Quantum Mechanics and Molecular Spectroscopy
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Lecture – 23
Spectral Line Shapes

Hello, welcome to the lecture number 23 of my course quantum mechanics and molecular spectroscopy. In the last lecture class, we were looking at the transition moment integral and its connection with the absorption spectrum. So, let us quickly review that.

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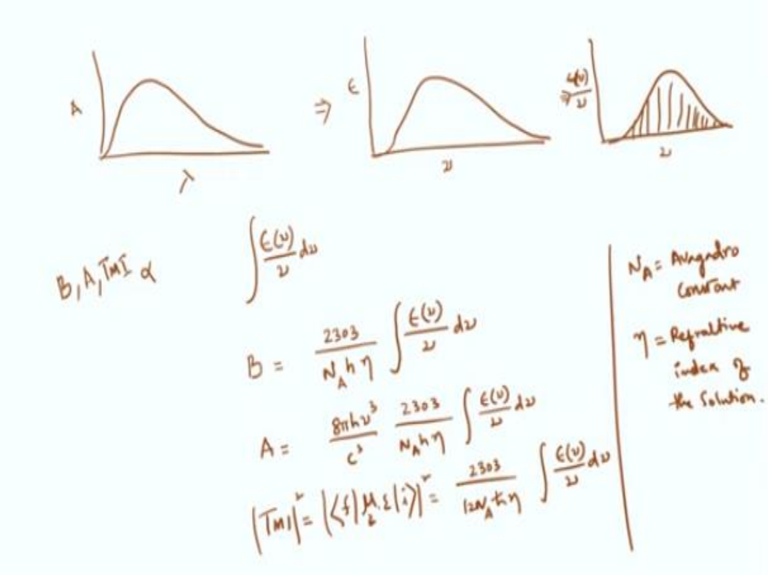

$B, A, |TMI|^2 \propto \int \frac{\epsilon(\nu)}{\nu} d\nu$

$B = \frac{2303}{N_A h \eta} \int \frac{\epsilon(\nu)}{\nu} d\nu$

$A = \frac{8\pi h \nu^3}{c^3} \frac{2303}{N_A h \eta} \int \frac{\epsilon(\nu)}{\nu} d\nu$

$|TMI|^2 = |\langle f | \mu_z \cdot \epsilon | i \rangle|^2 = \frac{2303}{12 N_A \hbar \eta} \int \frac{\epsilon(\nu)}{\nu} d\nu$

N_A = Avogadro constant

η = Refractive index of the Solution.

So if you have an absorption spectrum which you usually record as a function of lambda and you get absorbance A, so something like that. Then this can be transformed as a function of epsilon as a function of nu, so you get some other spectrum, different shape, and this when as epsilon of nu by nu as a function of nu you get another spectrum okay. So, it is the same spectrum that is plotted in a different way.

Then integral epsilon of nu by nu d nu which is nothing but area under this curve okay is proportional to the Einstein’s B coefficients, A coefficients, transition moment integral okay. So, I will write down the exact equation. So B = 2303 divided by NA h eta integral epsilon of nu by nu d nu and A will be equal to 8 pi h nu cube by c cube 2303 by NA h eta epsilon of nu by nu d nu.

And finally, your TMI that is nothing but your transition between the final state mu dot epsilon along z axis i equals to modulus of this square or rather TMI square = 2303 by 12 NA h bar eta integral epsilon of nu by nu d nu okay. Now in this case of course your NA is Avogadro constant and eta is refractive index of this solution okay. One thing that you must remember the refractive index of the solution is not same as refractive index of the solvent.

Of course, if you use very low concentrations, then you can approximate refractive index of the solvent equal to refractive index of the solution okay. So, this is what we looked at in the last lecture.

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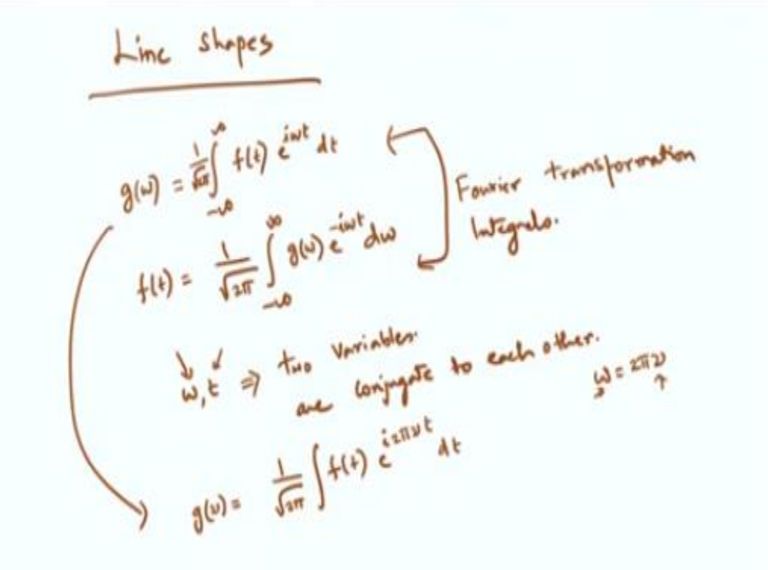

Line shapes

$$g(\omega) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} f(t)\, e^{i\omega t}\, dt$$

$$f(t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} g(\omega)\, e^{-i\omega t}\, d\omega$$

Fourier transformation Integrals.

$\omega, t \Rightarrow$ two variables are conjugate to each other.

$\omega = 2\pi\nu$

$$g(\nu) = \frac{1}{\sqrt{2\pi}}\int f(t)\, e^{i2\pi\nu t}\, dt$$

Now in this lecture, I am going to take a look at what is known as line shapes okay. This is more of a descriptive, we will not derive much anything, but I want to describe the line shapes, but before we go into line shapes I want you to understand one thing. So for example if you have a function okay g of omega and this is given by integral minus infinity to plus infinity 1 over root 2 pi f of t e to the power of i omega t dt.

If you have an integral and another integral where f of t = 1 over root 2 pi minus infinity to plus infinity g of omega e to the power of -i omega t d omega. Now if you have two such integrals, these are called Fourier transforms, Fourier transformation integrals. Now you can see the two variables that I am using omega and t these are the two variables and these two variables you can see are inverse with respect to or conjugate to each other, two variables are conjugate to each other okay.

That means whatever is there in time and its inverse is frequency, so time and frequency are conjugate with respect to each other okay. Now one can also write this slightly in different way. So g of nu = 1 over 2 pi f of t e to the power of i, now you know omega is equal to 2 pi nu, so 2 pi nu t dt, so all I am saying is that I am trying to you know instead of using the angular frequency I could use a linear frequency okay.

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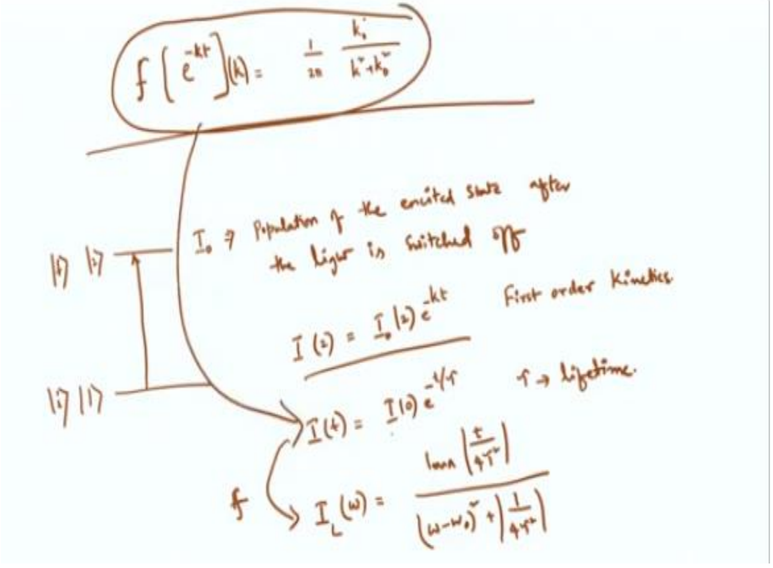

Now it turns out that if you have an exponential function okay, now let us just think of it this way okay, if you have an exponential function e to the power of -kt okay. If you have function e to the power of -kt and this e to the power of kt if you take a Fourier transform of it, Fourier transform of this function okay, then it turns out that this function will be nothing but in variable k 1 over 2 pi k0 divided by k square + k0 square okay.

Now why am I talking about this, I will come to that. Now let us suppose you have an excited state and a ground state, so I can call it as 1 or i and this as 2 and this as f okay. Now excite, go here and the population so what you had is initially you had some population okay, let us say call it as I0 that is the population of the excited state after the light is switched off okay. Once you switch off the light what will happen? It will decay.

So your I of the state 2 will be equal to I0 of state 2 okay e to the power of -kt okay. Now k is here again exponential decay okay. So, this is nothing but your first order kinetics okay or one could really write it as I of t = I0 or I of 0 into e to the power of -t by tau and where we call tau as the lifetime okay. In such scenario, what you will see that I Lorentzian of omega will be equal to.

Now we have to understand one thing is that when you have an exponentially decaying function you can get a Lorentzian function as a Fourier transform okay. Now if you get Fourier transform, then what you get is Imax of t by 4 tau square divided by omega – omega 0 square + 1 over 4 tau square modulus okay. Now this is not very difficult, you can use this formula and plug it in here and then you will be able to get this.

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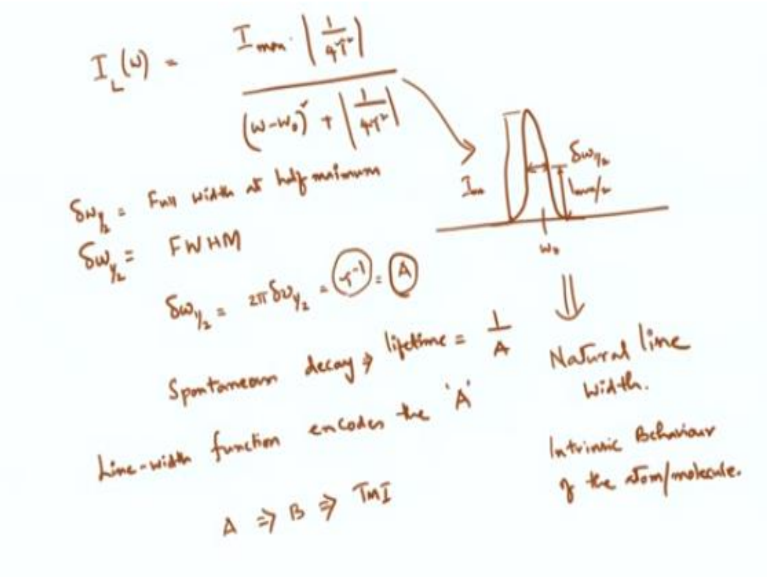

$$I_L(\omega) = \frac{I_{max}\cdot\left|\frac{1}{4\tau^2}\right|}{(\omega-\omega_0)^2 + \left|\frac{1}{4\tau^2}\right|}$$

$\delta\omega_{1/2}$ = Full width at half maximum

$\delta\omega_{1/2}$ = FWHM

$$\delta\omega_{1/2} = 2\pi\delta\nu_{1/2} = \boxed{\tau^{-1}} = \boxed{A}$$

Spontaneous decay ⇒ lifetime $= \frac{1}{A}$

Line-width function encodes the 'A'

A ⇒ B ⇒ TMI

Natural line width.

Intrinsic Behaviour of the atom/molecule.

Now let us look at this little more carefully. When I say that my I Lorentzian of omega equals to I max into multiplied by 1 by 4 tau square divided by omega – omega 0 square + 1 by 4 tau square modulus okay. Now when I plot this function, it will look something like this. So this is my omega0 okay, so this will be like this and this width is called delta omega half, so this is called half because if the total height is Imax and this height is Imax by 2.

So delta omega half is nothing but full width at half max, also known as FWHM, delta omega half okay and it turns out this value will be nothing but delta omega half will be equal to 2 pi delta nu half, this is nothing but tau inverse, this is nothing but A okay. We know that for a spontaneous decay process, the lifetime is nothing but inverse of the, for spontaneous lifetime equals to 1 over A.

You can go back and check in one of the earlier lectures okay. So, just by estimating this, we can get the value of A. So the line width function encodes the A. What is A? Your Einstein coefficient A, but we know once we know A, from A we know how to get B, and from B we also know how to get TMI. So, just by measuring the line width, one can get the lifetime and the Einstein's coefficient A okay.

So it is rather easier to understand that one can measure all the quantities or estimate the quantities like transition moment integral, Einstein's coefficient A, Einstein’s coefficient B just by measuring the spectra, either in the time domain or in the frequency domain. Of course, in the time domain I can measure tau, from there I can get A, from there I can get the line width or the full width at half max okay. All these quantities are interrelated.

Of course, there is one problem in measuring these quantities directly, one thing that these are called what is known as natural line width okay. That means this function we should be able to fit it to a Lorentzian. If it is a not a Lorentzian, then we would not be able to extract these parameters okay. So, this will only happen if it is a natural line width. That means the spectrum is not getting influenced by any other external factors but is a pure spectrum of the molecule itself.

So, this is what I will call as intrinsic behavior and when do we get? If you can somehow isolate an atom or a molecule from the external influence of other molecules of its kind or from the solvent, only then you will be able to understand this or under the approximation that the solvent has very little role to play okay. However, in the presence of solvents or any other molecules or the molecules of the same kind, this approximation can break down quite easily.

So, in such scenario when you do not get Lorentzian line shapes, all these quantities cannot be extracted okay. Now in general, one finds that there are other effects like temperature and because of the temperature there are molecular speeds okay which are given by Maxwell-Boltzmann distribution in the gas phase, in the solution they are given by the path length or mean free path.

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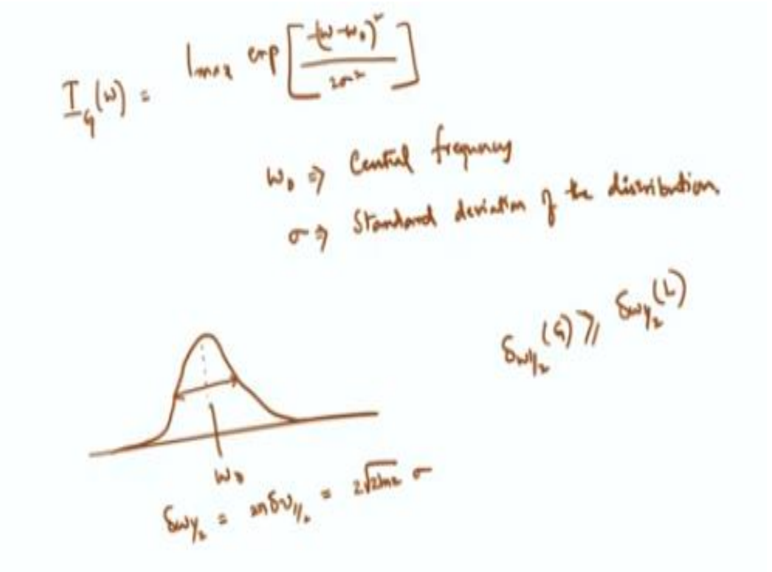

$$I_G(\omega) = I_{max} \exp\left[\frac{-(\omega-\omega_0)^2}{2\sigma^2}\right]$$

$\omega_0 \Rightarrow$ Central frequency

$\sigma \Rightarrow$ Standard deviation of the distribution

$\delta\omega_{1/2}(G) \geq \delta\omega_{1/2}(L)$

ω_0

$\delta\omega_{1/2} = 2\pi\delta\nu_{1/2} = 2\sqrt{2\ln 2}\,\sigma$

So in such scenario, the line shape is given by a Gaussian function IG of omega = I max into exponential – omega – omega 0 whole square divided by 2 sigma square okay. Now in such scenario, your omega 0 is the central frequency and sigma is the standard deviation of the distribution. So, for example you could have, so this is your omega 0 you could have a Gaussian distribution which looks like this.

And this is your omega 0 okay and you have value of sigma that you can calculate, in such scenario delta omega half is equal to nothing but 2 pi delta omega nu this is given by 2 lon 2 into sigma okay that is your FWHM in this case will be there and you will see that all of these will always be more than. So let us say delta omega half of a Gaussian distribution will always be greater than delta omega half of the Lorentzian distribution because that is a natural line width.

So Lorentzian is a natural line width and Gaussian distribution comes because of external influences and when external influences come in then the peak width increases okay. So always natural line width is the most narrowest line width that is why it is called natural line width and you cannot go below that. In fact it is actually controlled by the uncertainty principle okay, you cannot go below that.

But generally you never reach that value, you always have line widths which are wider than the natural line width that is because the atom or a molecule in question is always getting influenced by the external parameters, could be temperature, could be influence of the next molecule, intermolecular interactions or the solvent effect okay, any of this such external parameter.

So, it could be greater or greater than or the worst-case scenario it should be greater than or equal to. So, the natural line width is the narrowest line width any transition will have okay.

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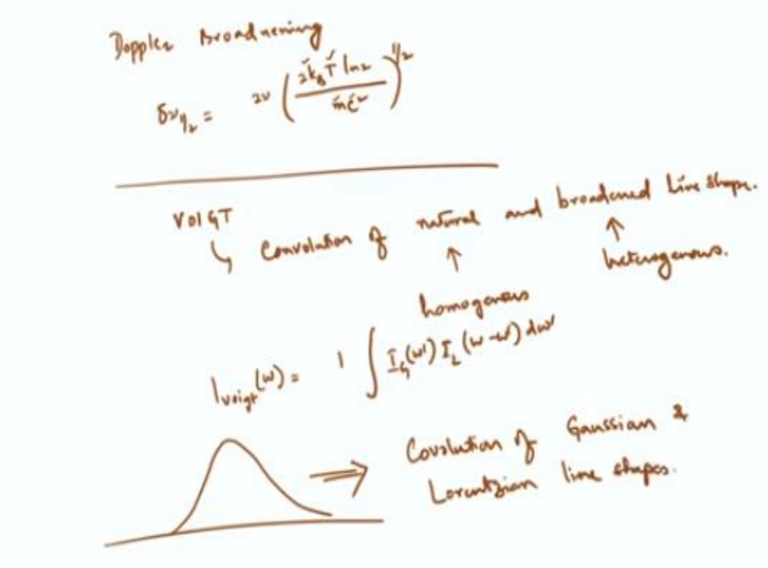

Doppler Broadnening

$$\delta\nu_{1/2} = 2\nu\left(\frac{2k_BT\ln 2}{mc^2}\right)^{1/2}$$

VOIGT

↳ Convolution of natural and broadened line shape.

natural ↑ homogeneous

broadened ↑ heterogeneous.

$$I_{voigt}(\omega) = 1\int I_G(\omega')I_L(\omega-\omega')\,d\omega'$$

⟹ Covolution of Gaussian & Lorentzian line shapes.

Now sometimes in the gas phase what you have a doppler broadening because you know atoms and molecules are moving around. When you have doppler broadening, then you have delta nu half is given by 2 nu into 2 kBT ln 2 divided by mc square to the power of half and of course you can clearly realize it will depend on the temperature, it will depend on the mass and it will depend on the speed of light okay.

So, this is the temperature dependent because you know temperature will affect the molecular speeds. So the doppler broadening will depend on the temperature okay. Now there is something called Voigt profile. Now this Voigt profile is basically a convolution of natural and broadened line shapes. It turns out this natural line is also called homogeneous and this is heterogeneous. Homogeneous because it is intrinsic to the molecule.

Heterogeneous because it is getting influenced by the external parameters. When you have a combination I Voigt of omega is given by I integral of IG omega prime Il omega – omega prime d omega prime okay, so it is a convolution okay. So, essentially the entire line shape, so if you have some shape something like that, then it is a convolution. That means the product function of the Lorentzian line shape and the Gaussian line shape and that is called a Voigt profile.

Unfortunately, when you do not have Lorentzian line profile, you will not be able to get information about the transition moment integral or A or B. So only when you have homogeneous line widths can the experimentally measurable quantities be equated to or experiment measurable quantities can be connected to the theoretically evaluated quantities such as transition dipole, Einstein A coefficient and Einstein B coefficients.

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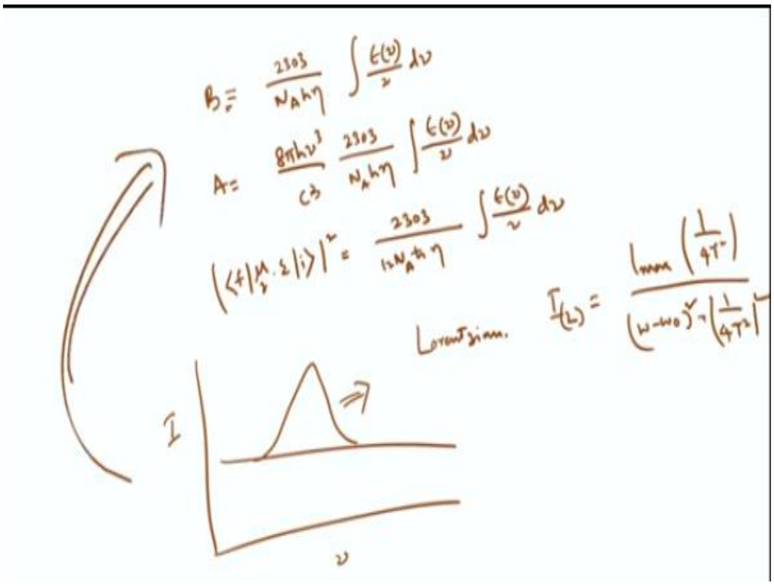

Therefore when I write such equations by NA h eta integral epsilon of nu by nu d nu or A = 8 pi h nu cube by c cube 2303 divided by NA h eta integral epsilon of nu by nu d nu and f mu z epsilon i modular square equals to 2303 divided by 12 NA h bar eta epsilon nu by nu d nu. When you write all these quantities and you have a band okay, this is nu versus intensity and this band must be Lorentzian.

So that means IL = Imax 1 by 4 T square divided by omega – omega 0 whole square + 1 by 4 T square. So only if you have this shape, all this will be right, otherwise not. So, we can only evaluate or only connect the theoretically valid quantities such as Einstein coefficient A, Einstein coefficient B, transition moment integral, etc. to the experimentally absorbed spectra only if you have a Lorentzian line shape, otherwise we cannot okay. We will stop here and take it up in the next lecture. Thank you.