Spectroscopy chemistry

Infrared [Vibrational] Spectroscopy

Topics

① Basic Introduction
② Simple Harmonic Oscillator
③ Anharmonic Oscillator [Anharmonicity]
* MORSE POTENTIAL ENERGY DIAGRAM.
④ Infrared Instrumentation.
* Fourier Transform Infrared Spectroscopy [FTIR]
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⑤ Interpretation of IR Spectrum
⑥ Application of IR Spectroscopy.

The term Vibrational Spectroscopy is used to describe the techniques of infrared and Raman Spectroscopy.

☆ **Introduction :-** Infrared Spectroscopy is a very powerful technique which uses electromagnetic radiation in the infrared region for the determination and identification of molecular structure as well as having various quantitative application within analytical chemistry.

☆ Simple Harmonic Oscillator (Vibrational Motion)

The Vibrational motion resembles the motion observed for a ball attached to a Spring i.e. harmonic ascillator which obeys Hook's law.

Hook's law relates the restoring force

$$F = -fx$$

$$V(x) = -Fdx \quad \text{or} \quad V(x) = \int fx\,dx$$

Thus $$V(x) = \frac{1}{2} fx^2$$

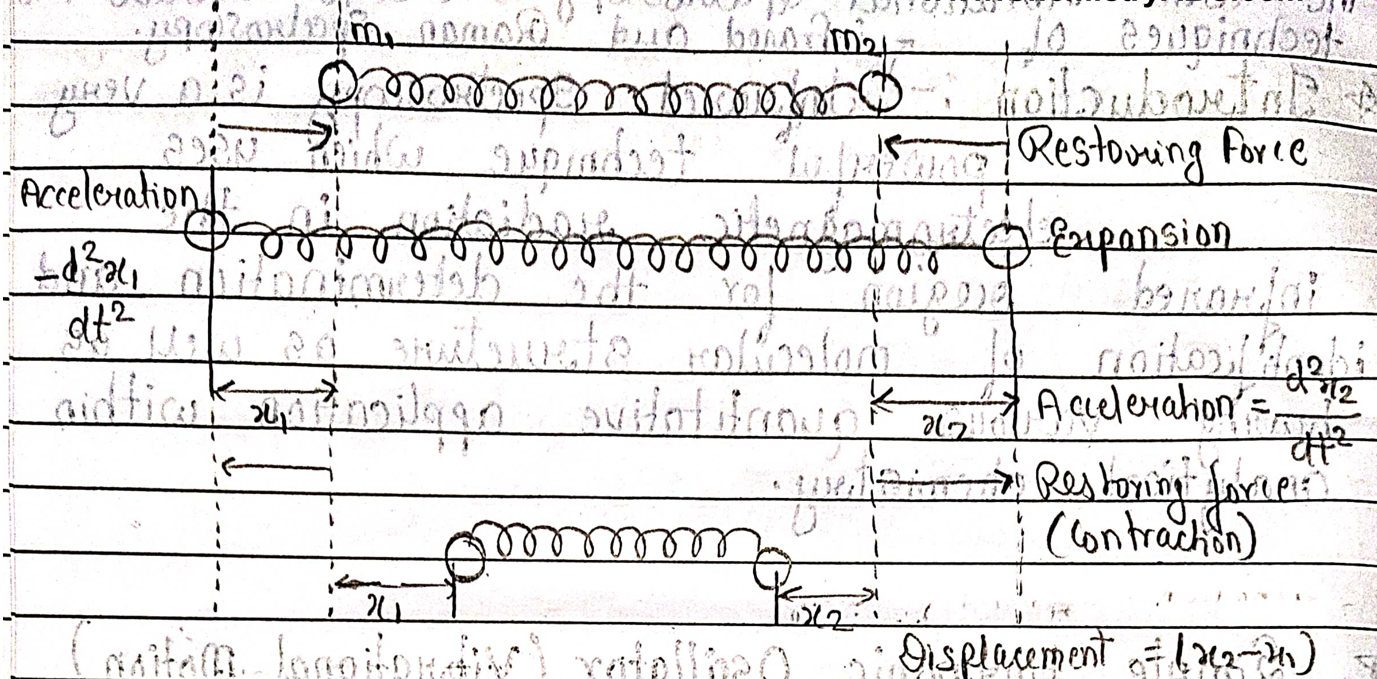
Application of Newton's second law gives the fimiliar equa of Simple harmonic oscillator (SHO). The equa. of motion according to classical mechanics is

$$f = md^2x/dt^2$$

Hence restoring force $m\dfrac{d^2x}{dt^2} = -fx$

The general equa is $x = x_0 \sin(2\pi\nu_0 t + \delta)$

Vibrational Motion of diatomic molecule :- Consider Vib. of a System of two Particles Such as diatomic molecule attached to a Spring. The only mode of Vibration is expansion and Contracting of Spring or a bond between two atoms in a molecule.



Vibration of a diatomic molecule.

The restoring force is

$$f = -f(x_2 - x_1)$$

Newton's law

$$-m_1\frac{d^2x_1}{dt^2} = -f(x_2-x_1) \quad + m_2\frac{d^2x_2}{dt^2} = -f(x_2-x_1)$$

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{f}{\mu}} \quad \text{———} ①$$

$$V(x) = \frac{1}{2}f(x_2-x_1)^2 \quad \text{———} ②$$

Substituting it in the Schrodinger wave equa. gives

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{h^2}\left(E - \frac{1}{2}fx^2\right)\psi = 0 \quad \text{———} ③$$

where the displacement $x = (x_2 - x_1)$ Thus the vibrational energy of diatomic molecule is

$$E_v = h\nu_0\left(v+\frac{1}{2}\right) : v = 0,1,2,3\ldots \quad \text{———} ④$$

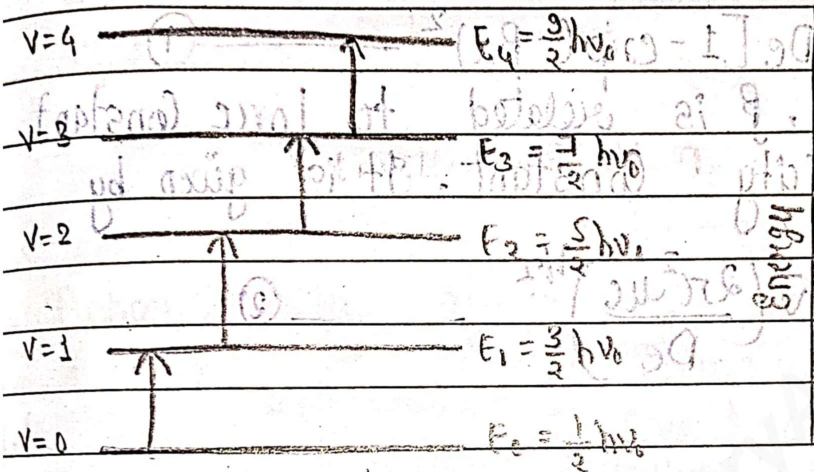
$$E_v(cm^{-1}) = \frac{E_v}{hc} = \left(v+\frac{1}{2}\right)\bar{\nu}_0\ cm^{-1} \ ; \ v = 0,1,2\ldots\ldots \quad \text{———} ⑤$$

Different values of Vibrational quantum numb.

$V = 0 \; ; \; E_0 = \frac{1}{2}\bar{\nu}_0 \; cm^{-1}$

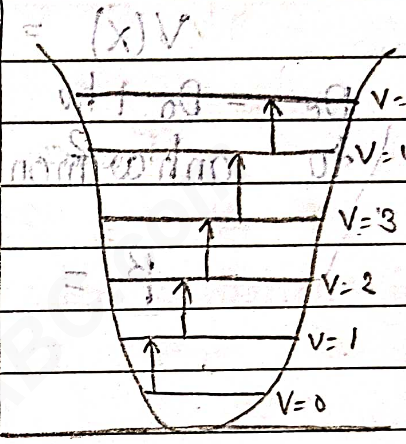
$V = 1 \; ; \; E_1 = \frac{3}{2}\bar{\nu}_0 \; cm^{-1}$

$V = 2 \; ; \; E_2 = \frac{5}{2}\bar{\nu}_0 \; cm^{-1}$



Vibrational transitions

ⓐ Energy levels



Vibrational levels are equally spaced.

ⓑ Transition between the Vib. energy level.

Applying Selection rule $\Delta\upsilon = \pm 1$ from equa. ⑤ we get

$$\bar{\nu}_{v \to v+1} = \frac{\Delta E}{hc} = \left(v+1+\frac{1}{2}\right)\bar{\nu}_0 - \left(v+\frac{1}{2}\right)\bar{\nu}_0$$

for emission $\bar{\upsilon}_{v+1 \to v} = \bar{\nu}_0 \; cm^{-1}$

$$\boxed{\bar{\nu}_{v \to v+1} = \frac{1}{2\pi c}\sqrt{\frac{f}{\mu}} = \bar{\nu}_0}$$

Zero point energy :- The lowest energy of a quantum mechanical harmonic oscillator is not zero but equal to $\frac{1}{2}h\nu$. It is referred to as Zero point energy and it has its Consequence in the Heisenberg Uncertainty Principal.

☆ Anharmonic Oscillator (Anharmonicity)

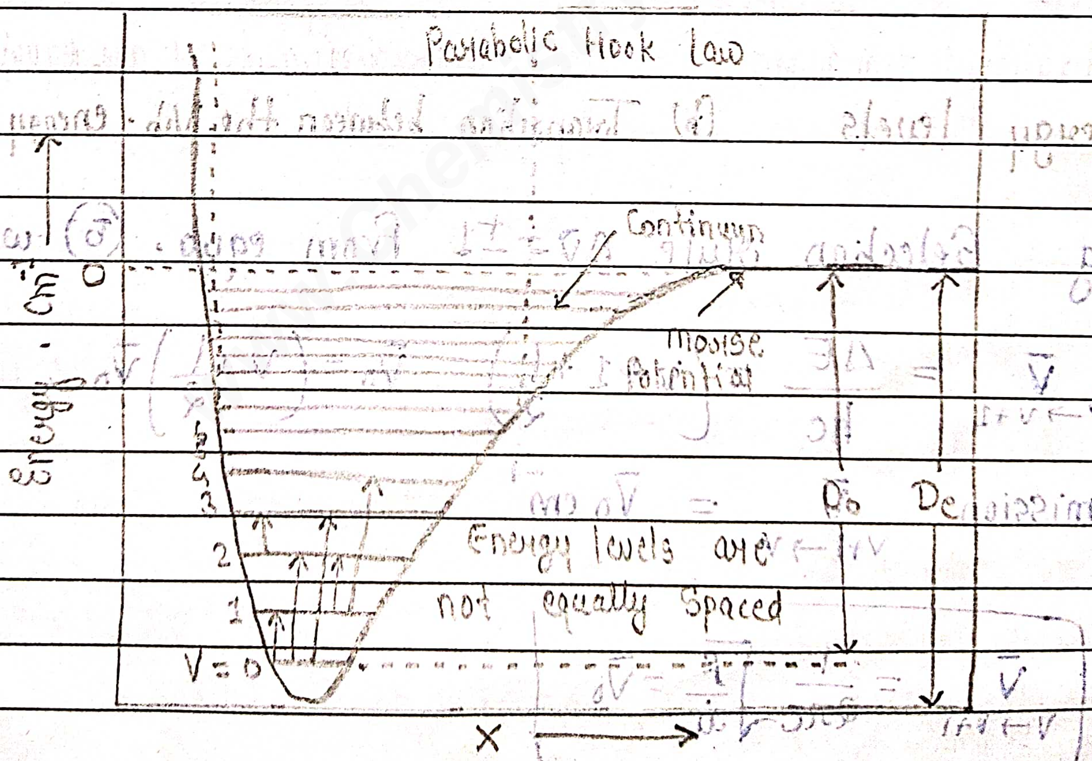
MORSE POTENTIAL ENERGY DIAGRAM.

P.M. Morse (1929) suggested an empirical expression for the potential energy of an anharmonic diatomic oscillator called morse function:

$$V(x) = D_e[1-\exp(-\beta x)^2] \text{ ——— } ①$$

$D_e = D_0 + \frac{h\nu}{2}$, β is related to force constant and to anharmonicity constant. It is given by

$$\beta = \bar{\nu}\left(\frac{2\pi^2 \mu c}{D_e}\right)^{1/2} \text{ ——— } ②$$



Morse potential energy function of an anharmonic oscillator.

$$E_v = \left(v+\frac{1}{2}\right)h\nu - x_e\left(v+\frac{1}{2}\right)^2 h\nu \quad \text{(Joules)}$$ ③

In terms of wave num. (cm^{-1}), the equa. ③ is expressed as

$$\frac{E_1}{hc} = \left(v+\frac{1}{2}\right)\bar{\nu} - x_e\,\bar{\nu}\left(v+\frac{1}{2}\right) \text{cm}^{-1}$$ ④

where x_e is the anharmonicity constant. It is small, positive and equal to

$$x_e = \frac{\bar{\nu}}{4} D_e$$ ⑤

Anharmonicity affects the molecular Vibrations in two ways.

1. Transitions
2. Overtones

For transition $\Delta v = \pm 1$

$$\Delta E = E_1 - E_0$$

$$\Delta E = \left[\frac{3}{2}h\nu_0 - x_e\left(\frac{3}{2}\right)^2 h\nu_0\right] - \left[\frac{1}{2}h\nu - x_e\left(\frac{1}{2}\right)^2 h\nu_0\right]$$

$$= h\nu - 2x_e h\nu$$

or in cm^{-1} $\frac{\Delta E}{hc} = 2\bar{\nu}_2(1-2x_e)$

Generally $\frac{\Delta E_v}{hc} = \bar{\nu}_v = \bar{\nu}_0 - 2(v+1)x_e\bar{\nu}_0 \text{ cm}^{-1}$

For transition $v \rightarrow v+1$, successive line lie $2\bar{\nu}_0 x_e(v+1)$ apart

Overtones :- If a Single quantum number changes by ±2, the transition is said to be First Overtone.

For transition $\Delta v = \pm 2$

$$\Delta E_v = E_2 - E_0 = \left[\frac{5}{2}h\nu_0 - x_e\left(\frac{5}{2}\right)^2 h\nu_0\right] - \left[\frac{1}{2}h\nu_0 - x_e h\nu_0\left(\frac{1}{2}\right)^2\right]$$

$$= 2h\nu[1-3x_e]$$

$$\frac{\Delta E}{hc} = 2\bar{\nu}_0(1-3x_e)\ cm^{-1}$$

If $\Delta v = \pm 3$, it is referred to as Second overtone.

$$\Delta E_v = E_3 - E_0 = 3h\nu_0 \cancel{(1-4)}(1-4x_e)$$

$$\frac{\Delta E}{hc} = 3\nu_0(1-4x_e)\ cm^{-1}$$

If $\Delta v = \pm 4$ third overtone

$$\Delta E_v = E_4 - E_0 = 4h\nu_0(1-5x_e)$$

$$\Delta E/hc = 4\bar{\nu}_0(1-5x_e)\ cm^{-1}$$

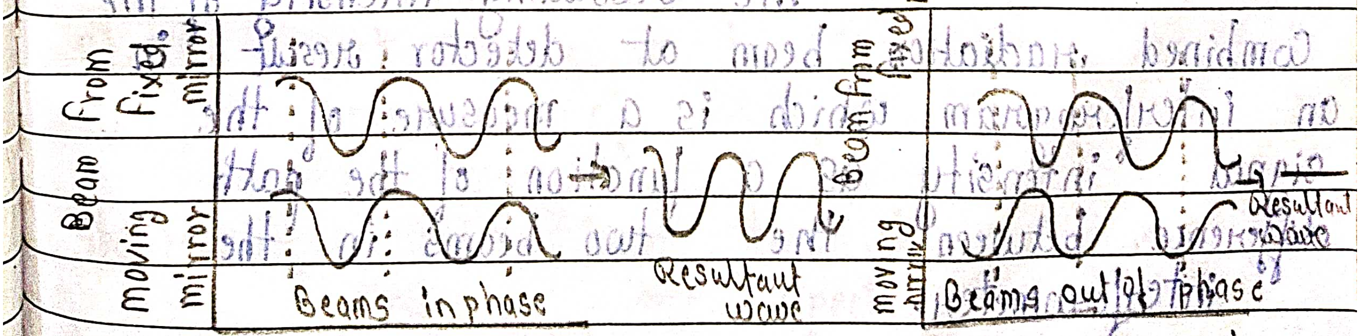
☆ **Infrared Instrumentation** :- The infrared instrumentation has diverged into two classes - dispersive and interferometric.

Fourier Transform Infrared Spectroscopy (FTIR)
Interferometry OR FTS.

Principle :- The principal of interferometry is the Simple interference of radiation where the absorption spectrum is obtained through the interference technique. Two Radiation beams with the same wavelength (λ) and amplitude lead to optical interference.

① If the radiation beams are in phase the beams will interfere constructive and the resultant amplitude will be twice as high.

② If the radiation beams are out of phase by $(\frac{1}{2})(2n+1)\lambda$ the beams will interfere destructively ~~Cancelled~~ Cancelling out each other.



ⓐ Constructive interference increase Radiation power ⓑ Destructive interference decrease radiation power

Constructive and destructive interference for a single wavelenght

FTIR Spectrometer :- It consists of :- ① an optical system which ~~has~~ uses an interferometer and ② a computer which stores data, performs computation on the data and plots the spectra.

FT spectrometer consists of two perpendicular mirrors, one of which is a stationary mirror and the other a movable mirror. Between these two mirrors is a beam spilitter set at 45° from the initial position of the movable mirror. A parallel beam of radiation from the infrared source is passed on to the mirrors through the beam splitter.

The beam splitter divides the beam and transmits half the incoming radiation to the fixed mirror and the other half to the movable mirror. The composition of beam splitter depends on the spectral region.

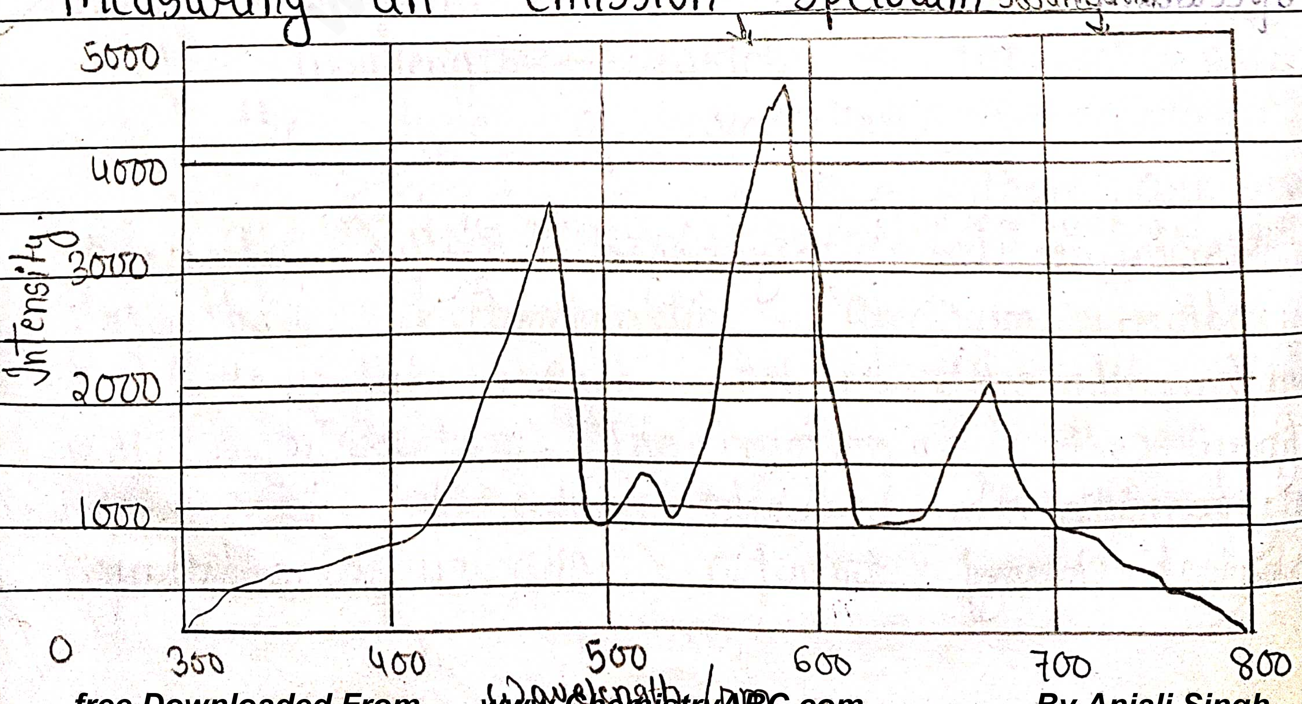
The resulting intensity of the combined radiation beam at detector result in an interferogram, which is a measure of the signal intensity as a function of the path difference between the two beams in the interferometer.

✲ Fourier - Transform (F.T) Spectroscopy :-

Fourier transform Spectroscopy is a measurment technique whereby Spectra are collected based on measurements of the coherence of a radiative Source, using time domain or Space domain measurments of the electro-magnetic Radiation or other type of Radiation. It can be applied to a variety of types of Spectroscopy including Optical Spectroscopy, infrared Spectroscopy (FTIR), nuclear magnetic resonance (NMR), mass Spectrometry and electron Spin resonance Spectroscopy.

The term F.T Spectroscopy reflect the fact that in all these techniques a FT is required to turn the raw data into the actual Spetrum and in many of the cases in Optics involving interferometers is based on the wiener-khinchin theorem.

Measuring an emission Spetrum



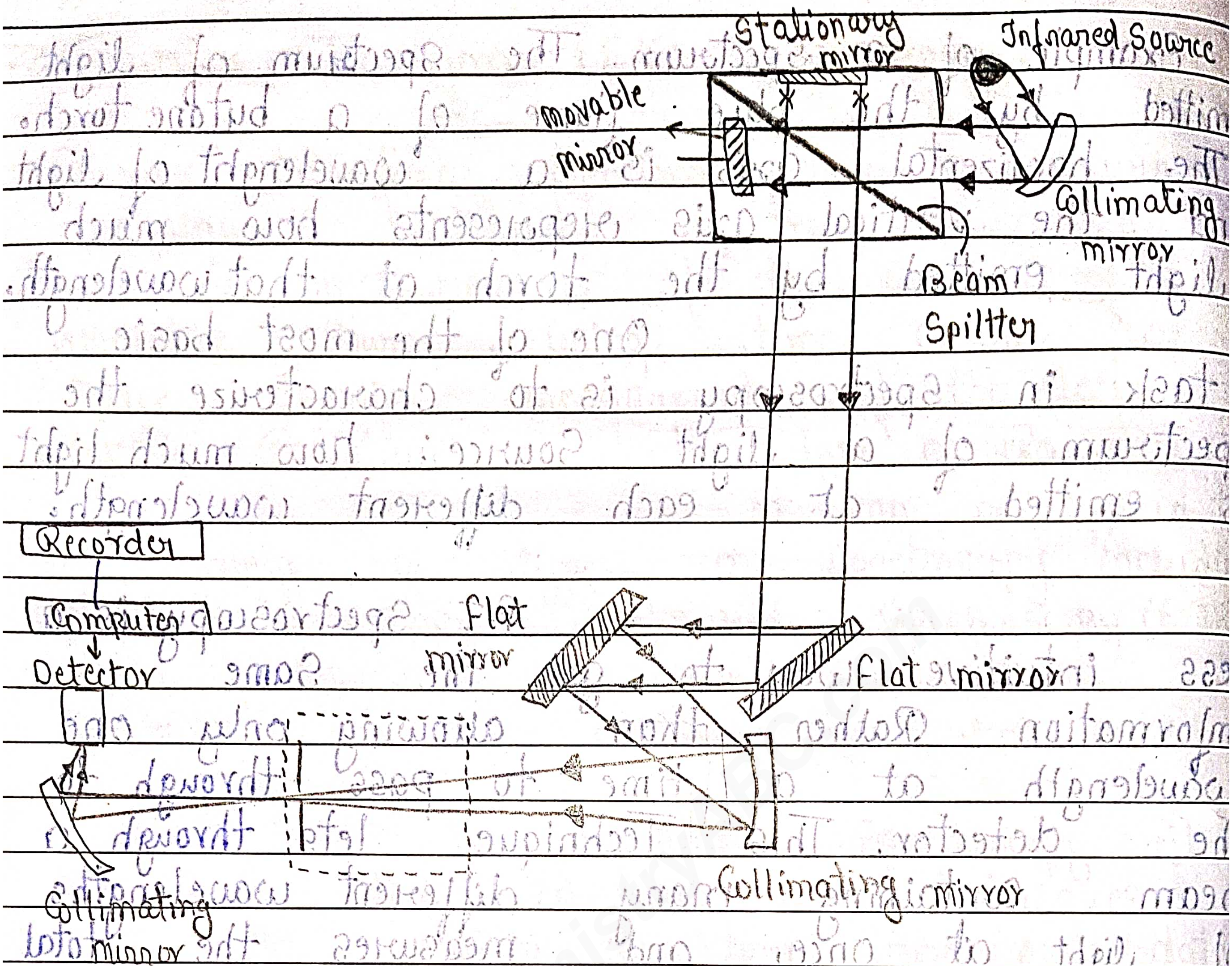
A Example of a Spectrum. The Spectrum of light emitted by the blue flame of a butane torch. The horizental axis is a wavelenght of light and the vertical axis represents how much light emitted by the torch at that wavelength.

One of the most basic task in Spectroscopy is to characterize the Spectrum of a light Source: how much light is emitted at each different wavelength.

F.T Spectroscopy is a less intuitive way to get the Same information Rather than allowing only one wavelength at a time to pass through to the detector, This Technique lets through a beam containing many different wavelengths of light at once, and measures the total beam intensity. Next the beam is modified to contain a different Combination of wavelengths giving a Second data point. This process is repeated many times. Afterward a Computer takes all this data and works backwards to inter how much light there is at each wavelength.

Measuring an absorption Spectrum :-

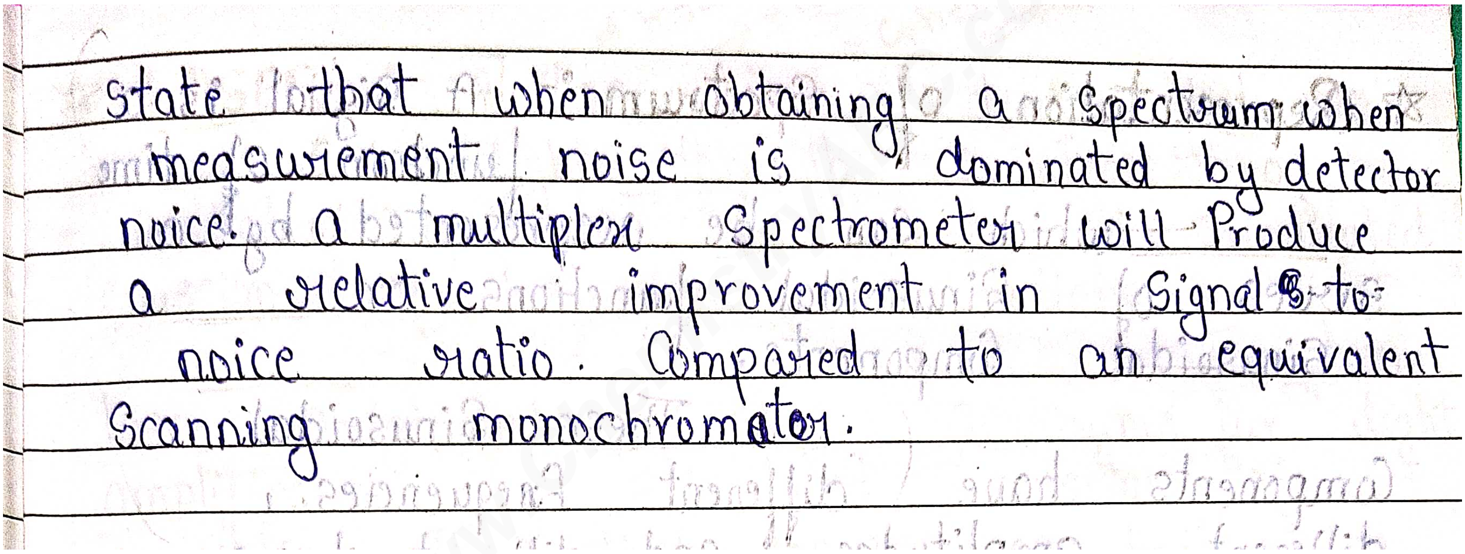
The method of F.T. Spectroscopy can also be used for absorption Spectroscopy. The Primary example is ~~FT~~ FTIR spectroscopy a Common technique in Chemistry.



Schematic diagram of a FT infrared Spectrophotom

The FT Spectrometer is just a michelson interferometer but one of the two fully reflecting mirros is movable, allowing a variable delay to be included in one of the beams.

Fellgett Advantage :- (multiplex advantage) :- One o the most important advantage of FT Spectroscopy was shown by P.B. Fellgett an early advocate advantage of the method. The Fellgett advantage also known as the multiplex Principle.



state that when obtaining a spectrum when measurement noise is dominated by detector noice. a multiplex Spectrometer will Produce a relative improvement in Signal-to-noice ratio. Compared to an equivalent Scanning monochromator.

The interferograms are most difficult to interpret and they are converted to the normal infrared spectra by fourier transformation.

Advantages :-

1. Multiplex Advantage (fellgett advantage) :- The concurrent examination of the detector signal for all the spectral elements is known as multiplex or fellgett advantage.

2. By FTIR it is possible to measure the whole spectrum with high resolution ($<0.001\ cm^{-1}$) in a few seconds.

Interpretation of IR Spectrum

There are no rigid rules for interpreting an infrared spectrum. However, certain requirements must be met before an attempt is made to interpret a spectrum.

1) The spectrum should be that of a pure compound.
2) The spectrum must be adequately resolved.
3) The method of sample handling must be specified.
4) Always start from the higher frequency end of the spectrum.

5) To distinguish between intermolecular and intramolecular hydrogen bonding, the spectrum of the sample are scanned at two different concentration. Various solvents may be used to study association effects.

✰ Application of IR Spectroscopy :-

1) IR is widely used in industry as well as in research. It is a simple and reliable technique for measurement, quality control and dynamic measurements.
2) it is also employed in forensic analysis in civil and criminal analysis.
3) Drug analysis
4) Testing the breath of suspected drunken drivers for ethanol.

✰ Rotation - Vibrational Coupling :- occurs when the rotation frequency of an object is close to or identical to a natural internal vibration frequency.