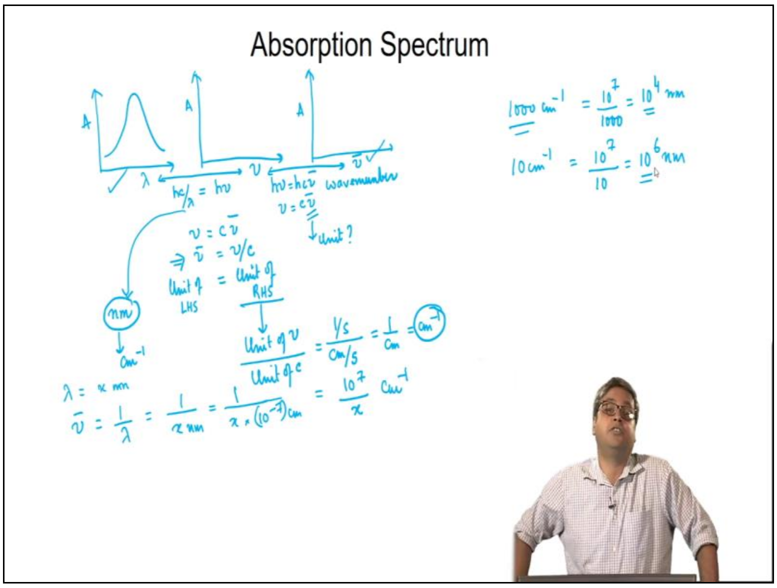
Fundamentals of Spectroscopy

dr Sayan Bagchi
Physical and Material Chemistry division, NCL Pune
dr. Anirban Hazra
department of Biotechnology
Indian Institute of Chemistry, IISER Pune

Lecture – 9
Lineshape Analysis

Hello everyone welcome to this lecture in the last lecture we have discussed how we can obtain an absorption spectrum.

(Refer Slide Time: 00:31)



Absorption Spectrum

$hc/\lambda = h\nu$

$h\nu = hc\bar{\nu}$ wavenumber

$\nu = c\bar{\nu}$ unit?

$\nu = c\bar{\nu}$

$\Rightarrow \bar{\nu} = \nu/c$

Unit of LHS = Unit of RHS

$\frac{\text{Unit of } \nu}{\text{Unit of } c} = \frac{1/s}{cm/s} = \frac{1}{cm} = cm^{-1}$

nm → cm^{-1}

$\lambda = x$ nm

$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{x\ nm} = \frac{1}{x \times (10^{-7})cm} = \frac{10^7}{x}\ cm^{-1}$

$1000\ cm^{-1} = \frac{10^7}{1000} = 10^4\ nm$

$10\ cm^{-1} = \frac{10^7}{10} = 10^6\ nm$

We had mentioned that if you plot absorbance obtained from a spectroscopy experiment against wavelength lambda we can obtain an absorption spectrum. Although conventionally absorbance is plotted against wavelength we can also plot absorbance against frequency as these are interchangeable. So, we can write h nu equals hc by lambda. Moreover we can also plot absorbance against wave number.

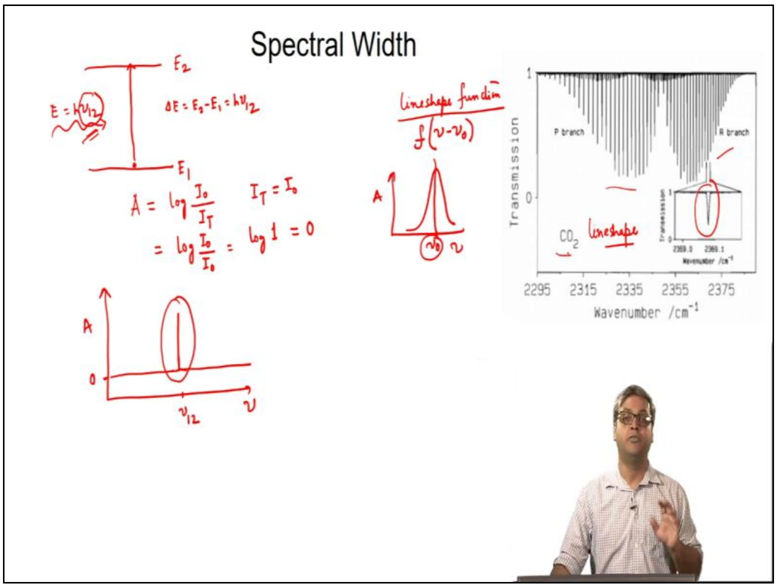
Wave number is denoted by nu bar a new bar is related to frequency because h nu equals hc nu bar or we can write nu equals c nu bar. So, the next question is what is the unit of q bar because we can write nu equals c nu bar or rearranging this equation we can write nu bar equals nu by c. So, we know the unit of the left hand side is equal to the unit of the right hand side. So, in order to find the unit of nu bar we have to find the unit of the right hand side and the unit of the right hand side is unit of nu by unit of c that is 1 by second by centimeter per second this gives 1 by centimeter or centimeter inverse.

So, centimeter inverse is the unit of nu bar and also lambda is normally represented in the unit of nanometers. So, let us look into the relation between nanometer and centimeter inverse. So, let us say the wavelength lambda equals x nanometer, so in centimeter inverse the wave number will be 1 by lambda that is 1 by x nanometer that is 1 by x times 10 to the power - 7 centimeter equals 10 to the power 7 by x centimeter inverse.

Later we will discuss about different forms of spectroscopy like UV visible spectroscopy infrared spectroscopy microwave spectroscopy and we will see that we get different spectroscopy depending on the wavelength of the light or the frequency of the light interacting with the matter. Conventionally when we plot our UV visible spectrum we use wavelength in the x axis however when we plot an infrared spectrum conventionally we plot wave numbers on the x axis this is just a convention used for convenience such that the values plotted on the x axis and not very large numbers.

So, let us see what do I mean by that for example 1000 wave numbers is a typical higher frequency so if we convert this number into nanometer it will be 10 to the power 7 by 1000 equals 10 to the power 4 nanometer, so 10 to the power 4 is a larger number than 1000. Similarly 10 wave numbers is a typical energy gap involved in a microwave transition, so this amounts to 10 to the power 7 divided by 10 that is 10 to the power 6 nanometer which is a very, very large number.

(Refer Slide Time: 05:28)



Spectral Width

So, far we have explained the absorption process by saying we have a molecule in a stationary state of energy E1 and when light of energy equals h nu 12 interacts with the molecule then the molecule goes from the stationary state with energy E1 to another stationary state of energy E2 such that Delta e or E2 - E1 equals h nu 12 apparently only one frequency is involved that is nu 12 in the transition process or in other words in terms of experiments if we use a polychromatic light source that is light having many, many frequencies we can expect that only one frequency that is nu 12 should be absorbed by the matter.

So, in all other frequencies where light is not absorbed absorbance is given by A equals log I 0 by I T and because in the other frequencies light is not absorbed by the matter so I T for those frequencies will be equal to I 0, so absorbance we can write log I 0 divided by I 0 equals log 1 that is 0. The absorbance should only be non0 at the frequency nu 12 so this can be represented in a spectrum so again we are plotting absorbance versus frequency and let us say this is my frequency nu 12.

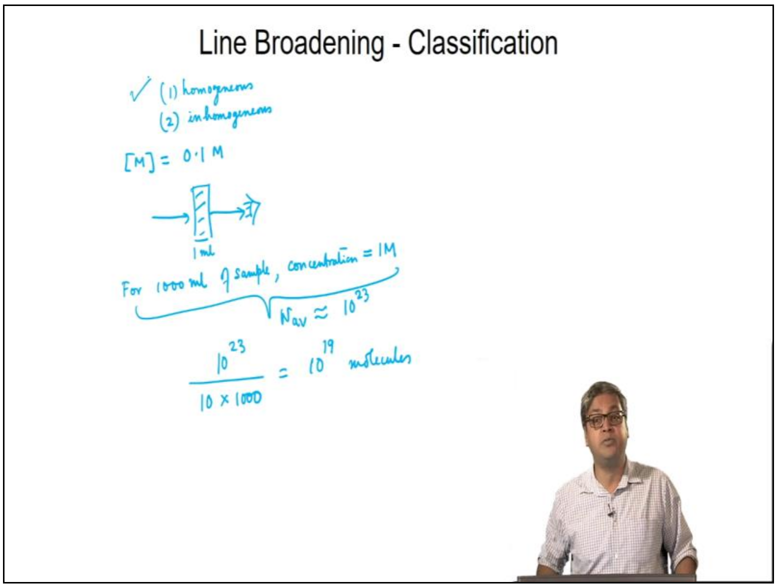
So for all other frequencies the absorbance will be 0 and only at nu 12 the absorbance will be non0 however it has been seen from experiments that the spectroscopic lines are not as infinitely sharp as shown in the plot. But they are more or less broad additionally we should realize that as the light sources polychromatic that is the light consists of many frequencies thus multiple transitions can be obtained from the same sample.

So, this is a spectrum where the lines are associated with the anti symmetric stretching mode of carbon dioxide. At high resolution the spectrum seems to consist of multiple lines from multiple transitions so if we expand the scale or if we zoom into one particular line the line with a per N narrow feature is observed to have a definite width and a characteristic shape. The shape of the line spectrum is known as line shape.

As this shape is a function of frequency the line shape can be represented using a line shape function which is given by f nu - nu 0 where nu 0 is the frequency corresponding to the maximum absorbance. So, nu 0 is also known as the peak position for a single peak corresponding to a transition the shape of this spectrum is symmetric with respect to nu 0. So, the observation of the width and line shape from the carbon-dioxide spectrum immediately raises two questions.

One what are the possible functional forms of these shapes and number 2 what physical processes are responsible for these shapes.

(Refer Slide Time: 10:25)



Line Broadening - Classification

✓ (1) homogeneous

(2) inhomogeneous

$[M] = 0.1\ M$

$$\underbrace{\text{For 1000 ml of sample, concentration} = 1M}_{N_{av} \approx 10^{23}}$$

$$\frac{10^{23}}{10 \times 1000} = 10^{19} \text{ molecules}$$

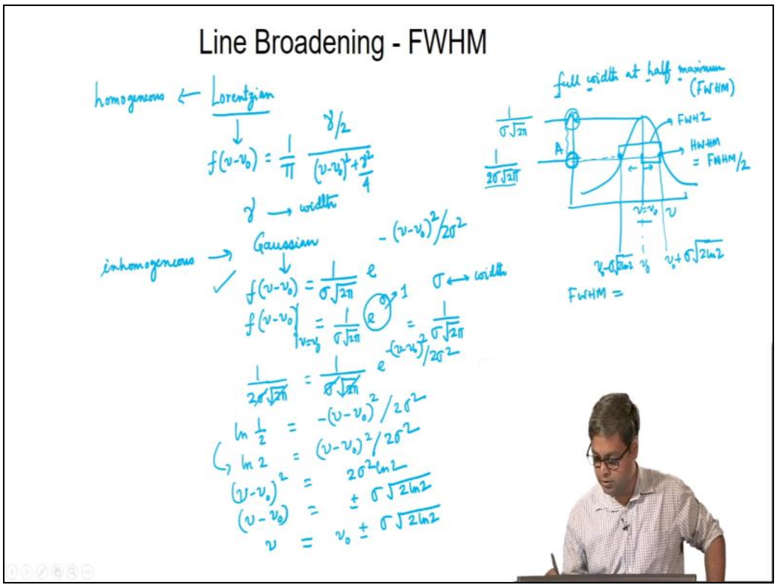
Line shape functions fall into 1 of the 2 general categories one is homogeneous and the second is in homogeneous. A homogeneous line shape occurs when all the molecules in the system have identical line shape functions. Here we should understand that we have an ensemble of molecules in the sample solution on which we shine light during the spectroscopy experiment. So, let us say we have made a sample solution of concentration equal to 0.1 molar and let us say the volume of the container which is placed in the direction of light so that the light is passed to the container and goes through the detector.

So, the volume of this container is 1 milliliter so we know that for 1000 milliliter of sample with concentration equal to 1 molar we have a Avogadro number of molecules which is approximately equal to 10 to the power 23 molecules. But now in our solution we have a volume of 1 milliliter and a concentration of 0.1 molar so the number of molecules we have during the experiment is 10 to the power 23 divided by 10 times 1000 equals 10 to the power 19 molecules.

Thus if all the molecules are affected the same way all our homogeneously affected during the light matter interaction they will have the same line shapes and we will have homogeneous broadening or homogeneous line shape function. For example if the absorbing species in the gas phase is subjected to high pressure then all the molecules are found to have an identical pressure broadened line shape for a particular transition pressure broadening of a transition is thus say to be a homogeneous broadening.

In contrast if the sample is dissolved in a liquid solvent then this order inherent in the structure of the liquid provides different solvent environments for the solute. As each solute experiences a slightly different environment they have a slightly different spectrum. The observed absorption spectrum from the experiment is made up of all the different spectra for the different molecular environments and it is said to be in homogeneously broadened.

(Refer Slide Time: 13:49)



Line Broadening - FWHM

homogeneous ← Lorentzian

$$f(\nu-\nu_0) = \frac{1}{\pi}\frac{\gamma/2}{(\nu-\nu_0)^2+\frac{\gamma^2}{4}}$$

$\gamma \rightarrow$ width

inhomogeneous → Gaussian ✓

$$f(\nu-\nu_0) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(\nu-\nu_0)^2/2\sigma^2}$$

$\sigma \longleftrightarrow$ width

$$f(\nu-\nu_0)\Big|_{\nu=\nu_0} = \frac{1}{\sigma\sqrt{2\pi}}\, e^{0} = \frac{1}{\sigma\sqrt{2\pi}}$$

$$\frac{1}{2\sigma\sqrt{2\pi}} = \frac{1}{\sigma\sqrt{2\pi}} e^{-(\nu-\nu_0)^2/2\sigma^2}$$

$$\ln\frac{1}{2} = -(\nu-\nu_0)^2/2\sigma^2$$

$$\ln 2 = (\nu-\nu_0)^2/2\sigma^2$$

$$(\nu-\nu_0)^2 = 2\sigma^2\ln 2$$

$$(\nu-\nu_0) = \pm\sigma\sqrt{2\ln 2}$$

$$\nu = \nu_0 \pm \sigma\sqrt{2\ln 2}$$

full width at half maximum (FWHM)

FWHM =

In general the homogeneously broadened spectrum can be represented by a Lorentzian. So, the Lorentzian line shape function represents homogeneously broadened spectrum. The Lorentzian line shape function is given by f nu - nu 0 equals 1 by pi gamma by 2 nu - nu 0 squared + gamma squared by 4 so here gamma is the parameter specifying the width of the spectrum. The inhomogeneously broaden spectrum is given by a Gaussian line shape function.

And the Gaussian line shape function can be written as f nu - nu 0 equals 1 by Sigma root over 2 pi E to the power - nu - nu 0 squared by 2 Sigma squared, here Sigma is related to the width of the spectrum. So, we can quantify width of the observed spectrum in terms of full width at half maximum. This is also written as FWHM from the initial alphabets of full width at half maximum. So, let us try to understand how to obtain full width half maximum or F W H M from a spectrum.

So let us say we have an absorption spectrum so we are plotting absorbance versus frequency. So, first thing we have to find out what is the absorbance at nu equals nu 0 because at nu 0 the absorbance is maximum. Once we find the maximum value of absorbance we have to find what is half of that maximum value and once we find that half of the maximum value of absorbance we have to find the values of the frequency that corresponds to half of the values of the absorbance.

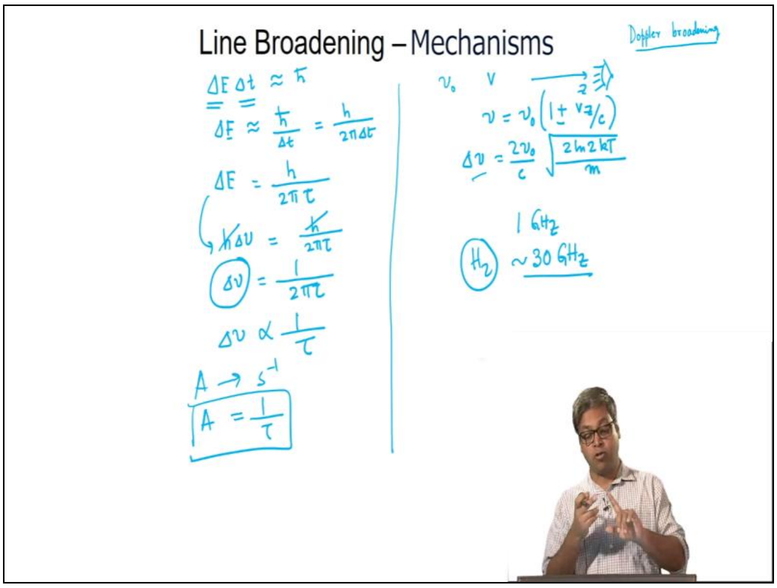
So because we are considering a spectrum which is symmetric about nu 0, so we will have two such frequencies one on the left and one on the right of your 0. So, now the frequency difference between these two points is the full width half maximum. Now instead of taking this frequency difference if we take the frequency difference between nu 0 and one of these frequencies which has half the maximum absorbance then that is given by half width at half maximum and because the spectrum is symmetric half width at half maximum equals full width at half maximum by 2.

So, if the functional form of the line shape is known we can find the functional form of the full width at half maximum. So, let us look into the Gaussian functional form. So, we have to evaluate this function at nu equals nu 0 so at nu equals nu 0 f nu - nu 0 becomes 1 by Sigma root over 2 pi E to the power 0 because E to the power 0 is 1 so this is 1 by Sigma root over 2 pi. So, now that means the maximum absorbance is 1 by Sigma root over 2 pi.

So, the absorbance at half the maximum absorbance value is 1 by 2 Sigma root over 2 pi. So, now we have to find the frequency at which the absorbance is 1 by 2 Sigma root over 2 pi, so we can write 1 by 2 Sigma root over 2 pi equals 1 by Sigma root over 2 pi E to the power - nu - nu 0 squared by 2 Sigma squared. So, we will cancel out this so we have or we can write ln half equals - nu - nu 0 squared by 2 Sigma squared.

So, we can also write from this equation ln 2 equals nu - nu 0 square by 2 Sigma squared or nu – nu 0 squared equals to Sigma squared ln 2 or nu - nu 0 equals + - Sigma root over 2 ln 2. So, now we needed to find nu, so nu equals nu 0 + - Sigma root over 2 ln 2. So what does it mean so I have nu 0 so this frequency is nu 0 + Sigma 2 ln 2 and this is nu 0 - Sigma 2 ln 2 so the full width half maximum equals to Sigma root over 2 ln 2.

(Refer Slide Time: 20:50)



Line Broadening – Mechanisms

Doppler broadening

$\Delta E \Delta t \approx \hbar$

$\Delta E \approx \frac{\hbar}{\Delta t} = \frac{h}{2\pi \Delta t}$

$\Delta E = \frac{h}{2\pi\tau}$

$\cancel{h}\Delta\nu = \frac{\cancel{h}}{2\pi\tau}$

$\Delta\nu = \frac{1}{2\pi\tau}$

$\Delta\nu \propto \frac{1}{\tau}$

$A \rightarrow s^{-1}$

$\boxed{A = \frac{1}{\tau}}$

$\nu_0 \quad v \quad \xrightarrow{z}$

$\nu = \nu_0\left(1 \pm v_z/c\right)$

$\Delta\nu = \frac{2\nu_0}{c}\sqrt{\frac{2\ln 2\, kT}{m}}$

1 GHz

H_2 ~30 GHz

So, now let us look into the physical processes that lead to broadening of the spectrum one of them is due to quantum mechanical effects this arises from the Heisenberg's uncertainty principle between energy and time which is given by Delta E delta T is of the order of h cross, so Delta E is the uncertainty in energy and delta T is the uncertainty in time. The expression tells us that if the system survives in a quantum state for a finite time the energy of the state in principle cannot be known with accuracy better than Delta E which is given by h cross by delta T or h by 2 pi delta T.

Now let us think about spontaneous emission when we excite a molecule to a higher energy state Einstein hypothesized that the molecule will spontaneously decay from the higher energy state. If the molecule on average say decays after time tau so tau is the time the molecule survives in the excited state then tau is known as a lifetime and we can write delta E equals h by 2 pi tau and for Delta E we can write h Delta nu equals h by 2 pi tau can cancel out h so Delta nu equals 1 by 2 pi tau.

So here Delta nu is the uncertainty in frequency which gives rise to a broadening of the spectrum along the frequency axis. Thus the spectral broadening or delta nu is inversely proportional to the lifetime if the life time is short the spectrum will be broad and vice versa we have discussed that a is Einsteins coefficient for spontaneous emission. The unit of A is second inverse that is inverse of the unit of time.

It can be shown that E is equal to 1 by lifetime or 1 by tau. Moreover lifetime can be affected by interactions between the quantum state and the surrounding particles that is collisions. In the condensed phase the occurrence of collisions are greater than that in the gas phase. As these collisions are inelastic in nature they reduce the lifetime of the excited state. A similar case happens when pressure is increased increase in pressure increases the number of collisions and thus reduces the lifetime.

In all these cases the spectral line shape is Lorentian and thus these factors lead to homogeneous broadening. One of the most common examples of gas phase inhomogeneous broadening occurs due to Maxwell Boltzmann distribution of molecular velocities and is called Doppler broadening. When viewed from the frame of the atom the Doppler effect results in light energy shift or shift in the frequency of light when the source is moving either toward or away from the observer.

When a source emitting radiation with frequency nu 0 moves with a velocity V and the observer is placed in the Z direction that is the detector in is in the Z direction then the observer detects the radiation with a frequency not equal to nu 0 but nu which is equal to nu 0 1 + - Vz divided by c but this plus and minus sign is related to an approaching or receding source. It can be shown that the full width half maximum Delta nu equals 2 nu 0 by c root over 2 ln 2 k T where T is the temperature divided by M.

So we see that Delta nu or full width half maximum of the Doppler broadening has an expression similar to what we had obtained for a Gaussian line shape. Thus Doppler broadening is inhomogeneous broadening and gives rise to a Gaussian line shape. We can see that the Doppler width is proportional to the square root of temperature and inversely proportional to the square root of mass. For example the Doppler width is 1 gigahertz for a UV visible transition at room temperature.

However for hydrogen the mass is small and the Doppler width is approximately much bigger that is approximately 30 gigahertz. So, finally I would like to end by mentioning that all these processes the Doppler effect the collisions the quantum mechanical effect that is lifetime happens simultaneously and thus the spectral line shape is never perfectly Gaussian or Lorentzian but is a convolution of Gaussian and Lorentzian line shape function and is given by the void function or the profile of the spectrum is known as for it profile.