UNIT-3 MPHYCC-10

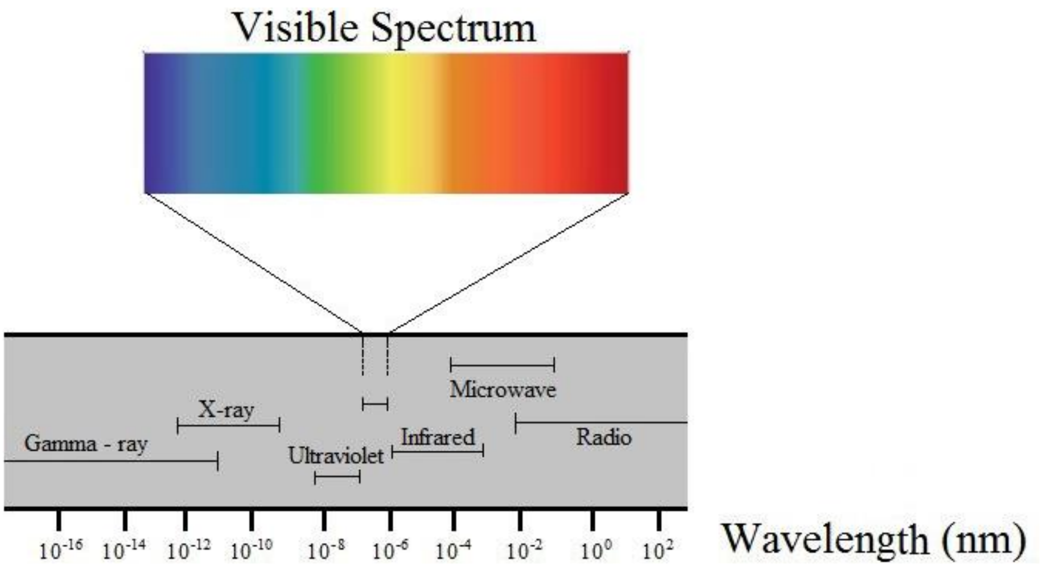
Infrared Spectroscopy

Submitted by:

Dr. Gargi Tiwari

Dept. of Physics

Infrared (IR) spectroscopy is one of the most common and widely used spectroscopic techniques employed mainly by inorganic and organic chemists due to its usefulness in determining structures of compounds and identifying them.



Introduction

Infrared (IR) spectroscopy is one of the most common and widely used spectroscopic techniques. Absorbing groups in the infrared region absorb within a certain wavelength region. The absorption peaks within this region are usually sharper when compared with absorption peaks from the ultraviolet and visible regions. In this way, IR spectroscopy can be very sensitive to determination of functional groups within a sample since different functional group absorbs different particular frequency of IR radiation. Also, each molecule has a characteristic spectrum often referred to as the fingerprint. A molecule can be identified by comparing its absorption peak to a data bank of spectra. IR spectroscopy is very useful in the identification and structure analysis of a variety of substances, including both organic and inorganic compounds. It can also be used for both qualitative and quantitative analysis of complex mixtures of similar compounds. The use of infrared spectroscopy began in the 1950's by Wilbur Kaye. He had designed a machine that tested the near-infrared spectrum and provided the theory to describe the results. The year this method became accepted in the field was in the late 1960's.

Absorption Spectroscopy

There are three main processes by which a molecule can absorb radiation and each of these routes involves an increase of energy that is proportional to the light absorbed. The first route occurs when absorption of radiation leads to a higher rotational energy level in a rotational transition. The second route is a vibrational transition which occurs on absorption of quantized energy. This leads to an increased vibrational energy level. The third route involves electrons of molecules being raised to a higher electron energy, which is the electronic transition. It's important to state that the energy is quantized and absorption of radiation causes a molecule to move to a higher internal energy level. This is achieved by the alternating electric field of the radiation interacting with the molecule and causing a change in the movement of the molecule. There are multiple possibilities for the different possible energy levels for the various types of transitions.

The energy levels can be rated in the following order: electronic > vibrational > rotational. Each of these transitions differs by an order of magnitude. Rotational transitions occur at lower energies (longer wavelengths) and this energy is insufficient and cannot cause vibrational and electronic transitions but vibrational (near infra-red) and electronic transitions (ultraviolet region of the electromagnetic spectrum) require higher energies.

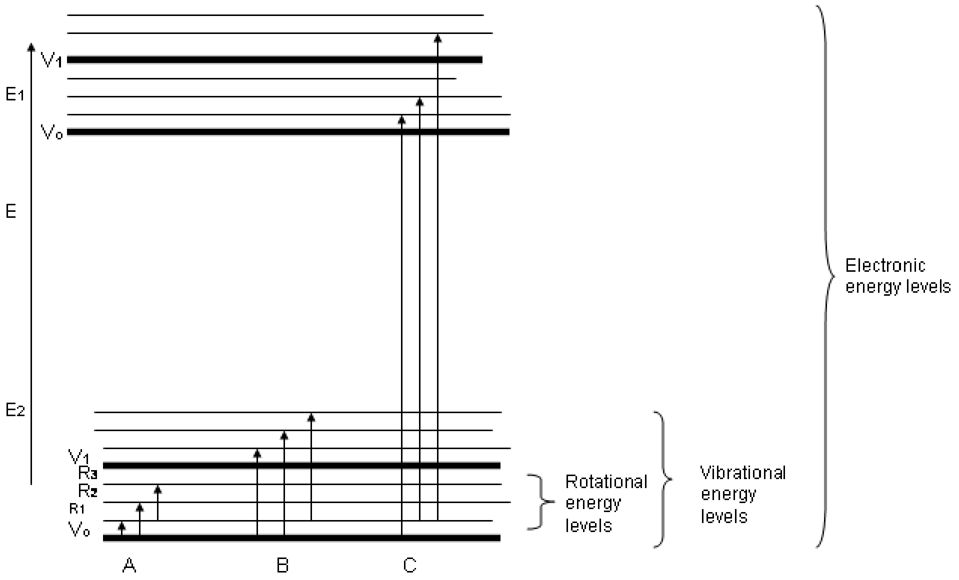


Figure 1: Energy levels for a molecule. Possible transitions that occur: (A): Pure rotational Transitions, (B) rotational-Vibrational Transitions, (C) Rotational-Vibrational-Electronic Transitions

The energy of IR radiation is weaker than that of visible and ultraviolet radiation, and so the type of radiation produced is different. Absorption of IR radiation is typical of molecular species that have a small energy difference between the rotational and vibrational states. A criterion for IR absorption is a net change in dipole moment in a molecule as it vibrates or rotates. Using the molecule HBr as an example, the charge distribution between hydrogen and bromine is not evenly distributed since bromine is more electronegative than hydrogen and has a higher electron density. HBr thus has a large dipole moment and is thus polar. The dipole moment is determined by the magnitude of the charge difference and the distance between the two centers of charge. As the molecule vibrates, there is a fluctuation in its dipole moment; this causes a field that interacts with the electric field associated with radiation. If there is a match in frequency of the radiation and the natural vibration of the molecule, absorption occurs and this alters the amplitude of the molecular vibration. This also occurs when the rotation of asymmetric molecules around their centers results in a dipole moment change, which permits interaction with the radiation field.

Diatomic Molecular Vibration

The absorption of IR radiation by a molecule can be likened to two atoms attached to each other by a massless spring. Considering simple diatomic molecules, only one vibration is possible. The Hook's law potential on the other hand is based on an ideal spring

$$F = -kx \qquad (1)$$

$$-\frac{dV(x)}{d(x)} \qquad (2)$$

this results in one dimensional space

$$V(x) = \frac{1}{2}k(r - r_{eq})^2 \qquad (3)$$

One thing that the Morse and Harmonic oscillator have in common is the small displacements ($x=r-r_{eq}$) from the equilibrium. Solving the Schrödinger equation for the harmonic oscillator potential results in the energy levels results in

$$E_v = (v + \frac{1}{2})\, h v_e \qquad (4)$$

with v=0,1,2,3,...,infinity

$$v_e = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{5}$$

When calculating the energy of a diatomic molecule, factors such as anharmonicity (has a similar curve with the harmonic oscillator at low potential energies but deviates at higher energies) are considered. The energy spacing in the harmonic oscillator is equal but not so with the anharmonic oscillator. The anharmonic oscillator is a deviation from the harmonic oscillator. Other considered terms include; centrifugal stretching, vibrational and rotational interactions have to be taken into account. The energy can be expressed mathematically as

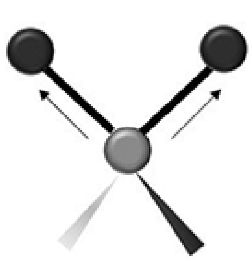
$$E_v = (v + \tfrac{1}{2})\mathrm{h}\nu_e - (v + \tfrac{1}{2})^2 X_e \mathrm{h}\nu_e + B_e J(J + 1) - D_e J^2\,(J + 1)^2 - \alpha_e\,(v + \tfrac{1}{2})\mathrm{J(J{+}1)} \tag{6}$$

Harmonic Oscillator anharmonicity Rigid Rotator centrifugal stretching ro-vibrational coupling

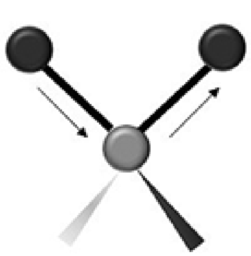
The first and third terms represent the *harmonicity* and rigid rotor behavior of a diatomic molecule such as HCl. The second term represents anharmonicity and the fourth term represents centrifugal stretching. The fifth term represents the interaction between the vibration and rotational interaction of the molecule.

Polyatomic Molecular Vibration

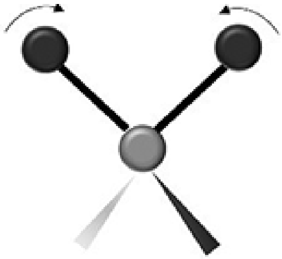
The bond of a molecule experiences various types of vibrations and rotations. This causes the atom not to be stationary and to fluctuate continuously. Vibrational motions are defined by stretching and bending modes. These movements are easily defined for diatomic or triatomic molecules. This is not the case for large molecules due to several vibrational motions and interactions that will be experienced. When there is a continuous change in the interatomic distance along the axis of the bond between two atoms, this process is known as a stretching vibration. A change in the angle occurring between two bonds is known as a bending vibration. Four bending vibrations exist namely, wagging, twisting, rocking and scissoring. A CH_2 group is used as an example to illustrate stretching and bending vibrations below.



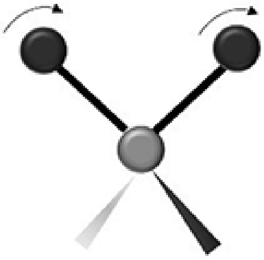
Symmetric stretching



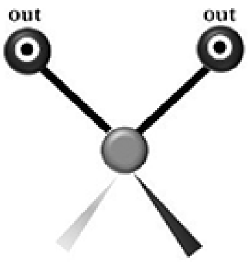
Antisymmetric stretching



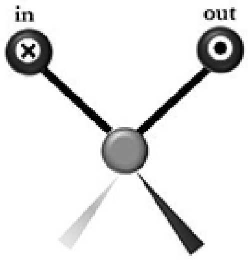
Scissoring



Rocking



Wagging



Twisting