Fundamentals of Spectroscopy

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Lecture – 11
Spectroscopic Timescales

Hello everyone welcome to this lecture in the previous lectures we have talked about the rates of transitions. The rates tell us there is a timescale associated to these transitions the time scales depend on the frequencies of the photons. As an outcome of the time dependent perturbation Theory calculation, the perturbation time is related to the energy difference between the two levels or the perturbation time depends on Delta E.

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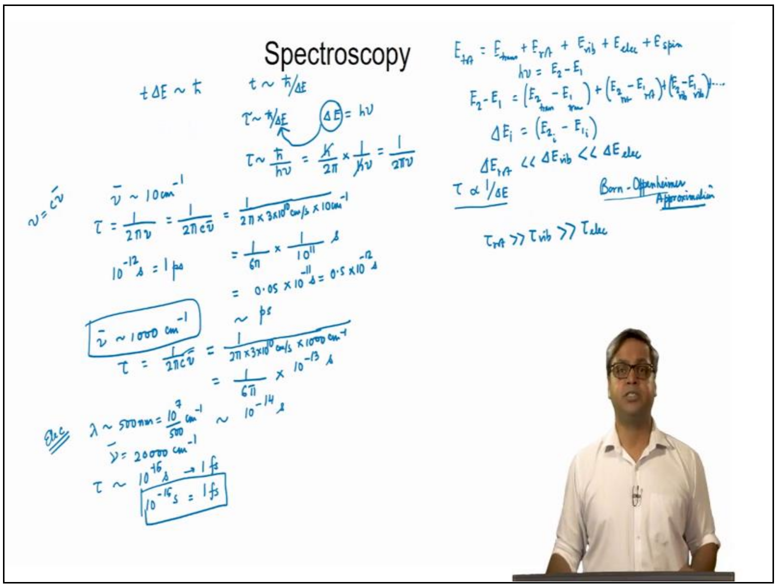

Spectroscopy

$t\Delta E \sim \hbar$

$t \sim \hbar/\Delta E$

$\tau \sim \hbar/\Delta E \qquad \boxed{\Delta E} = h\nu$

$\tau \sim \frac{\hbar}{h\nu} = \frac{\cancel{h}}{2\pi} \times \frac{1}{\cancel{h}\nu} = \frac{1}{2\pi\nu}$

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

$\bar{\nu} \sim 10\,\text{cm}^{-1}$

$\tau = \frac{1}{2\pi\nu} = \frac{1}{2\pi c\bar{\nu}} = \frac{1}{2\pi \times 3\times10^{10}\,\text{cm/s} \times 10\,\text{cm}^{-1}}$

$10^{-12}\,s = 1\,ps \qquad = \frac{1}{6\pi} \times \frac{1}{10^{11}}\,s$

$= 0.05 \times 10^{-11}\,s = 0.5 \times 10^{-12}\,s$

$\sim ps$

$\boxed{\bar{\nu} \sim 1000\,\text{cm}^{-1}}$

$\tau = \frac{1}{2\pi c\bar{\nu}} = \frac{1}{2\pi \times 3\times10^{10}\,\text{cm/s} \times 1000\,\text{cm}^{-1}}$

$= \frac{1}{6\pi} \times 10^{-13}\,s$

$\sim 10^{-14}\,s$

Elec

$\lambda \sim 500\,\text{nm} = \frac{10^{7}}{500}\,\text{cm}^{-1}$

$\bar{\nu} = 20000\,\text{cm}^{-1}$

$\tau \sim 10^{-16}\,s \rightarrow 1\,fs$

$\boxed{10^{-15}\,s = 1\,fs}$

$E_{tot} = E_{trans} + E_{rot} + E_{vib} + E_{elec} + E_{spin}$

$h\nu = E_2 - E_1$

$E_2 - E_1 = (E_{2_{trans}} - E_{1_{trans}}) + (E_{2_{rot}} - E_{1_{rot}}) + (E_{2_{vib}} - E_{1_{vib}}) \ldots$

$\Delta E_i = (E_{2_i} - E_{1_i})$

$\Delta E_{rot} << \Delta E_{vib} << \Delta E_{elec}$

$\tau \propto 1/\Delta E$

Born-Oppenheimer Approximation

$\tau_{rot} >> \tau_{vib} >> \tau_{elec}$

So, if the perturbation time is t we can write t times Delta E is in the order of h cross or the perturbation time we can write is in the order of h cross by delta E as the spectral transition happens during this perturbation time the value of t or the perturbation time is thus a characteristic of a particular transition. The spectroscopy provides the definition of a time scale for a particular transition. So, the time scale tau is of the order of the time of transition.

So, we can write tau is of the order of h cross by delta E from Bohr condition we get Delta E equals h nu so if you put this Delta E value in this expression what we find is tau is of the order of h cross by h nu that is h by 2 pi times 1 by each nu, so we cancel age we have 1 by 2 pi nu, so this tells us that transition from one stationary state of the matter to another stationary state happens within the time taken for a complete oscillation of the light wave.

So a frequency of oscillation of light that is nu is less the time scale will be more or if the frequency of oscillation of light is more the time scale will be less. For example the rotational frequency is smaller than the vibrational frequency. We can show the rotational timescale or time taken for a rotational transition is larger than the vibrational time scale or time taken for a vibrational transition. So, for a rotational transition nu bar is of the order of 10 wave numbers.

So we know that the time scale tau is given by 1 by 2 pi nu and because nu equals C nu bar we can write 1 by 2 pi c nu bar. so now let us put in the values that is 1 by 2 pi times 3 times 10 to the power 10 centimeter per second times 10 wave numbers. So, what we get is 1 by 6 pi times 1 by 10 to the power 11 second, so that is 0.05 times 10 to the power -11 second, so we can write 0.5 times 10 to the power -12 seconds and because 10 to the power minus 12 seconds equals 1 Pico seconds.

So, we can write the time scale is in the order of Pico seconds. So, now if we look into a vibrational transition the new bar is in the order of 1000 wave numbers or in other words the new bar is 100 times larger for a vibrational transition than the new bar for a rotational transition. So, for vibrational transition the time scale equals 1 by 2 pi c nu bar and we can write 1 by 2 pi times 3 times 10 to the power 10 centimeter per second times 1000 centimeter inverse so this will be 1 by 6 pi times 10 to the power -13 seconds.

So, this will be in the order of 10 to the power -14 seconds so we see that the wave number for a vibrational transition is 100 times more compared to the wave number for a rotational transition. And if we look into the time scale the time scale for a vibrational transition is 100 times faster than a rotational transition. So, now let us look into an electronic transition so for the electronic transition we can write lambda let us say lambda is 5 horn nanometre.

So let us convert this nanometer to wave numbers so this is equivalent to 10 to the power 7 by 500 wave numbers, so this is 20,000 wave numbers. So, we see the wave number for electronic transition is 20 times more compared to the wave number for our vibrational transition and if we do the same calculation of time scale we will get the time scale for electronic transition to be the order of 10 to the power -15 seconds that is 1 fem to second.

Because 10 to the power -15 seconds it was one frame per second. So, the total energy of a molecule can be written as E total equals E translational plus E rotational plus E vibrational plus E electronic plus a spin. So, the total energy of a molecule can be written as a sum of different modes of molecular motions this assumes the different modes of motion of a molecule are independent. Thus for absorption of light the Bohr condition as we know can be written as h nu equals E 2 – E 1 where the subscripts 1 and to indicate the initial and the final States respectively.

So considering that we can separate this motions for example rotation vibration electronic etc we can write E 2 - E 1 equals E 2 translational minus E 1 translational plus E 2 rotational minus E 1 rotational plus E 2 vibrational minus E 1 vibrational and so I am so forth for the other terms. So, classification of various spectroscopic transitions by various regions of electromagnetic radiation as we discussed earlier is possible because Delta E i that is given by E 2i - E 1i well I can be rotational vibrational or electronic motion. So, this Delta E i are largely different for the ith mode of motion.

In general we know that Delta E rotational is much less than Delta E vibrational and this is much less than Delta E electronic. So, this means because the time scale is inversely proportional to Delta E this means Tau rotational is greater than greater than tau vibrational which is much larger than tau electronic. Thus when the time scale of a spectroscopic process differs appreciably one can separately treat different modes of motion.

This approximation as we know is known as Born-Oppenheimer approximation this enables want to separate electronic motion from nuclear motion which is very important in electronic structure calculation. Similarly one can separate nuclear motion in two separate modes like vibration rotation and translation it has to be kept in mind that this is an approximation and hence under certain conditions this approximation is not valid.

These cases are described as the breakdown of Born-Oppenheimer approximation but when we discuss a specific form of spectroscopy we just focus on a particular energy level in other words we considered one motion to be independent of other degrees of freedom this means we do not consider any interaction between different modes of motion. For example rotation and vibration are considered as independent modes of motion.

However later when we discussed rotational and vibrational spectroscopy in detail we shall discuss one such case of the breakdown of Born-Oppenheimer approximation we will see that rotation and vibrational modes are only approximately independent. So, this brings us to the end of this particular module where we discussed about the concepts and principles that are common to different kinds of spectroscopy.

We started by asking the question what is spectroscopy then we briefly talked about the history of spectroscopy. We learned about light the dual nature of light that is the wave nature and the particle nature of light. We discussed about the different spectroscopic transitions like absorption spontaneous emission and stimulated emission. We have covered Einstein's coefficients and the relation between them. So, because quantum mechanics is needed to describe matter whose energy levels are quantized you have been introduced to the basic concepts of quantum mechanics.

Then we have talked about transition moment integral and Fermi's golden rule. We saw that the transitions are forbidden if the transition moment integral equals 0 in other words we introduced the concept of selection rules. Then you got a flavour of time-dependent perturbation theory and derived Fermi's golden rule then we compared spectroscopic transitions to chemical reactions and derived Beer-Lambert law that is when you were introduced to the terms absorbance and molar extinction coefficient.

Then we discussed about how an absorption spectrum is actually obtained from a spectroscopic experiment. We then talked about the line shapes of the absorption spectrum the homogeneous and the inhomogeneous line shape functions we learnt about how to obtain FWHM or full width at half maximum and the different functional forms of the line shape functions. We also talked about the different physical processes giving rise to spectral line broadening or line broadening mechanisms.

From there on we discussed about the different forms of spectroscopy based on different regions of the electromagnetic spectrum. Finally today we discussed about time scales for the spectral transitions and how the timescales differ for different spectroscopy. We also talked about approximate separation of the different modes of motion in a molecule that is Born-Oppenheimer approximation.

So in the next modules you will study different forms of spectroscopy like rotational spectroscopy, vibrational spectroscopy etcetera in greater details. You will see that the concepts covered in this first module will appear time and again during our discussions in the later modules. So, finally we will end this module and this lecture by solving a few more problems.

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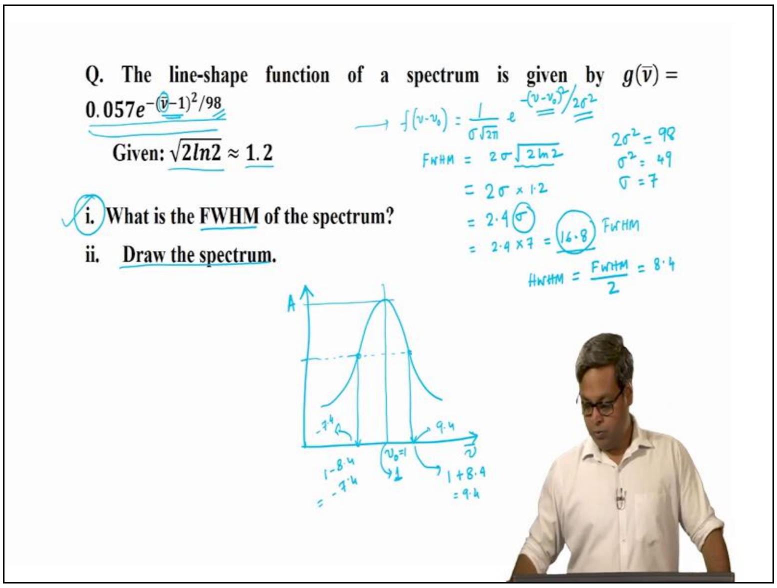

Q. The line-shape function of a spectrum is given by $g(\bar{\nu}) = 0.057e^{-(\bar{\nu}-1)^2/98}$

Given: $\sqrt{2ln2} \approx 1.2$

i. What is the FWHM of the spectrum?

ii. Draw the spectrum.

So, here is the first problem the line shape function of a spectrum is given by this expression and it is also given that root over 2 ln 2 equals approximately equal to 1.2, so the question is number one what is the full width at half maximum of the spectrum and number 2 is draw the spectrum. So, if we look at this expression this reminds us of the expression for the Gaussian lines of function so where we wrote f nu - nu 0 equals 1 by Sigma root over 2 pi E to the power - nu - nu 0 squared divided by 2 Sigma squared.

So, we have to find out the full width at half maximum or FWHM. So, for a Gaussian range of function we have seen FWHM is given by 2 sigma root over 2 ln 2, so the value of 2 ln 2 is given. So, the full width of half maxima will be 2 sigma times 1.2 that is 2.4 sigma. So, now what is the value of Sigma that we have to find out. So, if we compare this expression with the Gaussian line shape function we see 2 sigma squared that is this part is equal to 19.

So, 2 Sigma squared equals 98 so Sigma squared equals 49 or Sigma equal 7, so Sigma can only be positive so the full width at half maximum will be 2.4 times 7 that is 16.8. So, this is the full width half maximum that we have been asked in question number 1, so this is done. So, now draw the spectrum, so if we draw again a spectrum so absorbance is on the y-axis and we are plotting nu bar because you see nu bar is given in the expression nu bar that is wave number on the x-axis.

So let us draw the spectrum, so this is not the answer so we have to find out where is the peak so if we compare here is nu - nu 0, so normally the peak is at new zero but here is given nu bar - 1 so this nu 0 equals 1 here so the value of the peak position or the value of nu bar is 1. So, we know full width half maximum is 16.8 that means half width half maximum is full width half maximum divided by 2 equals 8.4.

So, this is the maximum absorbance, so let us say this is half the maximum absorbance and these are the 2 points corresponding frequencies, so the question is what are this corresponding wave numbers. So, this is 1+ 8.4 that is 9.4, so this is 9.4 and the value here is 1 – 8.4 that is -7.4 that is –7.4. So, you see if we are given an expression you can compare that with one of the lines of functions that you have already studied and from there not only you can find the full width half maximum but you can also draw the spectrum and you know where the peak is you know at what frequency or at what wave number the intensity or the absorbance is half the maximum.

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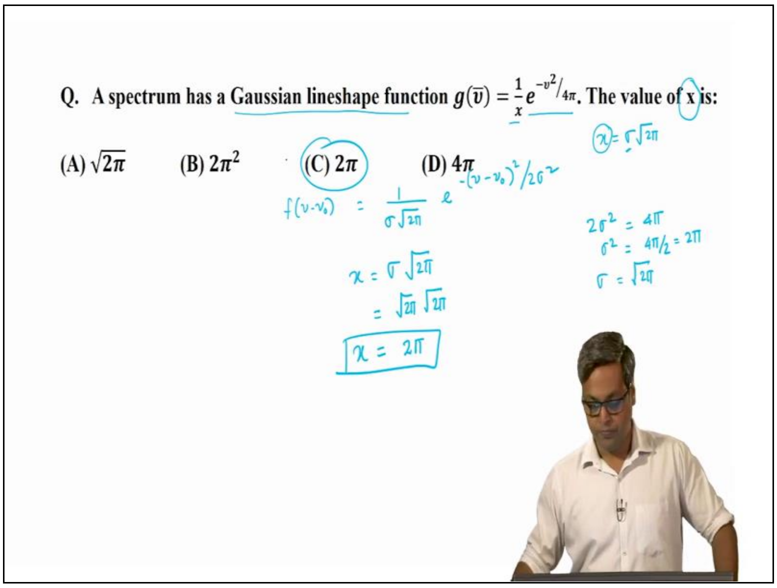

Q. A spectrum has a Gaussian lineshape function $g(\bar{v}) = \frac{1}{x} e^{-v^2/4\pi}$. The value of x is:

(A) $\sqrt{2\pi}$ (B) $2\pi^2$ [✓ (C) 2π] (D) 4π

$x = \sigma\sqrt{2\pi}$

$f(v - v_0) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(v-v_0)^2/2\sigma^2}$

$2\sigma^2 = 4\pi$

$\sigma^2 = 4\pi/2 = 2\pi$

$\sigma = \sqrt{2\pi}$

$x = \sigma\sqrt{2\pi}$

$= \sqrt{2\pi}\sqrt{2\pi}$

$\boxed{x = 2\pi}$

So, let us look into the next problem so in the next problem is a similar expression it has been given here that it is a Gaussian line shape function is given by 1 by x E to the power -nu square by 4 pi so you have been asked to find the value of x there are four choices ABCD so we will actually evaluate the value of x and c2 which answer does our value match so again we write that expression if nu - nu 0 equals 1 by Sigma root over 2 pi E to the power - nu - nu 0 squared by Sigma squared.

So, we can see two sigma squared equals 4 PI so we have to find the value of Sigma because x equals sigma root over 2 pi in other words if we know the value of Sigma then we will be knowing the value of x so 2 Sigma squared equals 2 pi we can write Sigma squared equals 4 PI by 2 equals 2 pi or Sigma equals root over 2 pi so the value of times is Sigma times root over 2 pi or root over 2 pi times root over 2 pi that is root over 2 pi squared that is 2 pi, so x equals 2 pi. So, our answer is c x equals 2 pi.

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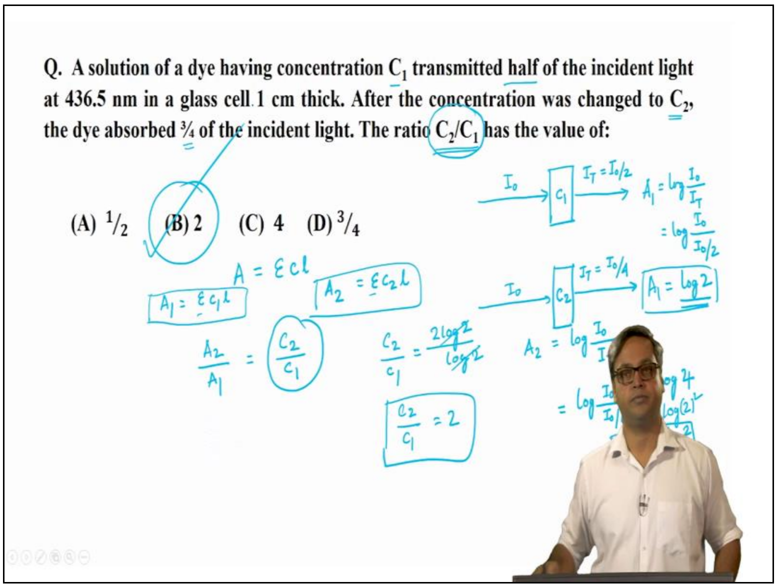

Q. A solution of a dye having concentration C_1 transmitted half of the incident light at 436.5 nm in a glass cell 1 cm thick. After the concentration was changed to C_2, the dye absorbed ¾ of the incident light. The ratio C_2/C_1 has the value of:

(A) $^1/_2$ (B) 2 (C) 4 (D) $^3/_4$

So, now let us look into the last problem a solution of a die having concentration C 1 transmitted half of the incident light at 436.5 nanometer in a glass cell 1 centimeter thick after the concentration was changed C2 the dye absorbed 3/4 of the incident light. So, you have been asked to calculate the ratio of C 2 by C 1 this is also a multiple-choice question. So let us figure out how we will find out the ratio C 2 by C 1.

So we have a sample and we have light a 0 falling on the sample and the transmitted light is half of I 0 because it says transmitted half of the incident right so I T equals I 0 by 2. So, in this case let us say because the concentration is one let us say the absorbance we denote by A 1 is for this first case is log as I 0 by I T equals log I 0 by I 0 by 2 it is log 2. We will just keep in this one will not simplify any further let us look into the second condition.

Now so in the first case the concentration was C 1 now the concentration has been changed to C 2 so I 0 falls on the solution and 3/4 of the incident light has been absorbed but what we care about here is not what has been absorbed but what is I T that is how much of the light is transmitted. So, if 3/4 of the light is absorbed then 1/4 of the light is transmitted. so I T equals I 0 by 4 in this case. So, I can write A 2 for the second case equals log I 0 by I T that is equals lock eyes 0 right eye is 0 by 4 that is log 4.

S o we know 4 equals 2 squared so I can write log 4 equals log 2 squared that means 2 log 2. So, in one case the absorbance is 2 log 2 and in the other case the absorbance is talked to. So, we know that absorbance equals epsilon C l from Vlr but law so we have two cases here. So, in one case we can write A 1 equals epsilon C 1 l and in the second case I can read A 2 equals epsilon C 2N see the path length remains the same during the experiment both the experiments.

And the epsilon does not change because we have the same sample but just we have changed the concentration. So, from these two equations we can write A 2 by A 1 equals C 2 by C 1, so we need to find this C 2 by C 1 so that should be equal to A 2 by A 1, so C 2 by C 1 equals A 2 that is 2 log 2 divided by A 1 that is log 2. So, log 2 log 2 cancels so C 2 by C 1 equals 2. So, this is our answer this message with B so the answer is B.