Lanthanide/Actinide Luminescence Spectroscopy-I

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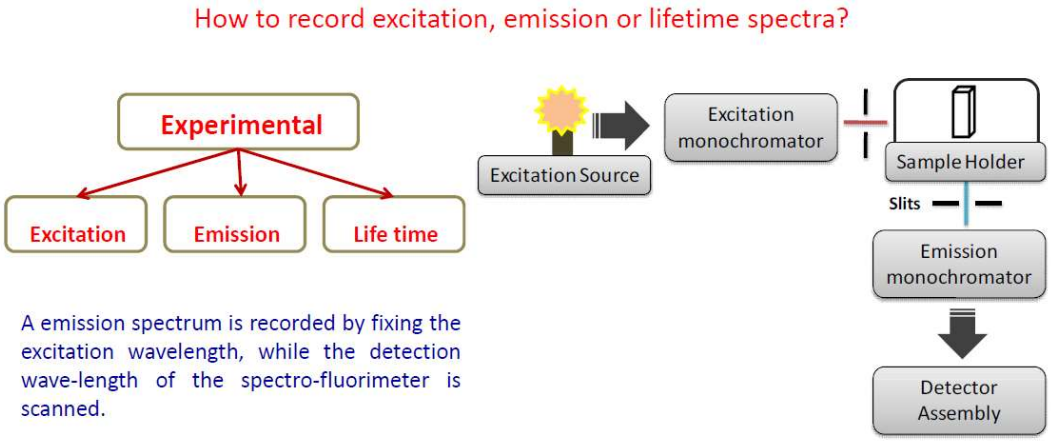
Week – 11
Lecture – 52

Hello everyone, and welcome back to the series of lectures on actinide chemistry,

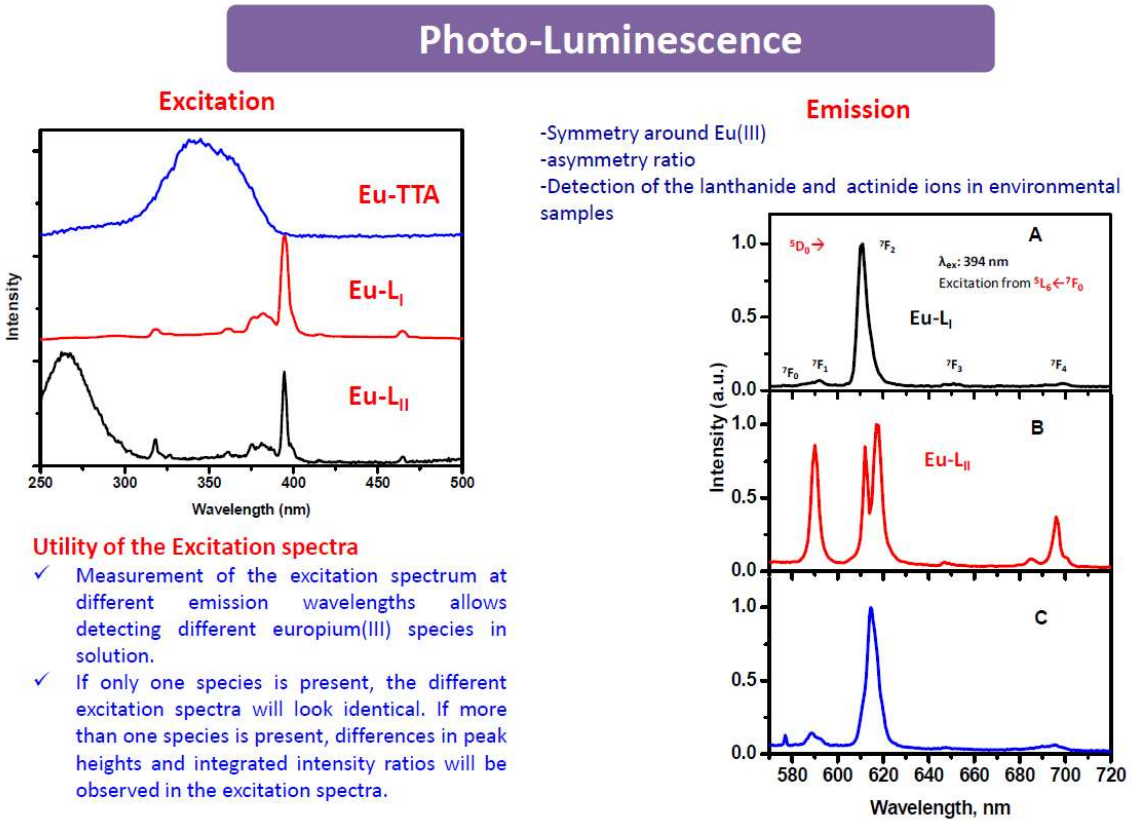


In the last lecture, we studied the spectroscopic aspects of lanthanide and actinides. In continuation to that, we will try to understand some of the utilities of emissions spectroscopy.

We have also discussed in the last slide of the last lecture how we can record the excitation, emissions, and lifetime spectra. The excitation source we are using electromagnetic waves or is UV-vis (source) light. The spectroscopy is generally called photoluminescence, PL in short. So in this photoluminescence, we excite with the source, and then we measure the emission, and we'll try to extract some information from the recorded excitation, emission as well as the lifetime spectra. So, in brief, I have told you how to measure these excitation spectra. To measure the excitation spectra, you have to fix the emission wavelength and scan the excitation monochromator, and then you'll get some peak at that fixed emission wavelength. Suppose, Take an example of Europium (III), and for this excitation peak maxima comes around 394 nm.

So, this is the excitation spectra in which the emission wavelength is fixed. what I'll do in emission spectra Since, I know the peak giving the maximum excitation I'll fix the excitation source at this peak (wavelength), and then I record the emission spectra. So by that, we have information about the excitation spectra, and we have information about the emission spectra. We'll take this (excitation) maximum, and this (emission) maximum, and will fix these two maxima, and record the decay half-life or the half-life of the decay life of the complex that we are interested in.

So as I showed you, how can measure excitation and emission spectra? So what is the information that we can get from these excitation spectra?



I've shown you several excitation spectra that I've taken from Google so you can see there is a difference when you start from A (top (blue)) to C (down (black)). You can say sometimes you are getting, and most of the time we are getting a peak in this red region (red circle), and that is the excitation spectra of Europium (III) with some complex so you are getting a peak at 394 (nm). But if you look carefully, there is a difference in the

excitation spectra of A to C. The peak position and broadness are different in different spectra. So, what does this suggest, and what kind of information we can draw from this kind of spectra?

Let us assume that, you have two complexes and then one complex. Let'ssay is Eu-LI, and the other complex you can say like Eu-LII.let us arbitrarily assign Eu-LI to one spectrum and Eu-LII to other spectra. So just by looking at these spectra, I can say that there is a difference in different wavelength regions. It says that these sharp transitions(near 394 nm) are present in both spectra. We also know that the f-f transitions are sharp but you can see these transitions(< 350 nm) are not sharp this is a broad transition. These are not-f transitions rather they are charge transfer bands or charge transfer transitions. So what we can say from this charge transfer transition or charge transfer band is that out of these two assumed complexes, Eu-LI, and Eu-LII; that I have written just says Eu-LI, and Eu- LII this particular ligand that is LII has a better overlap or more overlap with to the europium compared to LI. So what the broad transition is doing, is a charge transfer meaning you are exciting the ligand, and the ligand is transferring its energy to the Europium center, and from there you are getting emission lines for Eu.

So, we can get this overlapping information between the L, and Eu orbitals from the excitation spectra. Even in certain complexes, the charge transfer band is so large or you can say so intense, for example, Europium with TTA (Thenoyltrifluoroacetone).

I hope you have heard the name TTA in your extraction classes. If you take the spectra of this (Eu-TTA complex) the charge transfer band is too huge, you can say that these transitions are just very small as compared to the charge transfer band. So, the information of the metal ligand or overlap can be seen from this kind of spectra.

Okay now you have some excitation spectra and then you are sitting on the excitation maxima let us say here or here whatever excitation maxima you choose and then you record an emission spectrum. So, suppose, I sit on some maxima and then I record this spectra, and suppose again I am just arbitrarily assigning it LI and LII and you get some kind of spectra like this Europium LI and LII. So what? just by seeing this spectrum, one thing is

very clear to me the spectra do not look very similar. So, I can say that? the environment around Europium in these two complexes is different.

What it is? we will see later but it is different, this is different from this. So, this is the direct information that we can get from emission spectra but we should do it very closely then we can see there are several transitions that I have marked here and you know that we start with $^5D_0$ and we give transition to $^7F_0$, $^7F_1$, $^7F_2$ and all these transitions are marked here. So let us say the first transition is 5D0 to 7F0. So many times, we just say this is J-0 and this is J-0. So many times, we just say it is like 0-0 transition and then I am also using the term like 0-0 transition.

So if you see this 0-0 transition then it is like 0-1, this is 0-2 like that you can name like that also. So the information that is there in the 0-0 transition. Let us see here the 0-0 transition but this is my 0-0 transition that happened to be found near 580 nm for europium. We also know that the transitions that we say that are coming from $^5D_0$ to $^7F_0$ to $^7F_1$. we have seen that there is a splitting of the J level. This J level will split into 2J+1 states that I have shown in the previous slides, I guess.

Eu(III) Luminescence

Symmetry class	J=0	J=1	J=2	J=3	J=4	J=5	J=6
Icosahedral	1	1	1	2	2	3	4
Cubic	1	1	2	3	4	4	6
Octagonal	1	2	3	4	6	7	8
Hexagonal	1	2	3	5	6	7	9
Pentagonal	1	2	3	4	5	7	8
Tetragonal	1	2	4	5	7	8	10
Trigonal	1	2	3	5	6	7	9
Orthorhombic	1	2	5	7	9	11	13
Monoclinic	1	2	5	7	9	11	13
Triclinic	1	2	5	7	9	11	13

- The crystal-field perturbation destroys the spherical symmetry of the free-ion and the $^{2S+1}L_J$ terms split up in a number of crystal-field levels.
- The extent to which the 2J + 1 degeneracy of a $^{2S+1}L_J$ term is removed depends on the symmetry class and not on the point group it self.
- For all point groups with in a symmetry class, the splitting of a J term is identical. For instance, the splitting of the $^{2S+1}L_J$ terms is the same for all tetrahedral groups (D_{4h}, D_4, C_{4v}, C_{4h}, C_4, D_{2d}, S_4).
- The differences between the different point groups are reflected in different selection rules or in different numbers of transitions that are allowed between two $^{2S+1}L_J$ terms.
- Lowering in symmetry results in a relaxation of selection rules and to an increase in the number of allowed transitions. For the point group C_1, no transitions are forbidden by the selection rules and transitions are allowed between all the crystal-field sub levels of two $^{2S+1}L_J$ terms.

Yeah, you can see that this J level depending on the symmetry can split maximum into 2J plus 1. So, when we say about the 0-0 transition what is the J value? J is 0. So 2J+1 will be 1. So you can say even in symmetries of different environments this transition cannot split. What is the use of this? Let us say I have a spectrum I have just recorded a spectra I am getting peaks like this and the reason that is maybe 577 nm to 579 nm or so I am getting these two peaks.

One thing I am sure this is not the splitting. Why? Because it is a 0-0 transition. So, what information it gives to me that there is at least the presence of two Europium species or two different emitting species of Europium are present in the complex. So, this kind of information I can directly get from this 0-0 peak.

Let us say the other peak that is 0-1 peak. The 0-1 peak can split into J plus 1 giving rise to 3. So, if you are having this peak as you can say in this spectra there is some splitting. Similarly, when you have 0-2 this can give you 5 peaks. So, it can split into a maximum of 5. This all depends on the symmetry around the Europium ion.

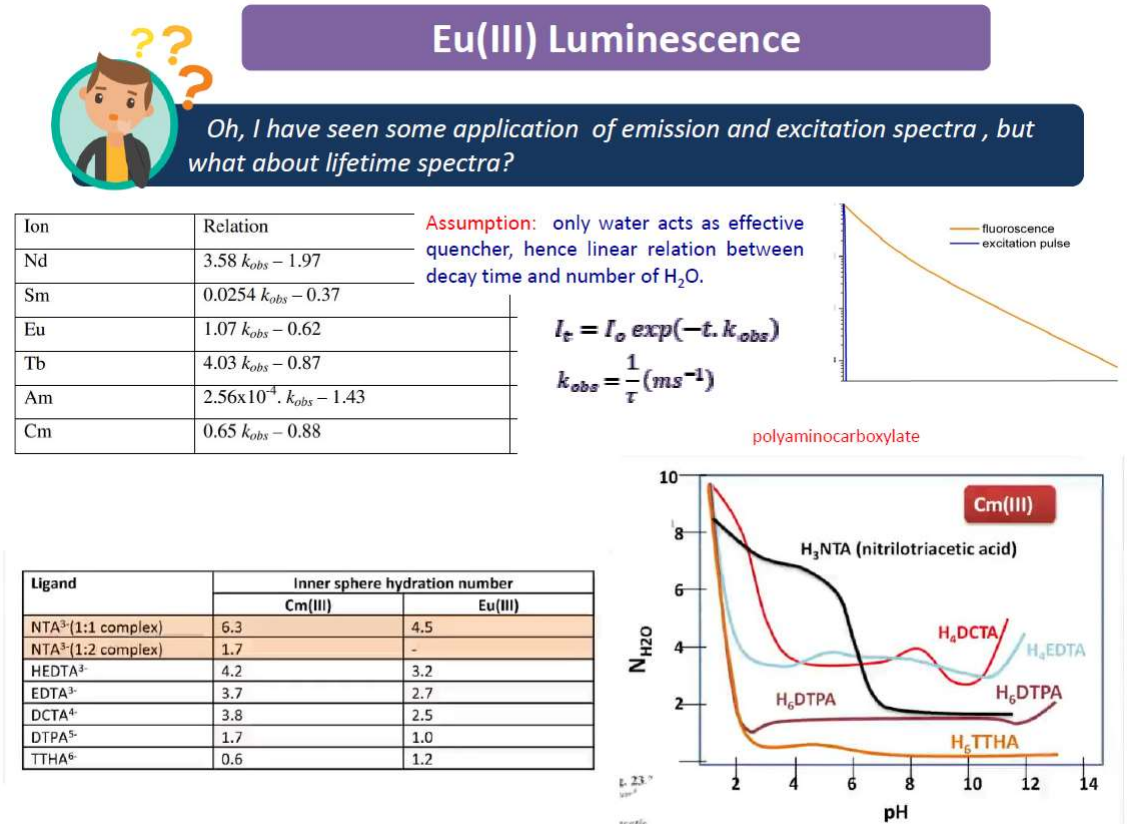
So lower the symmetry more the splitting. So, we can get information about the symmetry class if you know the splitting of all the lines and then you have to just see the table and suppose you have some system that has hexagonal symmetry and if you just see the first should be 1 then the second should be split into two, third should be 3. Likewise, if you see if you are matching with the splitting or your splitting of the pattern matches with this table then you can safely say that the symmetry around my Europium ion in this particular complex is hexagonal. You can get that information also from this. There is one more thing that we can know as asymmetry ratio.

Suppose we are having a transition 0-1 and then 0-2 and we are going to transition 0-1 transition. we have discussed is called a magnetic dipole whereas a 0-2 transition is called an electric dipole. We have also seen that these magnetic dipole transitions do not get much affected by the ligand environment. So, if we take the ratio of the electric dipole transition to the magnetic dipole transition, we are getting something that is called the asymmetry ratio.

We generally measure the ratio of the electric dipole transition with the magnetic dipole transition by taking the area under 0-2 transition divided by the area under 0-1 transition in a typical emission spectrum. For Eu(III) in water, if we take this ratio, it will be somewhere between 0.5 to 0.6. So generally, it happens that when there is an increase in this ratio for a given complex w.r.t. Eu in water, we say that the asymmetry around the Europium ion is higher in that complex.

So, asymmetry information of two Eu-L complexes can be found by using this asymmetry ratio. So now we can derive some information about the Eu-L complex. Now, we know this is the symmetry, and this is the kind of complexity that is there with Europium. Now

let's try to see how we can deal with the lifetimes. I'll come back to this slide after some time.



we can record the lifetime of the Eu-L complex in which we fix the excitation, and emission wavelength, and record lifetime. We fix both these wavelengths, at required wavelengths, and then we give an excitation pulse, and then we monitor the decay with time to get a decay curve. we can simply use the equation given below,

$$N\ (H_2O) = 1.07\ /\tau\ (\text{in ms}) - 0.7$$

After fitting the experimental decay to either mono or biexponential decay equations to get τ. Depending on the nature of the complex, we can get different lifetimes but generally, we start with a mono-exponential fitting, and then suppose we are not able to fit it then we go for the biexponential, and rarely to triexponential, but generally we restrict ourselves to a maximum of biexponential only. But theoretically, we can fit the decay curve in different orders of exponential (decay) functions until we get a good fit. We do not go beyond, bi or tri-exponential decay because if you are using a very high exponential then it may give a

good fit but it is logically not very valid. So, why the lifetime is decreasing or varying in different complexes? Let's assume for the lanthanide case or actinide, the decrease in lifetime is mainly because of the coordinated water. It is the OH vibrations of the water molecule, so most of the time we assume that the decay in the lifetime is mainly concerned with the vibration of the OH oscillators of the water. If water is the only responsible ion (molecule) or the molecule for the excited state decay then we can directly relate the number of water molecules in the primary sphere to the lifetime of the excited state. It has been done in the literature, and this is the linear relation.

$$N\ (H_2O) = 1.07\ /\tau\ (\text{in ms}) - 0.62$$

This linear relation directly relates the number of water in the primary hydration sphere to the decay lifetime. So you have to just fit the experimental decay curve, and from the decay constant you can use this equation, and from this equation, you can get the number of water in the primary hydration sphere. For Europium, it so happens that the decay lifetime in water is around 110 μs which gives 8-9 water molecules in the primary sphere. So, for Europium, we get 8-9 water molecules with a lifetime of around 110 μs. What is the utility of this? Let us assume that you have Europium in water, with let us say 8 water molecules, and then you add a ligand to the system.

Suppose, the ligand is bidentate, what will happen? We assume that it will just go, and bind to the Eu (III) ion so that now the ligand is where you can say out of the 8 positions two positions are occupied by the ligandmolecule. Now, if I just measure the lifetime of this molecule, we will get the number of the water molecule which, we are getting 8 in the case of the Europiumaqua system or the aqua hydration sphere this should be reduced to 6. So if the hydration number is reduced to 6 we can say yes there is some complex formation. Similarly, suppose you increase the ligand concentration or the pH depending on the nature of the ligand you may be getting a 1:2 (M:L) complex assuming again a bidentate ligand then 4 water molecules should be replaced, and then by putting this equation, you should be able to get 4 water molecules only.

So to exemplify that, I've given you the example of a complexation with some polyaminocarboxylate. This is for curium, and then again for the curium, you can see this

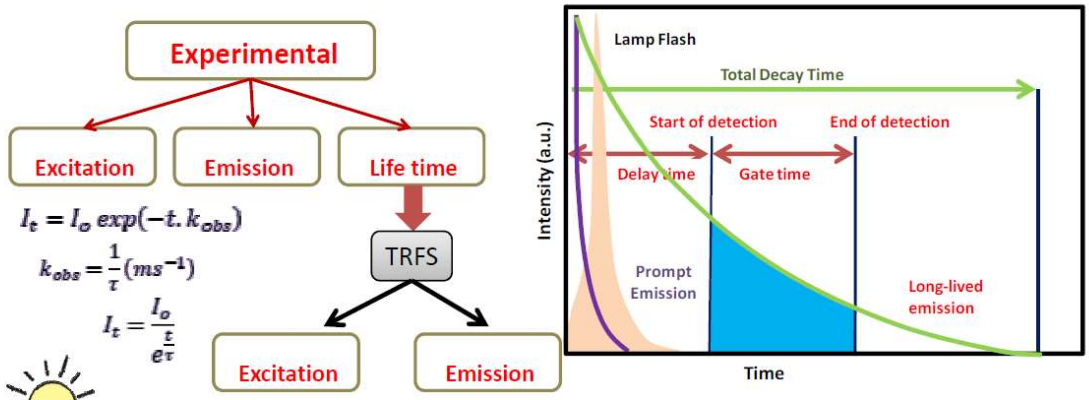
is the equation. These are the different polyaminocarboxylate ligands, and if you see the first case here in the graph, which is the hydration number of around 9 to 10 for Eu (III) aqua ion, and the moment you add the ligand at pH 2 there is a sharp decrease in the number of water molecules in the first hydration sphere of Eu.

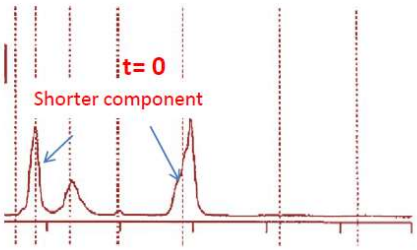
What does it mean? that at this pH there is a strong complexation or that now the ligand is complexed, and most of your water molecule has been removed. Compared to that if you see other curves, the number of water molecules in the primary hydration sphere is still intact in some complexes, and there are some water molecules in the primary hydration sphere. You can say that the denticity of the ligand will be affected by the denticity of the ligand.

Here you may have a 1: 1 complex or here maybe you have a 1:2 complex but whether it is 1:1 or 1: 2. we cannot say directly by this because that will depend on the denticity (of the ligand). Suppose you have a ligand which is having such as EDTA even with 1:1 it can remove mostly all the water molecules from the inner sphere of the metal ion. This is for NTAmide again you can see the two plateaus at a certain pH you have 1:1 if you increase the pH you get 1:2. So just by recording the lifetime at different pHs you can have information about the number of water in the primary hydration sphere, and you can also tell something about whether it is a 1:1 complex or 1:2 complex. Till now it is okay let us say we have only one species things are looking very easy now.

But suppose in a Eu-ligand system, we have more than one species suppose you have let us say two species few are 1:1, and few are 1:2. you have a complex mixture. In those cases what will happen is that instead of a mono-exponential curve you will get some curve which is which can easily be fitted into the biexponential curve. You will get a curve like this, and when you fit it into the mono-exponential you may not be getting very good fitting then you can go for the biexponential fitting to get statistically better fitting. So now you know from the lifetime data, that your system has more than one species based on the lifetime spectra. So I have information about the number of species in the system, but suppose I want to record the emission or excitation spectra of individual species. Remember that, the excitation, and emission spectra that we have recorded till now are in

a steady state. When I say steady state, it means there is nothing to do with the time. We have just exited the Eu-L complex with a given wavelength and recorded the emission. This recorded spectrum either emission or excitation are composite of contributions from both the species present in the solution... But, from the decay lifetime, we know there are two species, and suppose I am interested in getting the spectra of both species. What are the spectra of the short-lived or 1:1 complex, and what are the spectra of the long-lived or 1:2 complex?





Species	Lifetime (micro sec)	I(t) at 500 micro sec	
A	100	148	1%
B	500	2.72	63%

So, you have two species, and you want to know what is the contribution or rather what is the nature of the spectra of 1:1, and 1:2. For these kinds of cases, we cannot use the steady state emission profile. Why? Because there is no timing information, we cannot differentiate the two Eu-complexes based on this. But from the timing information that is the lifetime spectroscopy, we know that one species is decaying faster than the other.

For simplicity, I have assumed only two species. Let us say you have a system which is having two species one is decaying with a lifetime of 100 μs, and another with 500 μs. When I say lifetime, I mean the tau (τ) value is 100 μs. When we record the spectra,

and if you look it carefully. The species with 100 μs will decay first, and the species with 500 μs will have a long tail. Why? If you see these equations,

$$I_t = I_o \exp(-t.k_{obs})$$

$$k_{obs} = \frac{1}{\tau} \text{ , and } I_t = \frac{I_o}{\exp(t/\tau)}$$

Then we can say okay the species with τ = 100 is decaying very fast compared to the species with τ = 500, which is giving you a tail, and I want to record this spectrum. So initially with the steady state suppose I record spectra that look like the one in the slide, and these are the steady state spectra?

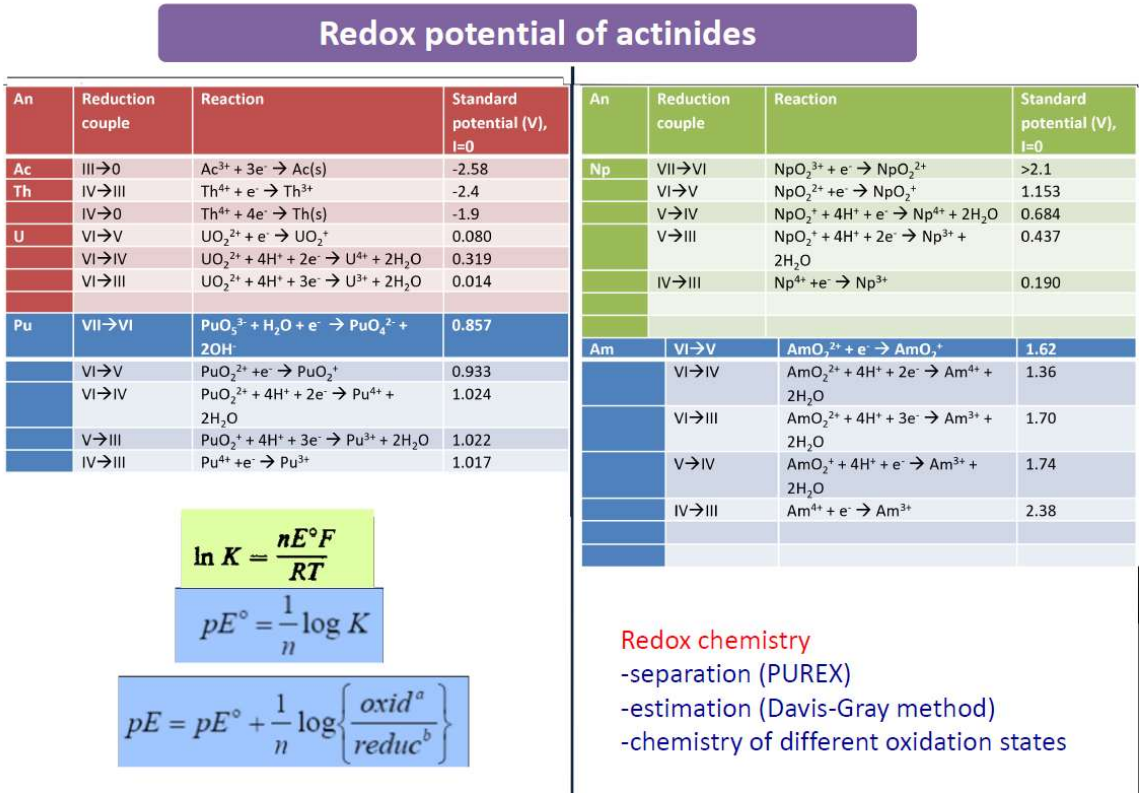
I have written t=0, and for simplicity, I assume that these two peaks this peak, and this shoulder is coming from the shorter component which is the 100 microsecond component, and the rest of the spectra is from the 500 microsecond component. So, what I want to record I want to record both I cannot do with the steady state. So now what I will do, I will do time-resolved fluorescence spectroscopy. In this, I will excite the Eucomplex with a wavelength, let us say at 394 (nm) in this case, and then I'll wait for a certain amount of time. Why wait? Because suppose I am excited at any particular time, and I am waiting till it gets decayed. That is waiting time. How it can help us? Let us say for τ= 100, andτ= 500 μs, and you are waiting for around 500 μs. In 500 μs you have given 5 lifetimes to decay for the 100 μs species, however for the 500-microsecond species you have given only 1 decay lifetime. The decay curve intensity is a combination of both 500, and 100 lifetime, and by giving the delay we'll try to differentiate the two species in the time domain. The below equation

$$I_t = \frac{I_o}{\exp(t/\tau)}$$

Suggests the decreased intensity at any time is inversely proportional to $e^{t/\tau}$. Where t is the waiting or delay time? So, in this case, t =500 μs.

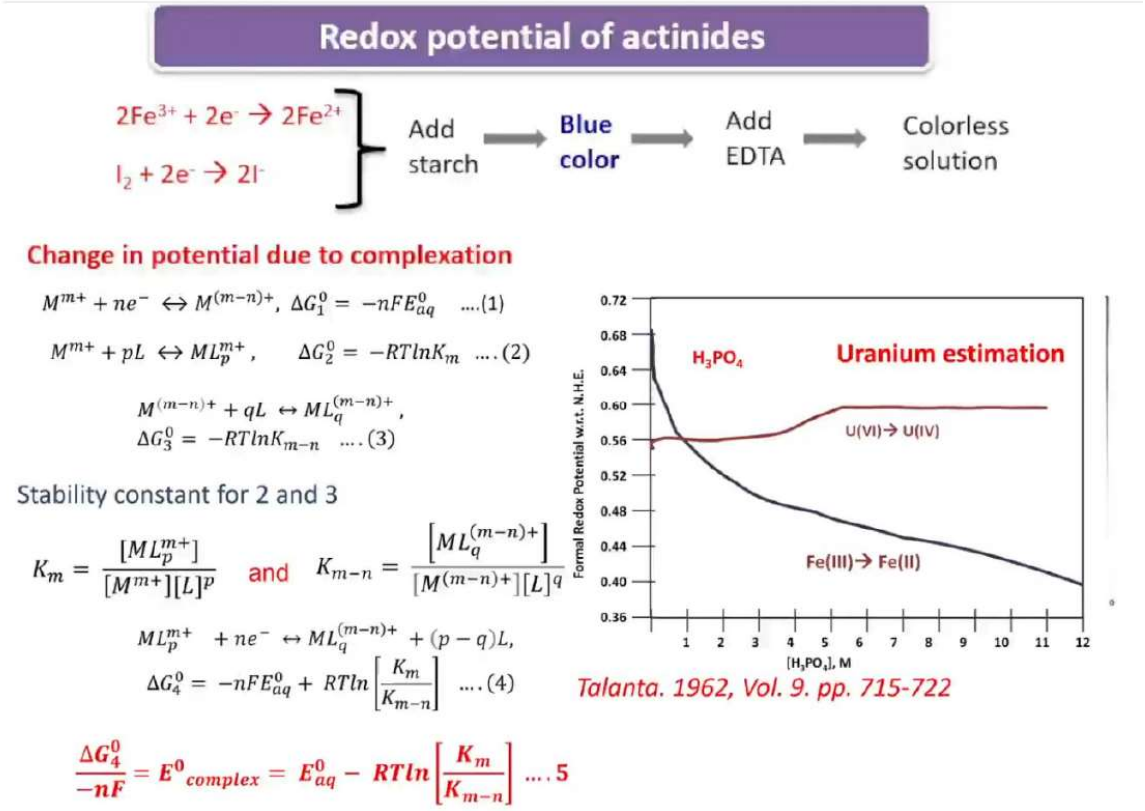
Let's assume the initial intensity is I_0 for both species, after 500 μs, the intensity of 100 μs will fall by e^5. I_0 divided by e^5, which means that there is a decrease of almost 148 times the shorter component whereas if you see the longer component, it has only one half-

life or one decay life. So for this, the decrease is just like 2.72 times. So, after 500 μs the signal from long-lived species is 63% but remains ~ 1% from the short-lived component. So, if you are giving decay, and are measuring after decay the profile which you will get is mainly dominated by the long-lived component. So I am expecting that this peak should be not there at the first peak then we are getting a second peak, and the shoulder should not be there, and where should be there a peak? So, if it is a spectrum of A + B then this should be spectra of B assuming that B has a lifetime of 500 μs. So, in this way, you know A + B you know B, and you can subtract (A + B) - B. This is not that direct we have to understand the quantum yields also but assuming that everything is similar for both the complexes I can say that you can just subtract it to get the A. So, you can record the excitation spectra as well as emission spectra using this time-resolved fluorescence spectroscopy.



So now you have some ideas and some applications of this spectroscopy. Now I just want to have a very brief discussion about the redox property that we have already discussed. I just want to give you some of examples the actinides. I have already discussed with you about this table what are the redox potentials of different actinides, and from this table, you

can easily see that some of the redox potentials are way on the higher side so let us say thorium is the highest so it is very difficult to reduce Th(IV) to Th(III) but some of the actinides such as the plutonium having redox all of around one-volt so there are a lot of chemistry a lot of redox chemistry can happen. So why do we need to require this redox chemistry many times it happens that we require it for the separation because most of the time our separation is based on the oxidation state of the metal ion, and you must have heard, and you must have listened to this PUREX process, many a time we play with the oxidation state for their (Actinide) determination that is the generally we do for the Uranium estimation using a Davis Gray method, and suppose you want to understand the chemistry of the different oxidation state even in those cases we want to have information about the redox potential so that we can play with the redox potential, and with a certain complexing agent or we can add some you know some different kind of redox couple that can either easily reduce or oxidize metal ion.



So to simplify, suppose I've given a very simple example let us say that from our class book chemistry suppose you are here having a couple of iron that is getting reduced to

Fe2+, and you have a couple that is between iodide, and iodine gas so suppose I take these two, and I mix them, and after that, I just add a drop of starch what I find then the color of the solution is beginning blue why the color of the solution is becoming blue because if you see this couple it so happens that the reduction potential of this is 0.77 the first one iron, and reduction potential of this is low let us say 0.54, it so happened that iron will get reduced whereas this will go oxidized to iodine gas, and when you are adding starch to the iodine gas it will make a complex that will be blue now to this blue color you add two drops of EDTA now what EDTAwill do?

EDTA can complex Fe^{3+} and Fe^{2+}, and the moment it complexes their redox behavior will change now the reduction couple is no more than 0.77 V rather it decreases to something like 0.12, and since the redox potential has been changed so the course of reaction will change, and you will geta colorless solution why because now there is no more iodine what you are getting is now iodine is getting reduced to iodide, and your iron is getting oxidized to Fe3+ so this is the variation in the redox couple I just want to emphasize just by the addition of some ligand how we can do it mathematically it is a very simple equation that I've taken from a paper. you can just easily see that suppose we have a redox couple that is the M^{n+} is going to $M^{(n-1)}$, and you can always write ΔG for that similarly suppose there is a complexation, for the complexation you can again write so this is the way you have started with oxidized one this is the product that reduced one again you can write for the complexation.

I am assuming that the L is a neutral ligand, and when you write this you can write the corresponding stability constants also that K_m, and K_{mn}, and with simple mathematical juggling what you found that you can easily write this equation, and if you closely look at this equation. then now you are not talking about the pure metal ion you are talking about the complexes the ML complex is getting reduced to ML_q complex with the total gain of n electrons so now we are talking about the redox potential of this particular couple, and if you see mathematically.

$$M^{m+} + ne^- \leftrightarrow M^{(m-n)+},\ \Delta G_1^0 = -nFE_{aq}^0 \quad ....(1)$$

$$M^{m+} + pL \leftrightarrow ML_p^{m+},\qquad \Delta G_2^0 = -RTlnK_m \quad ....(2)$$

$$M^{(m-n)+} + qL \leftrightarrow ML_q^{(m-n)+},$$
$$\Delta G_3^0 = -RTlnK_{m-n} \quad ....(3)$$

Stability constant for 2 and 3

$$K_m = \frac{[ML_p^{m+}]}{[M^{m+}][L]^p} \quad \text{and} \quad K_{m-n} = \frac{\left[ML_q^{(m-n)+}\right]}{[M^{(m-n)+}][L]^q}$$

$$ML_p^{m+} + ne^- \leftrightarrow ML_q^{(m-n)+} + (p-q)L,$$
$$\Delta G_4^0 = -nFE_{aq}^0 + RTln\left[\frac{K_m}{K_{m-n}}\right] \quad ....(4)$$

$$\frac{\Delta G_4^0}{-nF} = E^0{}_{complex} = E_{aq}^0 - RTln\left[\frac{K_m}{K_{m-n}}\right] \quad ....5$$

We found if you drive the equation for this you find that the relation between E and E^0 is complex.

The ratio of K_m /K_{mn} is the important term. Why? because now your potential is dependent on the stability of these two complexes as I've shown you in the EDTA example, the complexes of EDTA with Fe^{3+}, and Fe^{2+} must have different stability. so their stability constant must be different so which is more stable depending on that you will get a potential that is either left-shifted or right-shifted. The resultant potential may be more negative than the original one or maybe more positive than the original one. Generally, it so happens that when you are adding some kind of complexing agent some of the complexes get stabilized, and you'll get a reduction of the lower potential, and this is again just what I've shown you in the Davis-Gray method. it is a very important method in the estimation of uranium in the nuclear industries. here is what people have done they played cleverly with the redox potential of the iron complex iron couple, and uranium couple so if you see that the iron couple has a potential of around 60 millivolts in sulfuric acid but the moment you start adding phosphoric acid there is a decrease in the reduction potential whereas under similar condition.

if you see a couple of uranium it is almost unchanged, and rising so here if you see that the reduction couple of iron is higher side than the uranium whereas the reverse is true here what it means that here iron will try to reduce, and uranium will get oxidized whereas here uranium will get reduced so now you have U (VI) that will get reduced to U (IV) now U (VI) will get to U (IV). uranium will get reduced, and iron will get oxidized just by changing the media. we can see there is a huge effect of medium on the potentials, and just by playing the media we can play with the redox potential, and that is generally used to carry out different transformations that redox transformation even for the actinides but instead of metallic reducing or oxidizing agent.

Neptunium

Oxidation state of Neptunium ions		Chemical conditions	
Before treatment	After treatment	Redox reagents	Conditions
Np(III), Np(IV), Np(V)	Np(VI)	Ce(IV)	H_2SO_4, HNO_3
		MnO_4^-	H_2SO_4, HNO_3
		Aq(II)	$HClO_4$
		$HClO_4$	fuming
Np(III)	Np(IV)	O_2 air	
Np(V), Np(VI)	Np(VI)	Fe^{2+}	H_2SO_4,
Np(VI)	Np(V)	NH_2NH_2	1 M HNO_3
		H_2O_2	0.5 M HNO_3
Np(IV), Np(V), Np(VI)	Np(III)	Zn(Hg)	

Plutonium

$$2Pu^{4+} + 2NH_3OH^+ \leftrightarrow 2Pu^{3+} + N_2 + 4H^+ + 2H_2O$$

$$2Pu^{4+} + NH_3OH^+ \leftrightarrow 2Pu^{3+} + 3H^+ + 0.5N_2O + 0.5H_2O$$

We mainly prefer something that is the kind of more organic so hydroxyl amine hydrochloride or hydrazine or sometimes hydrogen peroxide are mostly used in changing this couple of actinides, and some of the reagents that are generally used for neptunium in the aqueous phase are given here, and similarly, for plutonium also have given here so this is just to make you understand that in different kind of media, the potential can shift here, and there, and this understanding of potential, and this understanding of their shifting with

different kind of reagents are generally used for their either selective reduction or selective oxidation, and these processes along with the extractant that we use are generally used for the separation chemistry or understanding the chemistry of lanthanides, and actinides into the aqueous phase, and with this, I just want to end the today's lecture.

Thank you very much you

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