Concepts of chemistry for engineering
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Lecture 45
Electronic Spectroscopy -II

We have learnt about electronic energy states. And we know how knowing the electron configuration including the spin states, we can talk about electronic energy states. And we are now going to talk about the transitions between these states, we are already familiar with n pi star and pi-pi star transitions.

And we had closed the discussion in the previous module saying that not all transitions are going to take place, some transitions are more probable some transitions are less probable, according to that the intensity of transition is defined. In that connection, we are going to study Lambert Beer’s law.

And then we will talk about different kinds of spectra that one could get, depending on the bond length of the ground and excited electronic states. And then we will talk about some other kinds of transitions. But before that, let us have a look at an actual spectrum reported in scientific literature.

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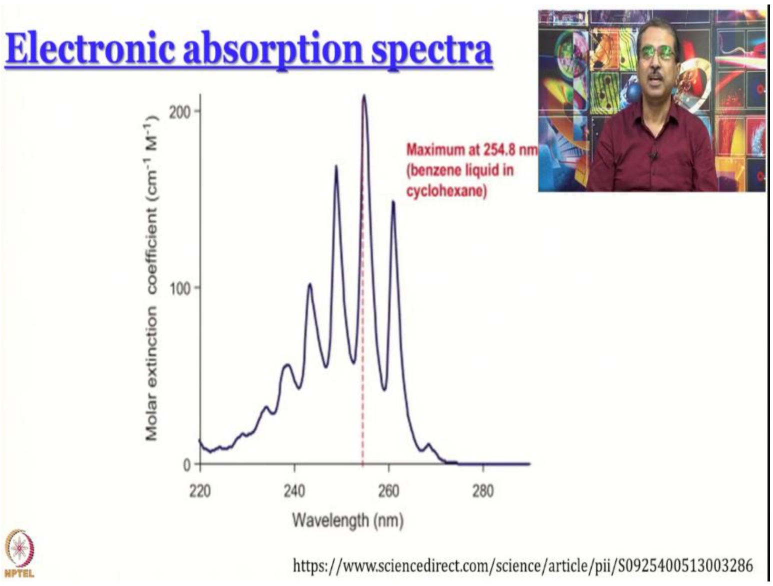

Electronic absorption spectra

Maximum at 254.8 nm (benzene liquid in cyclohexane)

https://www.sciencedirect.com/science/article/pii/S0925400513003286

This here is an absorption spectrum of benzene dissolved in cyclohexane. An aromatic compound dissolved in a non-aromatic organic solvent. So, since it is benzene, you might as well understand that this transitions that you see they are pi-pi star transition, because benzene does not have a nitrogen atom or oxygen atom or any such thing.

So, two things to note here are first of all, what is the y axis what is the x axis, x axis here is wavelength, x axis in a spectrum has to be something that is related to energy, it is conventional to use wavelength, because most of the measurements in the ultraviolet visible region is performed by using dispersive gratings or spectrometer detector kind of combinations.

And dispersive gratings work on the principle of as we know Bragg's Diffraction Law. So, there the diffraction is defined in terms of wavelength, but it is not very difficult to convert from wavelength to energy. When we do that, we have to do some correction called Jacobian correction to this but that is a different story altogether. The second thing is what is the y axis, three things that we have to discuss.

The y axis is molar extinction coefficient in $cm^{-1}M^{-1}$, we are going to learn about this. The third aspect is look at the spectrum, the spectrum is highly structured, why is the spectrum highly structured and are all spectra highly structured? By the time we are done today, we will know the answer to these questions.

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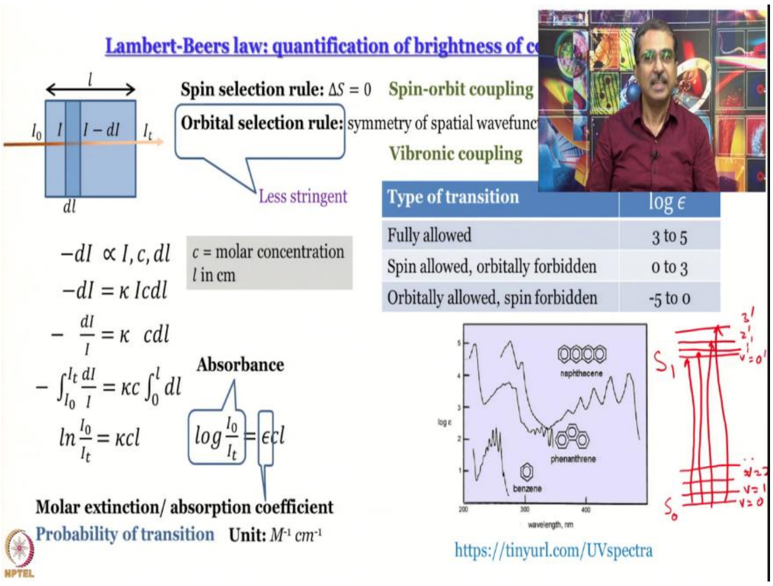

Lambert-Beers law: quantification of brightness of c

Spin selection rule: $\Delta S = 0$ Spin-orbit coupling

Orbital selection rule: symmetry of spatial wavefunc

Vibronic coupling

Less stringent

$-dI \propto I, c, dl$

$-dI = \kappa\, I c dl$

$-\frac{dI}{I} = \kappa\ \ c dl$

$-\int_{I_0}^{I_t} \frac{dI}{I} = \kappa c \int_0^l dl$

$ln \frac{I_0}{I_t} = \kappa c l$

c = molar concentration
l in cm

Absorbance

$log \frac{I_0}{I_t} = \epsilon c l$

Molar extinction/ absorption coefficient

Probability of transition Unit: $M^{-1}\ cm^{-1}$

Type of transition	log ϵ
Fully allowed	3 to 5
Spin allowed, orbitally forbidden	0 to 3
Orbitally allowed, spin forbidden	-5 to 0

https://tinyurl.com/UVspectra

But first, let us remember what we learnt in the last module. There are selection rules, spin selection rule, which is more stringent requires that there cannot be any transition between a singlet and triplet state and orbital selection rule which is less stringent is based on symmetry or spatial wave functions.

Spin selection rule can break down because of spin orbit coupling. orbital selection rule can break down by vibronic coupling. So, all those bands that you saw a little while ago, they are vibronic bands, they involve not only electronic levels, but also vibration level, we will come to that. But first before that, since, we are talking about transitions that are more probable and that are less probable, we need some means by which we should be experimentally able to determine which transition is more probable which transition is less probable.

And experimental parameter that tells us about the probability of transition and this is obtained in the form of Lambert- Beer's law. If you remember the y axis of the spectrum that we just saw, that is what it is, well Lambert and Beer's independently proposed something and then you combine them to get the law.

Let us say this rectangle is a sample, the length of the sample along the direction of propagation of light is L, intensity of light impinging on the sample is I_0, and intensity of light transmitted from the sample is I_t. So, what happens as the shading of the arrow also shows is that as light gets absorbed by the molecules that are there in the sample, it loses intensity, some of the light is absorbed, so it does not go out. So, intensity would decrease or an extinction to some extent would take place.

So, to find out the relationship between I_0 and I_t, what Lambert and Beer separately did was, they considered a thickness dl in the sample, in the direction of propagation of light and the intensity of light impinging on this small element, let us say that is I and intensity of light that emerges from this element let us say that is I-dI. That means, this narrow strip has caused a decrease in intensity by an amount dI.

So, Lambert and Beer, two scientists figure out that this (- dI) is proportional to three things; the intensity of light that impinges on that element, concentration of the sample, so how many molecules the light would have to pass through, and dl the thickness of this element. So, it is the proportionality, can be written very easily in terms of an equation.

But before that, one thing that we should say is that, in this treatment c is always written as molar concentration and l is always written in terms of centimeter, that is what gives us the unit. So, -dI, then is $\kappa.I.c.dl$, where Kappa (κ) is the constant of proportionality, not very difficult to figure out what has to be done dI/I,= $\kappa.c.dl$.

All we have to do now is integrate both sides, left side has to integrated from I_0 to I_t, right side has to be integrated from 0 to l. So, this is what we need to do. And when we do that right side is very simple, integral of dl between limit 0 and l is just l, left hand side is also simple dI/I integrated is going to be natural logarithm of I and the limits are I_0 and I_t anyway.

So, we get ln I_0/ I_t is equal to κcl. And since we are more comfortable working with logarithm to the base 10, it is not difficult to convert ln to log base 10, you just multiply by a constant, you do that you get log I_0/ I_t. Remember this log is base 10 is equal to εcl, this constant Kappa is multiplied by a number. And I will not say explicitly what the number is, I think all students of this course should know what it is, if you do not better check, better remember this value.

So, log I_0/ I_t is equal to εc*l*, c is concentration, *l* is length of the sample. What is there on the left-hand side, log I_0/ I_t that essentially tells us how much of the incident light has been absorbed, this is called absorbance. It is an extrinsic quantity depends on c and *l* also.

And what is epsilon (ε) ? Since, epsilon is multiplied by c and l the parameters that have got to do with how much of sample there is, how much of sample the photons have to pass through, epsilon is an intrinsic quantity, it is something that gives us an idea about how probable the transition is. So, this is called molar extinction coefficient or molar absorption coefficient, I always call it molar extinction coefficient.

But few years ago, I had a student who told me unequivocally that molar extinction coefficient is apparently outdated and I have to call it molar absorption coefficient. I like the term extinction because look at this arrow, it is light is getting extinguished to some extent. But anyway, molar absorption coefficient is the more modern term, both work. So, molar extinction or molar absorption coefficient tells us about probability of transition.

An experimental parameter that tells us how probable the transition is. In fact, with a little bit of theory, one can find a relationship between this experimentally observed quantity and the theoretically calculated probability of transition. This is worked out in many standard textbooks. Barrow is what I studied but then Barrow is out of print. So, you could study this from I think McQuarrie and Simon's book, and maybe even Atkins physical chemistry book.

By the way, I did not mention any textbook so far you can study all this from Atkins by and large. People who are interested in a little more, you can study Banwell’s molecular spectroscopy book, those who are interested in a lot more, I recommend molecular spectroscopy by Jack D. Graybeal. But that book is way beyond the scope of the current course.

Let is come back to this, we have this equation absorbance is equal to εcl. So, if I measure absorbance at different concentrations, then what happens absorbance should increase within a certain range. So, if I plot absorbance against concentration, if I know concentration, then the slope should give me epsilon. It is as simple as that.

Now, high absorbance, what does that mean? High absorbance means that very little light will emerge from the sample, so the sample is nearing opacity. I leave it to you to work out, what is the percentage of light that is transmitted, I_t/ I_0 multiplied by 100 when absorbance is 0.01, 0.1, 1 and 10. Please work this out. And I think you will understand why I would like you to do this.

Absorbance tells us how opaque or how transparent the sample is for that particular wavelength. What are the factors that epsilon depend upon? Definitely depends upon the wavelength. That is why in the spectrum that I showed you the plot was epsilon against wavelength or energy, because some transitions are more probable some transitions are less probable.

And if you remember the unit that was written in the spectrum, the unit was I think they are written in centimeter inverse per molar, I have written M^{-1} cm^{-1}, very easy to work out from this expression, left hand side absorbance has no unit please remember, absorbance has no unit, it is a logarithm of a ratio and there is no way it can have any unit, right hand side c has a unit, l has a unit. So, epsilon also has a unit M^{-1} cm^{-1}. So, this is Lambert Beer's law, epsilon tells us probability of transition.

Now, if we recall the kind of transitions that we know already, there are transitions that are spin forbidden, but allowed a little bit by spin orbit coupling. There are transitions that are maybe spin allowed, but are orbitally forbidden, allowed a little bit by vibronic coupling. So, and there are some transitions that are completely allowed, spin allowed as well as orbitally allowed.

The difference in the probability among these shows up very nicely in the comparative values of the epsilons, the molar absorption coefficients, and this table summarizes it quite nicely. For fully allowed transitions, spin allowed as well as orbitally allowed the molar extinction coefficient in M^{-1} cm^{-1} ranges from 10^3 to 10^5, I have taken log to the base 10 here, that is why it is 3 to 5.

For spin allowed transitions which are orbitally forbidden, they come next in line and epsilon ranges from 10 to the power 0, 1, 2, 3, 4, that kind of thing to 10 to the power 3000, 2000 so on and so forth. For orbitally allowed, but spin forbidden transition. As I said, if you remember, spin selection rule is more stringent. So, if epsilon ranges from 10^{-5} to 10^0 really, really small transitions, less intense transitions.

And I will not discuss this in detail. But this here is a collection of spectra of different aromatic hydrocarbons, benzene, phenanthrene, and naphthacene, I leave it to you to figure out which ones are fully allowed, which ones which of these transitions are spin allowed, which ones of these transitions are orbitally allowed, but what we are going to discuss today in the remaining 10-12 minutes is that why is it that they are all structured.

Even in the benzene spectrum that I showed you earlier. If you remember, they are all structured. So, why is it that they are structured? Why are the spectra structured? They are structured because see, we were talking about this, this is let us say the ground state S_0. And this is let us say S_1, the excited state, the electronic levels, but electronic levels are associated with vibrational sub levels.

And these levels are characterized by vibrational quantum numbers that range from 0, 1, 2 so on and so forth. And even S_1 they are characterized by vibrational levels. It is conventional to denote those quantum numbers by $v^/$ equal to, I will write $0^/$, $1^/$, $2^/$, $3^/$. Now, the difference between vibrational levels is high enough, so only these zeroth vibrational level of S_0 is populated at room temperature.

So, any upward transition has to originate in v equal to 0. But then, for vibronically allowed transitions, it is not as if only the $00^/$ transition will take place, $01^/$, $02^/$, $03^/$, all these transitions can take place with different probabilities. Sorry about my poor artistic skills, please remember that these vertical lines are all straight lines, they are not really the curvy lines that I have drawn.

But the point is for a given vibrational, for a given an electronic energy gap, there can be multiple transitions involving the vibrational sub levels of the higher electronic state and that is what we are going to dwell upon a little bit and that is what gives the structure to this absorption spectrum.

So, you can think that this S_{02}, in which direction is energy increasing from left to right wavelength increases, so energy increases from right to left. So, this one is S_0 to a well, v equal to 0 to $v^/$ equal to $1^/$ transition, this is v equal to 0 to $v^/$ equal to $2^/$, $3^/$, $4^/$ and so on and so forth.

And as you see that these vibronic transitions are not all equally probable. Also, there are two kinds of spectra in for naphthacene, you see the $00^/$ transition seems to be the most intense whereas, for benzene some other transition seems to be most intense, why is that so? That is what we learn in the next 10 minutes also.

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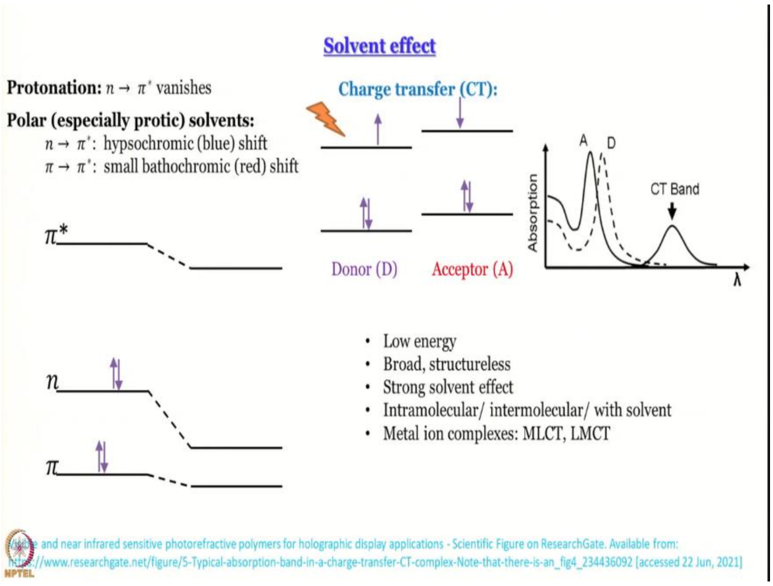

Solvent effect

Protonation: $n \rightarrow \pi^*$ vanishes

Polar (especially protic) solvents:

$n \rightarrow \pi^*$: hypsochromic (blue) shift

$\pi \rightarrow \pi^*$: small bathochromic (red) shift

Charge transfer (CT):

- Low energy
- Broad, structureless
- Strong solvent effect
- Intramolecular/ intermolecular/ with solvent
- Metal ion complexes: MLCT, LMCT

Visible and near infrared sensitive photorefractive polymers for holographic display applications - Scientific Figure on ResearchGate. Available from: https://www.researchgate.net/figure/5-Typical-absorption-band-in-a-charge-transfer-CT-complex-Note-that-there-is-an_fig4_234436092 [accessed 22 Jun, 2021]

But before that, one more thing that we want to talk about is solvent effect and how do you know which transition is what. First of all, we have discussed already that n pi star transitions are less probable. Because they are orbitally forbidden. So, if in a molecule you have a less probable transition in a little lower energy region, then you can think that it is n pi star transition compared to pi-pi star transitions which are expected to be stronger and in higher energy smaller wavelength region.

What happens if I add acid, where acid the lone pairs would get engaged with the proton. So, n pi star transition would gradually vanish, if you add enough acid, it will decrease with increasing acid amount, finally, it would vanish. For polar solvents n pi star transitions show blue shift or hypsochromic shift that means, they shift to higher energies, blue and red are relative terms.

pi-pi star transitions show very small bathochromic or red shift, why is that so, because, when you have these polar solvents, the energy levels get stabilized to different extents, the pi level gets stabilized to some extent, n level gets stabilized to a much greater extent, because in nonbonding orbitals, you have these electron pairs that are more strongly directed. So, it is easier for solvent to lower their energies.

pi star also gets stabilized to an extent that is greater than that of pi, because it is more delocalized but not as much as that of n, all these stabilizations they are not to scale, they are grossly over emphasized. So, what would I get in a polar solvent? Let us say left hand side, this is a situation in nonpolar solvent, right hand side situation is in a polar solvent, this n pi star gap is more than the n pi star stare gap in nonpolar solvent.

That is why in n pi star transition shows hypsochromic or blue shift, whereas pi-pi star transition can show a little small bathochromic shift because pi star is stabilized to a greater extent than pi. Another kind of transitions that take place very often are charge transfer transitions. What is that? Suppose you have a donor and acceptor, something that likes to donate electron something that likes to accept electron.

Let us say you have an organic molecule, some kind of a coumarin and let us say you have aniline, aniline is a good donor. And coumarin is a good electron acceptor. So, when they are close together, of course, they have to be in close proximity. So, we will see how they are brought in close proximity, then if to shine with the right amount of light, light wavelength of light, then there can be a transition from the donor to the acceptor.

So, these transitions always occur in low energies, because they take place only when the energy gap is not very large. They are broad and structureless. Why are they broad and structureless? Well, see this donor acceptor energy levels have two different systems relate to each other, they can have a big spread, that is why they are broad and they are structureless because this is unbound states.

So, there is no really vibration that holds them together, except for some very loose vibration involving the donor and acceptor moieties. So, they are broad and structureless. They show strong solvent effects, because there is a charge transfer charge separation. So, naturally when you have a polar solvent, it is going to stabilize charge transfer stage to a very large extent. And now, how do you get the donor and acceptor together?

One easy way of doing it is that if the solvent itself is either donor or acceptor, then the solute is surrounded by the donor or acceptor or whatever it might be, then you can have charge transfer with the solvent. Otherwise, if both solutes are involved in a charge transfer, then their concentration would better be very large, otherwise it does not happen. The third option is a donor and an acceptor that are bonded together that is when charge transfer can happen very easily.

In metal ion complexes, the charge transfer often involves the ligand as well as the metal depending on the direction of charge transfer, it is called metal to ligand charge transfer or ligand to metal charge transfer about which you might study a little more in your discussion of inorganic chemistry. But before leaving this slide, this here is a schematic representation of the absorption spectra.

Let us say this is the absorption spectrum of acceptor, this is the absorption spectrum of donor. Charge transfer band would appear only when donor and acceptor are present together in sufficiently high concentration or covalently bonded together. As you see, it appears at longer wavelength that is smaller energy. It is broad and it is structureless. These are the characteristics of charge transfer bands. So, we stop here and in the next module, we will talk about this time not structureless but structured absorption.