Fundamentals of Spectroscopy

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Lecture – 60
Electronic Spectroscopy - 4

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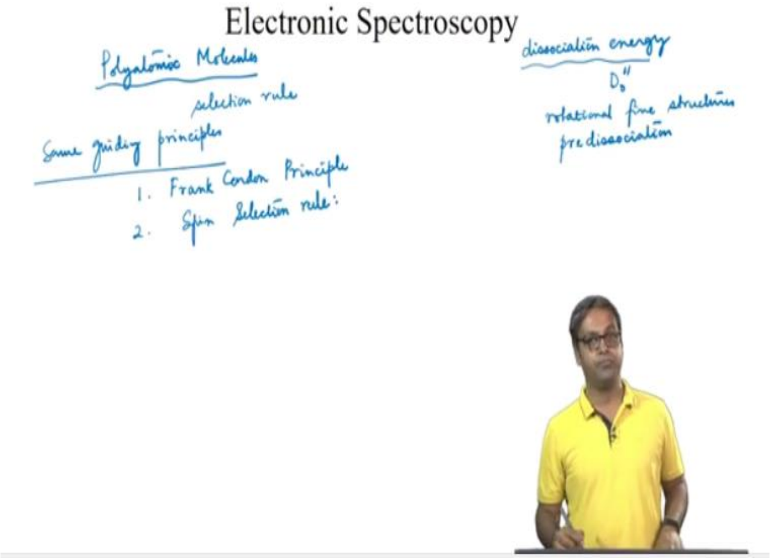

Electronic Spectroscopy

Polyatomic Molecules

selection rule

Same guiding principles

1. Frank Condon Principle
2. Spin Selection rule:

dissociation energy

D_0''

rotational fine structures

predissociation

Hello all; welcome to the lecture, in the last lecture we discussed dissociation energy and how to estimate the dissociation energy of the ground state that is D0 double prime, we also briefly looked into the rotational fine structures and we also talked about something known as pre-dissociation. So, in today's lecture we will discuss polyatomic molecules, so first of all it is difficult to derive the selection rules for polyatomic molecules.

But we should remember that the same guiding principles that we have seen in case of diatomic molecules should work for polyatomic molecules, so the same guiding principles should work which include for example, Franck–Condon principle and for example, the spin selection rule.

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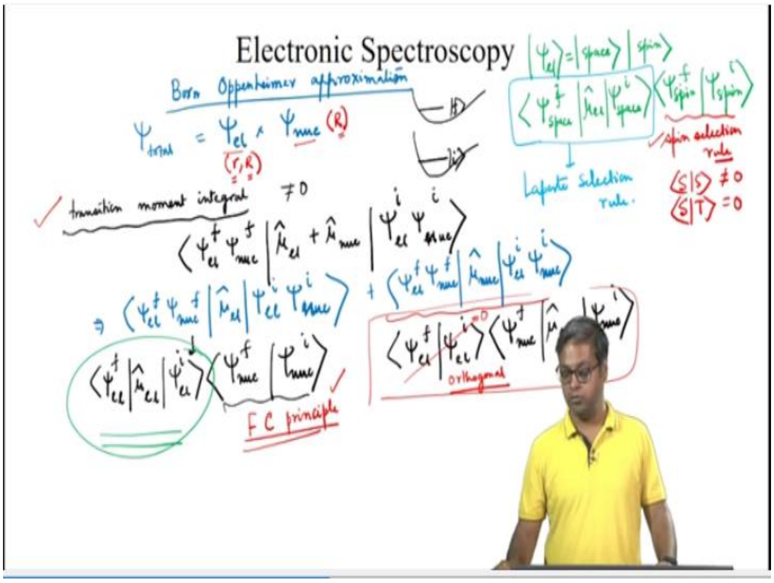

Electronic Spectroscopy

Born Oppenheimer approximation

$\Psi_{total} = \Psi_{el}(r,R) \times \Psi_{nuc}(R)$

transition moment integral $\neq 0$

$\langle \Psi_{el}^{f} \Psi_{nuc}^{f} | \hat{\mu}_{el} + \hat{\mu}_{nuc} | \Psi_{el}^{i} \Psi_{nuc}^{i} \rangle$

$\Rightarrow \langle \Psi_{el}^{f} \Psi_{nuc}^{f} | \hat{\mu}_{el} | \Psi_{el}^{i} \Psi_{nuc}^{i} \rangle + \langle \Psi_{el}^{f} \Psi_{nuc}^{f} | \hat{\mu}_{nuc} | \Psi_{el}^{i} \Psi_{nuc}^{i} \rangle$

$\langle \Psi_{el}^{f} | \hat{\mu}_{el} | \Psi_{el}^{i} \rangle \underbrace{\langle \Psi_{nuc}^{f} | \Psi_{nuc}^{i} \rangle}_{\text{F C principle}}$

$\langle \Psi_{el}^{f} | \Psi_{el}^{i} \rangle \langle \Psi_{nuc}^{f} | \hat{\mu} | \Psi_{nuc}^{i} \rangle$ $= 0$ orthogonal

$|\Psi_{el}\rangle = |space\rangle |spin\rangle$

$\langle \Psi_{space}^{f} | \hat{\mu}_{el} | \Psi_{space}^{i} \rangle \langle \Psi_{spin}^{f} | \Psi_{spin}^{i} \rangle$

Laporte selection rule.

spin selection rule

$\langle S|S\rangle \neq 0$

$\langle S|T\rangle = 0$

So, let us now revisit the Born-Oppenheimer approximation, so due to the Born-Oppenheimer approximation, the total wave function which is written as psi total can be written as the product of the electronic wave function that is psi electronic times the nuclear wave function that is psi nuclear and so I will write the psi electronics as r, R and psi nuclear as R. So, the nuclear wave function that is psi nuclear depends on the nuclear coordinates that is R.

And depends on both the vibrational and electronic quantum numbers of states, the electronic wave function that is psi electronic is a function of both nuclear that is R and electronic coordinates that is represented by r but only depends on the electronic quantum number or electronic states. So, now in order to understand the selection rule, let us look into the transition moment integral.

So, we have discussed this transition moment integral or how to obtain the selection rule from transition moment integral before in this course, so the transitions will be allowed as long as this integral is not equal to 0, so this transition moment integral for this case can be written as; so we have an initial state and we have a final state, so this is for one electronic level, this is for a different electronic level.

So, we can write psi electronic f for the final state, psi nuclear that is f for the final state then we have the dipole moment operator mu electronic plus mu nuclear, then psi electronic for the initial state, psi electronic or psi nuclear for the initial state. So, this is our transition moment integral, so because we can immediately see that we can split it into 2 terms, we can write this as psi electronic f psi nuclear f times mu electronic psi electronics i psi electronic or psi nuclear i, so this is my first term.

And the second term we can write as psi electronic f psi nuclear f, then mu nuclear then psi electronic i and psi nuclear for the initial state, so we have split this transition moment integral into 2 terms. Now, if we focus into the second term; so the second term here we can write this as this psi electronic final psi electronic initial and then we have this integral that is psi nuclear final mu nuclear psi nuclear initial.

So, this second term can be written this way and in this, this part is 0 and this is because 2 different electronic states are orthogonal and because they are orthogonal that becomes 0 and if this is 0, this entire part becomes 0. So, now let us look into the first term; so the first term can be written as from here, we can write psi electronic mu electronic, this is final then psi electronic initial times psi nuclear final psi nuclear initial.

So, the second part here gives rise to what we know as Franck Condon principle that means we are talking about the overlapping integral between the initial vibrational state of that electronic state and the final vibration of state of the final electronic state. So, now let us concentrate on this other part that means this part. So, the electronic wave function can be written as a product of the spatial part that means, psi el can be written as a product of the spatial part and that of the spin part.

So, I can write this, I will write this as psi space i then mu electronic psi space this is f, this is i psi spin f psi spin i, so we can write this because the transition dipole or the dipole moment operator is independent of the spin, so the spin part in this expression gives rise to what we know as spin selection rule. In other words, this SS is not equal to 0 but ST equals 0, so this reminds of the spin selection rule that is a singlet to singlet transition is allowed.

Whereas, a singlet to triplet transition is forbidden, so we see that we started from the Born-Oppenheimer approximation and then we looked into the transition moment integral and by dissecting this transition moment integral using the Born-Oppenheimer approximation, we reach the Franck-Condon principle and we reach the spin selection rule, so these are the 2 selection rules.

So, now we are actually left with this part, so this part of the expression gives rise to what is known as the Laporte selection rule. So, this selection rule holds for centro symmetric molecules.

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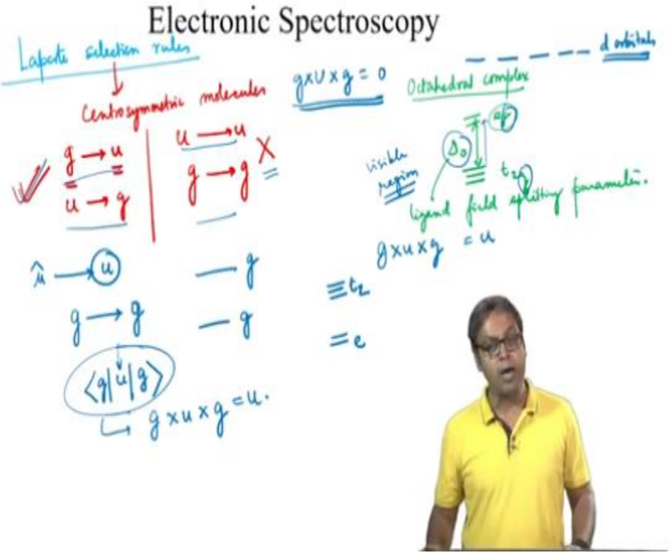
Electronic Spectroscopy

So, let us say we are talking about Laporte selection rules and this selection rule holds for centro symmetric molecules, so this selection rule states that the only allowed transitions are the transitions that are accompanied via change in parity, so that means some g to u, so we talked about this gerade and ungerade in one of the lectures on electronic spectroscopy, so this g to u or u to g transitions are allowed.

On the other hand, so these are allowed transitions, on the other hand u to u or g to g transitions are forbidden, so we should remember this dipole moment operator, if we look into the Cartesian coordinates of mu that means the x y and z components, so this x, y and z components of the dipole moment operator transforms like u or we can say this dipole moment operator transforms like u.

So, therefore if we have a g to g transition that means, the initial state is g, the final state is g, then the transition moment integral becomes something like g, u, g, so this means g times u times g and that is u, so the integral vanishes until this integrand is invariant under all symmetry operations. So, this integrand has to be g that means, if we do not think about this dipole moment operator, the other part should be u.

That is the reason this g to u or u to g is allowed and u to u and g to g is forbidden, so we can say that ug and or gug equals 0, so the integral is 0, so that is why it is forbidden. So, let us look into the consequence of this Laporte selection. So, we know in a free atom all 5 d orbitals are degenerate, so all the 5 d orbitals are degenerate. So, in a free atom they are degenerate but in a d metal complex where the immediate environment of the atom is longer spherical, the d orbitals are no longer degenerate.

For example, if we think about an octahedral complex, then this degenerate d orbitals will split into 2 sets; one is the triply degenerate orbitals known as t2g and the doubly degenerate orbitals known as eg, so this 3 t2g degenerate orbitals lie below this 2 eg orbitals and the difference in energy, this is denoted by delta 0 which is the ligand field splitting parameter.

So, this delta 0 is not large, so transitions between these 2 sets of triply degenerate and doubly degenerate orbitals typically occurred in the visible region of the spectrum for however, we can see for a d to d transition in an octahedral complex is like going from a, g to a g that means, we have g times u times g that is u and this is forbidden, so this can become allowed or weakly allowed as vibronic transitions, as a result of coupling to asymmetrical vibrations occur.

So, as it is not allowed or it is just weakly allowed, so due to this the octahedral complexes and less intensely coloured on the other hand, if you think about a tetrahedral complex; the tetrahedral complex has no center of symmetry and because it is not central symmetric, we do not have this Laporte selection rule. So, the tetrahedral complex splits into e and t2 where t2 lies above this e.

And because it is not centro symmetric we do not write eg or t2g but we write e and t2, so now the transitions become allowed and hence they are more intensely coloured than octahedral complexes. So, complex may absorb radiation as a result of transfer of electron from the ligand into the d orbitals of the central atom or the central metal ion or it can happen the other way around that is vice versa.

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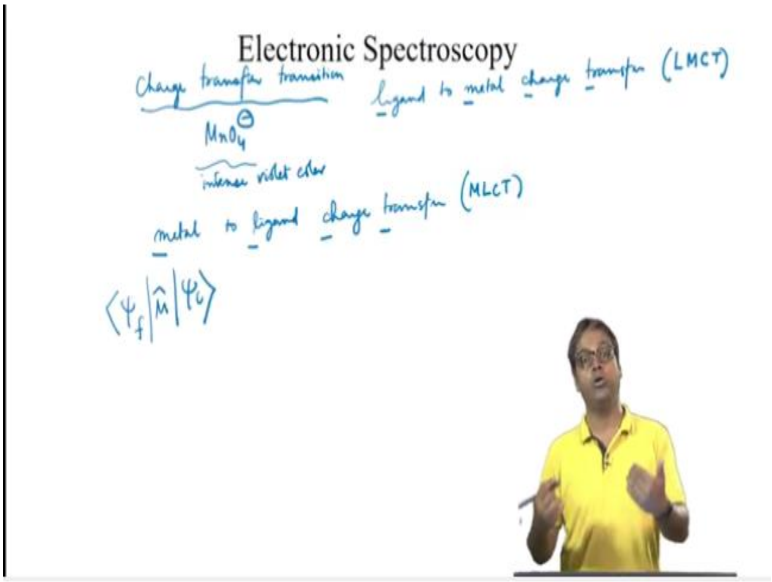

Electronic Spectroscopy

Charge transfer transition

ligand to metal charge transfer (LMCT)

$MnO_4^{\ominus}$

intense violet colour

metal to ligand charge transfer (MLCT)

$\langle \psi_f | \hat{\mu} | \psi_i \rangle$

And this is known as charge transfer transition, so in charge transfer transitions, the electrons move through a considerable distance and because the electrons move through a considerable distance this means the transition dipole moment may be large and because the transition dipole moment is large, the absorption is intense and this mode of chromophore activity is shown by, let us say for this permanganate anion that is MnO4 minus.

And accounts for this intense violet colour, so here or in permanganate, the electrons migrate from an orbital that is largely confined to the oxygen atom ligands to an orbital that is largely confined to the manganese atom, so this is an example of ligand to metal charge transfer. So, ligand to metal charge transfer which is represented by LMCT, so the reverse migration that is from a metal to the ligand is also possible.

So, in that case we will have a metal to ligand charge transfer, so it is known as MLCT, an example of this MLCT is the transfer of a d electron from the metal into the anti-bonding pi orbitals of an aromatic ligand. So, the intensities of this charge transfer transitions are proportional to the square of the transition dipole moment as we know that means, the usual way.

The transition moment can be thought of as a measure of the distance moved by the electron as it migrates from the ligand to the metal or from the metal to the ligand, so large distance of migration then corresponds to a large transition moment and because we have a large transition moment that means, a high intensity of absorption, however because this integrand is proportional to the initial and the final wave functions.

So, this transition moment integral we can write psi f dipole moment operator psi i, so this is proportional to the initial and the final wave functions, so this is 0 unless these 2 wave functions have nonzero values in the same region of space, so although this large distances of migration might favour high intensities, the diminished overlap of the initial and the final wave functions arising due to these large separations of metal and ligands favours low intensities.

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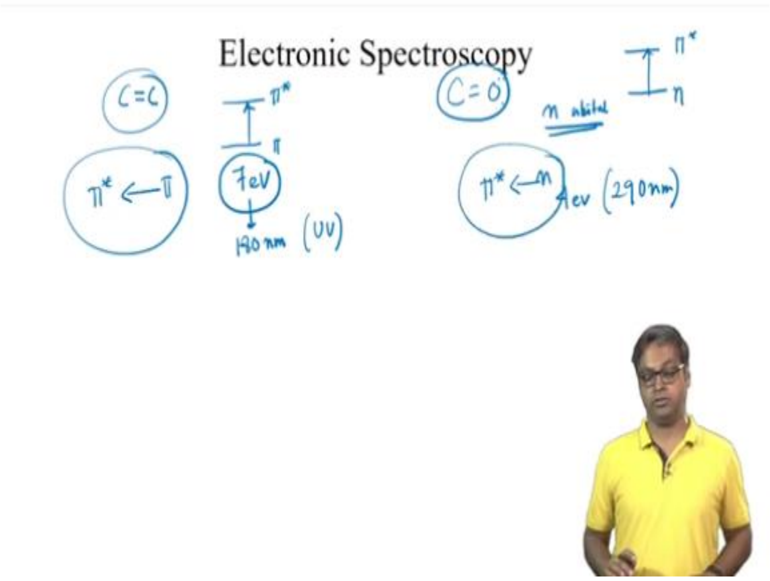

Electronic Spectroscopy

So, absorption by a CC double bond results in the excitation of the pi electron into the anti-bonding pi star orbital, so pi to pi star, so this chromophore activity is due to pi to pi star transition and the energy for this pi to pi star transition is around 7 electron volt for an unconjugated double bond and from this energy of 7 electron volt, if we do the back calculation, this corresponds to an absorption at 180 nanometer.

So that means in the ultraviolet region of this electromagnetic spectrum, so when the double bond is not unconjugated but is a part of a conjugated chain, the energy of the molecular orbitals like closer together and the transition moves to a longer wavelength, so it may even fall in the visible region because it is now traveling a longer wavelength, in case of this conjugated system is long enough.

So, on the other hand instead of this C double bond C, if you think about the C double bond O that is the carbonyl, so the transition responsible for the absorption in carbonyl compounds can be traced to the lone pair of electron on the oxygen atom and this electron pair is represented in molecular orbital theory to be the n orbital which is largely confined to 1 atom for example, in this case is the oxygen atom and not appreciably involved in the bonding.

So, upon excitation so one of these electrons gives rise to something known as n to pi star transition because the electron from the n orbital now goes to the pi star orbital, so we have this n to pi star transition and the typical energy is about 4 electron volt that is around 290 nanometer and because these transitions in carbonyls are symmetry forbidden, so this n pi star absorptions are weak.

So, we have talked about the different types of absorptions in polyatomic molecules, so we talked about the DD transitions in octahedral and tetrahedral complexes, we talked about the charge transfer transitions like MLCT or LMCT and finally, we talked about the pi to pi star and n to pi star transitions. So, this brings us to the end of this lecture and in the next lecture, we will discuss further about conjugated molecules and we will also discuss about the fate of the electronically excited molecule.