spectrum absorptions. In practice, however, infrared spectra do not normally display separate absorption signals for each of the $3n-6$ fundamental vibrational modes of a molecule. The number of observed absorptions may be increased by additive and subtractive interactions leading to combination tones and overtones of the fundamental vibrations, in much the same way that sound vibrations from a musical instrument interact. Thus, the number of observed absorptions may be decreased by molecular symmetry, spectrometer limitations, and spectroscopic selection rules.

Since IR spectroscopy can be used to help identify molecular compounds, in particular by showing what functional groups are present, it can be used to identify drugs and determine their purity, to test other consumer products and in forensic analysis to analyse fibres, paint samples, dyes, glass etc.

**Note: if a strong, sharp peak in the spectrum of a molecule is chosen then as the concentration of the molecule in the sample increases, the absorbance increases and so IR spectra can be used for quantitative analysis as well.

**Note: photon energies from the infrared region are not large enough to excite electrons but may induce vibrational excitation of covalently bonded atoms and groups.

**Note: if the sample is analysed in gas phase, then there are no intermolecular forces. Then, for example, the IR spectrum of ethanol as a gas would not show an absorption band for the hydroxyl functional group as there are no hydrogen bonds for gaseous ethanol.

**Note: the OH group in the carboxyl group and the OH group in an alcohol show broad peaks at a different range of wavelengths, with the OH group in the carboxyl group often overlapping with the C-H bond.