Interpretative Spectroscopy

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Lecture 60

Summary and conclusion

Hello everyone, I once again welcome you all to my last lecture in this series of interpretative spectroscopy. Today let me summarize and conclude about whatever we discussed about various spectroscopic aspects, problems, conditions, definitions and all those things in the last 59 lectures. So, this course is all about spectral interpretation and elucidation of the structure of known or unknown samples to understand about spectroscopic methods and their potential in chemistry and other science subjects.

General process for structural elucidation of an unknown sample, we have several avenues here. Of course, before that we have to ensure that we have a pure compound. Even by physical measurements such as melting point, boiling point we should be able to tell whether the compound is pure or not and first of all our objective is to make the compounds in their purest form and then the purity can be assessed and also the identity can be found out from the spectral interpretation by taking various spectra to ascertain the purity and the nature of the molecule.

We should always go for more than one type of spectroscopic or analytical means. When we have pure compound, we have several options as I mentioned CHN analysis is there, elemental analysis, mass spectrometry, NMR and they give you some idea about molecular formula. Before that once we know from mass fragment molecular ion peak, from that one using rule 13 and also hydrogen deficiency index we should be able to identify tentative formula and then we can identify functional groups using these methods and also substructures again using NMR and eventually x-ray if it is a solid compound. Molecular formula can also give you about saturation, unsaturation and also other groups extra and then we arrive at possible structures. We have to write all possible isomers, if there are any, and again go to the mercy of NMR, mass and IR to identify fragments and also different

positions of the chemical shifts and also stretching frequencies, we can write most possible structures and we can confirm it.

We use different type of radiations of electromagnetic waves in different instruments. All these are given here and of course corresponding energy in frequency is also given and also temperature of bodies emitting wavelength is also given here. It is a very useful electromagnetic spectrum. For example, the radio waves, microwaves, infrared, visible ultraviolet, x-rays and gamma rays. Gamma rays also comes in Mossbauer spectroscopy.

What is important is approximate time scale for structure determination with various techniques. This is very important because most of the molecules will be under dynamic process and also if the time scale does not suit, then we may not be seeing the information we are looking for. Electron diffraction 10 raise to minus 20 (10^{-20}). Whatever the dynamics that happens up to 10 raise to minus 20 (10^{-20}) can be analyzed. X-ray, 10 raise to minus 18(10^{-18}), UV 10 raise to minus 15(10^{-15}), visible 10 raise to minus 14 (10^{-14}) and IR and Raman 10 raise to minus 13 (10^{-13}) and ESR is coming down 10 raise to minus 4 (10^{-4}) to 10 raise to minus 8 (10^{-8}) and NMR 10 raise to minus 1 (10^{-1}) to 10 raise to minus 9 (10^{-9}) and fast kinetics 10 raise to minus 3 (10^{-3}) to 10 to 100 seconds, and for the physical separation, they should be stable for more than 100 seconds. Then by looking at the morphology we should be able to pick and separate the isomers, if they have different morphology or color. This is very important especially in NMR time scale if the dynamics is beyond this scale what happens, in order to see NMR for those, we have to either speed up or slow down the dynamic process. For example: we go for low temperature or high temperature NMR studies and this periodic table shows NMR active nuclei having non-zero nuclear spin and of course this color index is very useful in identifying.

Given in orange all have I equal to 1; red I equal to half, many are there. ^{1}H, ^{13}C, ^{31}P, ^{19}F and all those, even platinum, tungsten. Then 3 by 2 (3/2), we have quite a few 3 by 2 (3/2). Boron there is one 3 by 2 (3/2) and also 3. Then 5 by 2 (5/2), like this is a very useful periodic table with color code for identifying nuclear spin having different values and then nucleus with negative gyromagnetic ratio will have highest energy for the most positive M values this you should remember.

Let us look into the effect of magnetic field on nucleus in a more classical way. Nuclei behave like tiny bar magnets when they are subjected to magnetic field. What happens, some of them will be aligned with the field and some of them will be opposing the magnetic field, nevertheless because this induces a motion, because of this induced motion under magnetic field they will start precessing with respect to the applied magnetic field but they would never align with the magnetic field and they will be at an angle. Move this angle in such a way that, we flip it once, when we flip it what happens we can see nuclear transition. In order to do that one what we do is apply another magnetic field perpendicular to the applied magnetic field with its frequency corresponding to the precision frequency of this nuclei under the influence of the major magnetic field. When the resonance occurs, it will be flipping.

This is all about NMR. You see this is the axis here, this is the direction of applied magnetic field they are never aligned but they will be precessing with respect to that one. You can see that one and then how we can remove. Move this one away from this one increase the angle so that it comes here and it will flip. That means we can say that nuclear transition has occurred. We know that $\Delta s = \pm 1$, here and then the frequency with which they precess about the applied magnetic field is called Larmor frequency. The orientation is not allowed by quantum mechanics that mean aligning with the mag field is not allowed; they can never align with the magnetic field, that means they can always precess with an angle here, precision about Bnaught here and then when it is precessing, we are applying another magnetic field in a direction perpendicular to the applied magnetic field whose frequency should be the frequency of the precessing nucleus. In that case what happens, the flipping happens and then it will flip, means it is basically nuclear transition. We can correlate this one, since omega is angular so 2pinu ($2\pi\nu$). Then you can say nu equal to gamma by 2 pi into B_o($\mathbf{B_o}$).

$\boldsymbol{\omega} = 2\pi\nu$, $\nu = \boldsymbol{\gamma}\mathbf{B_o}/2\pi$

This is a very important equation. Here nu equal to gamma over 2 pi into B naught gamma over 2 pi into B naught ($\nu = \boldsymbol{\gamma}\mathbf{B_o}/2\pi$). gamma gyromagnetic ratio this how it is related and gamma is constant here 2 π is constant. That means ν is directly proportional to the applied

magnetic field that means increase in the magnetic field increases the frequency. In the absence of the magnetic field they have random orientation, the moment you apply magnetic field, they will try to align with the magnetic field are opposing the magnetic field and then you can see very nicely in this cartoon how nicely it is flipping due to the applied frequency in the direction perpendicular to the applied magnetic field. Resonance can be understood and this is constant for each nucleus and therefore hydrogen, it is 26.753 radians per tesla per second. That means here in a 14,092 gauss field a 60 megahertz proton is required to flip a proton.

One major difference between EPR and NMR is: so here magnetic field is kept constant and we are varying radio frequency, whereas in case of EPR microwave radiation is kept constant and magnetic field strength is varied that is the major difference, otherwise more or less they are very similar when it comes to selection rule.

Everything in this table is very important this gives about different nuclei, their spin natural abundance and magnetic ratio and also the corresponding NMR frequency.

To look into the multiplicity of the chemical shifts we use n plus 1 (n+1) rule here for that one we can use this Pascal triangle very readily and Pascal triangles are different for different spin system. This is for I equal to half, whereas this one is for I equal to 1 and also, we have I equal to 3 by 2.

When you are dealing with nuclei of different I values, this shows how a typical AB turn it into A2 system.

- **In the AB case, the middle energy levels are similar to A_2**
- **As these middle levels become closer, it becomes difficult to tell which nucleus has which m_I value.**
- **Similar to A_2 case consider the linear combination of the two wave functions.**
- **Since these new functions are mixtures, it is no longer possible to designate the transitions whether they are due to change in mI or A or B.**

- **As a result, by simply looking into spectrum it is no longer possible to determine the chemical shifts of A and B.**
- **General pattern of the AB spectrum depends on the $\Delta\delta$ of A and B and the corresponding *J* value.**
- **Spectra shown here are for *J* = 10 Hz and a variety of $\Delta\delta$ values.**
- **When $\Delta\delta$ is large relative to J, spectrum appears as a distorted doublets set.**
- **The intensity of the inner lines increases as J/ $\Delta\delta$ increases.**
- **At $\Delta\delta$ = 0, the spectrum is reduced to a single line as in case of A_2 system.**
- **Points to remember**
- In a first order spin system,
- **i) The $\Delta\delta$ must be greater than the *J***
- **ii) All chemically equivalent nuclei must also be magnetically equivalent.**
- **What is the meaning of chemically equivalent and magnetically equivalent**
- **Two or more nuclei are chemically equivalent if they can be interchanged by the operation of some symmetry elements of the molecule**

$\Delta\delta_{AB} = (\delta_1 - \delta_4)(\delta_2 - \delta_3)$ **and** $J = \delta_1 - \delta_2 = \delta_3 - \delta_4$

^{31}P NMR is very useful for studying reactions and reaction mechanism and especially when we are using phosphine in homogeneous catalysis for different type of organic transformations. Phosphorus compounds have very distinct chemical shift range with 100% abundance. Small quantity of sample is good enough and also there is no need to use even deuterated solvents that way in whatever the solvent we are doing we can take the liquid and we can check. We can do continuous reaction, we can do batch reactions and analyze the intermediates through variable temperature or time dependent NMR experiments.

This is a very interesting ^{15}NMR for cyclosporine A. we have 11 different types of nitrogen atoms and this beautiful spectrum was obtained in just one hour because of ^{15}N enriched sample. You imagine this is not enriched, we have a very minute percentage of ^{15}N and rest is ^{14}N and if you want to identify these things in a typical molecule that is not enriched, it would take 10 years to get this kind of spectrum.

This is a beautiful NMR spectrum of ^{199}Hg coupled to fluorine atoms. You see mercury is coupled in a very symmetric way in this centrosymmetric molecule. These two fluorines are coupling first to give a triplet and then these two will split each triplet into triplets and then we have CF_3 groups, six-fluorine are there; they split each line of triplet of triplets into a septet and we get this beautiful spectrum here. This is a triplet of triplets of septets.

This is another interesting molecule where we have one two three four five different types of NMR active nuclei. Just I have shown ^{31}P NMR spectrum here. It shows 48 lines. It is a triplet of doublets of doublets of quartets and this is a beautiful spectrum.

Let us move on to UV visible spectroscopy. This is a very important Beer-Lambert's equation, we are using here. A longer path length through the sample will cause more UV light to be absorbed, the greater the concentration of the sample, the more UV light will be absorbed and UV visible spectrum consists of absorbance A on y-axis and wavelength on the horizontal x-axis.

Different type of electronic transitions are shown here: sigma to sigma star is the highest one and then pi to pi star and then n to pi star. How this energy level would change with by changing the functional groups and also having conjugation and all those things we have already discussed. This we see routinely in alkanes, this we see in carbonyls and this we see in unsaturated compounds (pi to pi star) and this n to sigma star in O, N, S and halogen compounds and n to pi star in carbonyls.

Total angular momentum quantum number J

The total orbital angular momentum of an atom ($L=\Sigma l$), and the total spin angular momentum of an atom ($S=2s+1$) combine to form total angular momentum, a number that is quantized by the number J.

L and *S* do not necessarily have to be pointing in the same direction. Therefore *J* can range from *L*+*S* to |*L*–*S*|.

It is interaction between orbital and spin angular momentum quantum numbers.

Term symbols are very important so as microstates. We use the equation n factorial over r factorial into n minus r factorial $\frac{n!}{r!(n-r)!}$. n is the capacity of the sub shell so for d it is 10 electrons so 10!, for f you have 14 electrons so 14 factorial, P it is 6 factorial.

This is how you can find out the microstates and then in case of electronic spectra electrons may be promoted from one level to another one. That is what exactly happens, During electronic transition, what happens the low energy vibrational and rotational transitions will also occur, but the energy difference between the vibrational and the rotational is too close to be resolved in an electronic spectrum. That results in broadening and hence the bandwidths will be in the order of thousand to three thousand centimeter minus one.

In a free gaseous metal ion, d orbitals degenerate and no d-d transitions are observed. In a complex, degeneracy is lost and splitting into t_{2g} (t_2) and e_g(e) takes place.

Magnitude of Δ_o depends on the nature of the ligands and affects the energy of electronic transitions and hence the frequency of absorption maxima

Extent of splitting is related to the ligand positions in the spectrochemical series

In a free gaseous metal ion d orbitals degenerate and no d-d transitions are observed. In a complex, degeneracy is lost because of splitting and also mixing with the s and p orbitals. As a result, d-d transitions are allowed. Strictly speaking, d-d transitions are forbidden. The magnitude of Δo depends on the nature of the ligands and how that going to affect the energy of light on transitions and hence the frequency of absorption maximum. This depends not only on nature of the ligands but also on the nature of the metals and their position, whether 3d, 4d or 5d and also the charge on them. The extent of splitting is related to the ligand positions in the spectrochemical series, because of donor and acceptor properties. That you know, pure sigma donors, pure sigma donors and pi donors and pure sigma donors and pi acceptors. As I had mentioned earlier all d-d transitions can be simply

classified into four categories d^0, d^{10}: no transitions, colorless. If at all color comes, it has to be due to the charge transfer transition. In case of d^0 it has to be a ligand to metal, d^{10}- it has to be a metal to ligand and d^5 is unique here. It is Laporte forbidden as well as spin forbidden. As a result, those compounds are not colored. If at all color is there in case of tetrahedral complexes, it is pale in color and then other eight categories d^1 d^4 d^6 d^9 one electron, one less than half filled, one more than half filled, one less than completely filled. They show invariably one transition, whereas in case of d^2 d^3 d^7 d^8; two electrons, two less than half filled, two more than half filled and two less than completely filled, show invariably three transitions. In some cases, in homoleptic molecules because of closer space of two transitions, you may see just two transitions. That is what we see in case of hexaaquavanadium(III)$^+$ ($[V(H_2O)_6]^{3+}$). For example, here, I showed you mercuric iodide, HgI_2. HgI_2 is a d^{10} system, brick red color is due to the metal to ligand charge transfer. $KMnO_4$ or potassium dichromate metals are d^0, intense purple or orange color is there, that is again due to ligand to metal charge transfer. In case of bismuth triiodide, orange red color is due to metal to ligand charge transfer transition. In case of prussian blue it is metal to metal charge transfer transition. Since iodide has a very high polarizability, which results in the ionic charge getting easily transferred to the Hg^{2+} cation, this process releases energy which falls in the visible spectrum. As a result, they appear brick red in color hence the compounds like $KMnO_4$mercuric iodide etc are highly colored. Then selection rules are very important. Electronic transitions may be classified as intense or weak according to the magnitude of the **ε**, absorptivity coefficient, that corresponds to whether they are allowed or forbidden transitions. Allowed transitions have e maximum 10 raise to 4 (10^4) or more and probability of their occurrence is very high these are generally due to $\pi \rightarrow \pi^*$ star transitions. For example, 1,3-butadiene shows absorption at 217 nanometer and epsilon is about 20,900, represents an allowed transition.

What are the forbidden transitions? These are usually related to $n \rightarrow \pi^*$transition. For these transitions, epsilon-maximum is generally less than 10 raise to 4 (10^4) and then $n \rightarrow \pi^*$transition of saturated aldehyde or ketones exhibit a weak absorption of low intensity near about 285 nanometer and have the value of epsilon-maximum less than 100 is a forbidden transition.

The selection rule says Δl equal to plus or minus ± 1 have high absorbance and spin selection rule Δs equal to 0, that means during electronic transition, they should not change their spin. The upward spin should go to upward spin only, whereas in case of nucleus upward spin will become downward spin. That is the difference and then d-d transitions are strictly speaking Laporte forbidden (leoparda fermi done). Because of mixing what happened d-orbitals lose their identity and hence we see d-d transition. Nevertheless, if you look into it, d-d transitions are Laporte forbidden $\Delta l = \pm 1$. Epsilon value is 5 to 10 liters per mole per centimeter, very very low. That itself indicates these transitions are strictly speaking Laporte forbidden. So when transition metal forms a complex metal is surrounded by ligands, mixing of d and p orbitals may occur and as a result, transitions are no longer pure d-d in nature because of slight relaxation in Laporte rule, d-d transits are observed. Also, in case of octahedral complexes, which are highly centrosymmetric, what happens when the ligands are vibrating and often they come out of their mean position. As a result, they come out of their mean position which lac the center of symmetry. Mixing will occur and they show transitions. For example, tetrabromomanganate is tetrahedral and is colored. The hetero substituted pentamine chlorocobalt has unsymmetrical substitution and is colored, whereas this one if you look into homoleptic hexaaquacopper or hexaaquacobalt, which have centrosymmetry and no mixing of p and d orbits are there and they are not colored. However, the metal to ligand bond vibrates so that the ligand spends an appreciable amount of time out of their centrosymmetric equilibrium position. As a result, small amount of mixing occurs and low intensity transitions are observed.

In case of IR, this is very important

$$\nu = \frac{1}{\pi}\sqrt{\frac{f}{2m}}$$

How this stretching frequency is related to stretching force constant and the reduced mass of those two atoms involved in a bond.

The vibrational motions and frequencies of a structure containing several balls of different masses connected by springs with different force constants can be studied using classical mechanics which can be correlated with the motion of a molecule.

Simplest way to study polyatomic molecules is by treating various parts as diatomic species. This work well when one of the two atoms is not bonded to any other atom in the molecule.

This is an ideal simplified equation one can use comfortably to find out. If the stretching frequency is given, force constant can be found out very easily because other terms are constant. In a diatomic molecule we have to find out μ, reduced mass. It is m1xm2 by m1 plus m2 (m_1m_2/m_1+m_2).

For example: If you see here what happens when they are substituted. Here observed value is 2150, here it is ir inactive and also, they show different type of vibrations, wagging and twisting. The twisting mode produces no change in dipole moment and hence ir inactive in symmetrical modes. Here they show different type of vibrational motions. This is symmetric stretching and anti-symmetric, scissoring, rocking and wagging. These are all symmetric, these are all anti-symmetric. As I had mentioned this is the equation one can use comfortably. This is the simple derivative from Hook's law how they are related. This another simple equation

$$\overline{\nu} = 130.3\sqrt{\frac{f}{\mu}}$$

For example all the three equations are there. You can always examine because everything is given here: reduced mass, force constant, frequency. Simply apply and then verify this is for homework or assignment you can keep doing and of course some of them have shown here.

You can just look into it. A couple of examples I have included here. for C double bond C. When it comes to IR, carbonyl compounds very important and carbonyl compounds you know CO forms a sigma bond through the lone pair from carbon taken to appropriate metal orbitals: d_z^2 $d_{x^2-y^2}$. This is anti-bonding, pi star would interact with pi-symmetry orbitals from the metal d_{xy} d_{yz} or d_{xz} to generate anti-bonding and bonding. Bonding will be populated with electrons from the metal that we call it as back bonding and the same thing we call it as, in terms of a spectroscopy, charge transfer.

These two modes of bonding is mutually reinforcing the metal to carbon bond that is called synergistic effect. Charge removal through pi bonding leads to more extensive sigma bonding and charge donated through sigma bonding facilitates further back bonding. that is sigma donation will make electron deficient and back donation makes electrons rich and they will be acting in tandem. This is called synergistic effect and then it is very interesting to compare the stretching frequencies in these homoleptic molecules of having different electronic configuration, d^{10}-d^6 etcetera. If you notice here in case of nickeltetracarbonyl stretching frequencies are quite high, that means not much back bonding occurs here. Of course, this entire molecule survives only on back bonding. The MO diagram clearly shows that there is no sigma bond. Unlike $CrCO_6$, where we have well designated chromium to carbon sigma bonds, whereas here it is not there. That is the reason these compounds are very volatile and and very reactive and very sensitive compounds. They can readily decompose in fact $NiCO_4$ was made with an intention of getting pure nickel for catalytic purpose through decomposition and this is how this bond can vary here it can become if more electron density goes to the π*it becomes almost like a ketonic carbonyl group and then of course here I have shown for different substituted carbonyl groups four five and three and having different geometric isomers cis and trans, how many active IR bands are observed for COs. For example, here when you have three, you can have facial or meridional. In case of meridional you will see three, whereas in case of facial you will see two and of course these are all for homoleptic molecules.

This is about mass. This periodic table gives about natural abundance of different isotopes. This comes very handy in characterizing the compounds through mass spectrometry.

Here this is EPR, one should remember this equation very well from that one we should be able to calculate g. Similarly, you can compare it to coupling constant we see in case of NMR and then for a free electron this is 2.0023 and then of course here we consider only J equal to l plus s, whereas in case of electronic spectroscopy we consider both l plus s and l minus s. We should remember for g = h nu over betaH ($\frac{h\nu}{\beta H}$). H is the magnetic field strength. With increase in magnetic field the energy associated with the electronic spin also increases and it will go to higher frequency.

This is a typical epr spectrum is shown here. We have an odd electron. We have to use 2nI plus one rule and all of them have I equal to one. It splits into nine lines of this intensity. You can see, this is a beautiful spectrum. Of course, here I have not shown these things and hydrogen hyperfine splitting is not shown. This splitting shown here is due to four nitrogen here with I equal to one.

This example is about hyperfine splitting. You can see here, first this electron will be split from these two into a quintet because 2nI plus one proves it. Then we have four hydrogen atoms with I equal to half will split each one into a quintet. We will see quintet of quintets. This is a very beautiful hyperfine splitting spectrum. EPR spectrum of this anion is shown here.

Next question: For a radical, the magnetic field is 3810 Gauss. The frequency of the microwave is 9600 megahertz. what is the value of g factor.

g factor can be simply calculated

$h\nu = g_e\beta_B B_0$

Therefore, g = 1.8

This is how you can calculate the unknown quantity using this simple equation here.

This is again mass spectrometry. This gives various fragments and the corresponding mass one can see very nicely here and then of course if you have hydrogen index deficiency, we can find out first. We can use 13 rule and then 13 rule, will give you approximate molecular formula. From molecular formula, again apply hydrogen deficiency index and find out the tentative structural formula and then take the help of data obtained from various spectrometer to elucidate the structure

Isotopic patterns for compounds containing different elements also shown here. This is very important and also the ratio also one should remember. How it shows in case of hydrogen and phosphorus and fluorine you see only one, whereas carbon ^{13}C is 1.1% and nitrogen ^{15}N very small ^{17}O and then here 32. We will see and 34 so small quantity again 35 and 37. In case of metals, we see patterns which are very unique for each metal. You

can see something like this. If you have these things handy, when you have the spectrum, you should be able to identify even if the metal is unknown

The rule of 13 is very important as I said. Take the mass divided by 13 and the quotient, whatever the value will be the number of carbon atoms. Quotient plus this reminder will be the number of hydrogen atoms. You can have something like this and then for hetero atoms what happens if nitrogen is there you take out CH_2. For oxygen, take CH_4 and then sulfur is there, take C_2H_8 and phosphorus take C_2H_7 so that is 31 24 plus 7 31 and then if chlorine is there C_2H_{11}. If hydrogen deficiency is there you can also take C_3H minus that means every Cl you take take out three carbon atoms add one hydrogen atom and for bromine you can take out C_6H_7 and 127 iodine you take out $C_{10}H_7$. So this is how you can adjust the formula to arrive at tentative formula.

Some examples are shown here and possible candidates with hetero atoms and nitrogen rule is also you should remember a molecule with even number of molecular weight must contain either no nitrogen or even number of nitrogen. A molecule with odd number molecular weight must contain an odd number of nitrogen so you should remember these things when you are using rule 13.

So let me conclude now so far I had discussed several spectroscopy methods and several problems and of course at some point of time we had to conclude the lecture series and I hope this was very useful and many of you are interested in taking exams, competitive exams to get into higher studies or doctoral work or some of you may be doing doctoral work. One thing I am telling you, this learning never ends and also for students learning is the profession. When learning is profession your attitude has to be right. How to set your attitude to become a humble student is, you have to have first, these five entities in the profession of learning. You should have sincerity, honesty, dedication, discipline, and determination. When you inculcate these five entities in your profession of learning you will be having a right attitude to achieve whatever you want and to make a mark in whatever the subject you just embrace for your higher studies.

With this I wish you all the very best. Okay; you should remember: Bee greedy for learning and be content with earning, as far as you are a student, you should not think about earning

and also you can see here only one letter makes a difference between learning and earning. I will tell you again: be greedy for learning and be content with earning, I wish you all the very best, god bless you all, thank you.