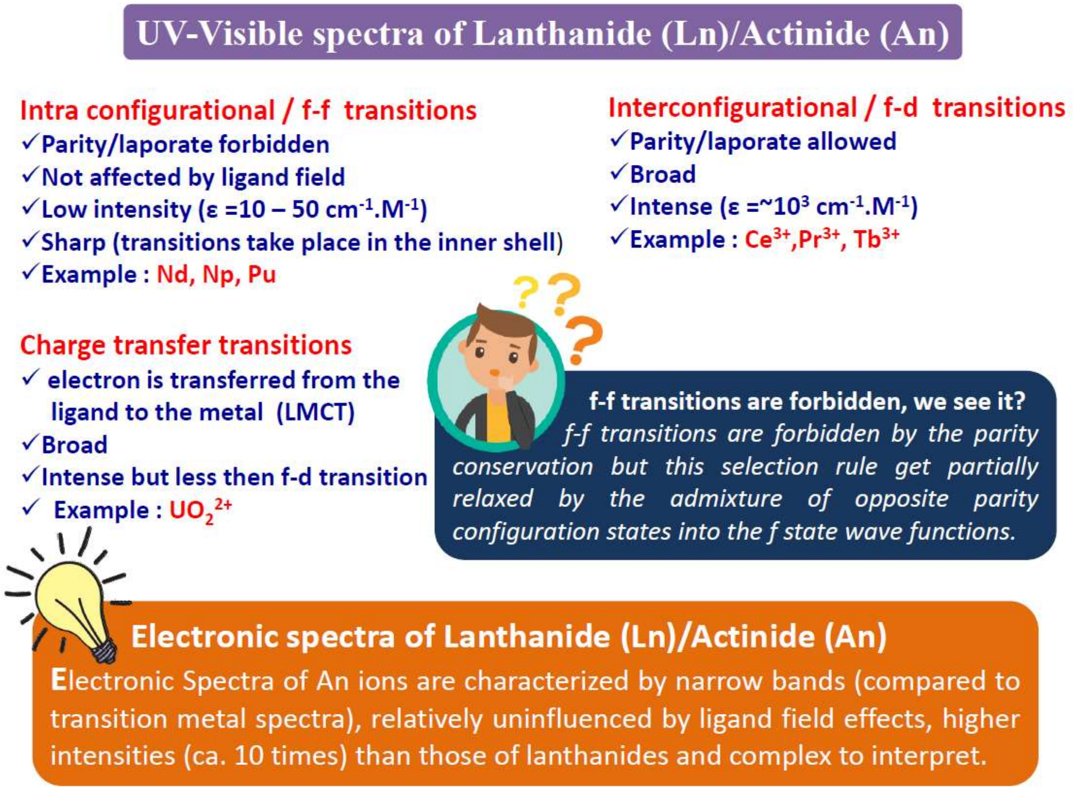
Course Name: Nuclear and Radiochemistry
Professor Name: Prof. P. K. Mohapatra
Department Name: Radiochemistry Division
Institute Name: Homi Bhabha National Institute
Week - 10
Lecture - 50

Hello everyone, and welcome back to the series of lectures on Actinide Chemistry.



UV-Visible spectra of Lanthanide (Ln)/Actinide (An)

Intra configurational / f-f transitions
- ✓Parity/laporate forbidden
- ✓Not affected by ligand field
- ✓Low intensity ($\varepsilon = 10 - 50\ cm^{-1}.M^{-1}$)
- ✓Sharp (transitions take place in the inner shell)
- ✓Example : Nd, Np, Pu

Interconfigurational / f-d transitions
- ✓Parity/laporate allowed
- ✓Broad
- ✓Intense ($\varepsilon = \sim 10^3\ cm^{-1}.M^{-1}$)
- ✓Example : Ce^{3+}, Pr^{3+}, Tb^{3+}

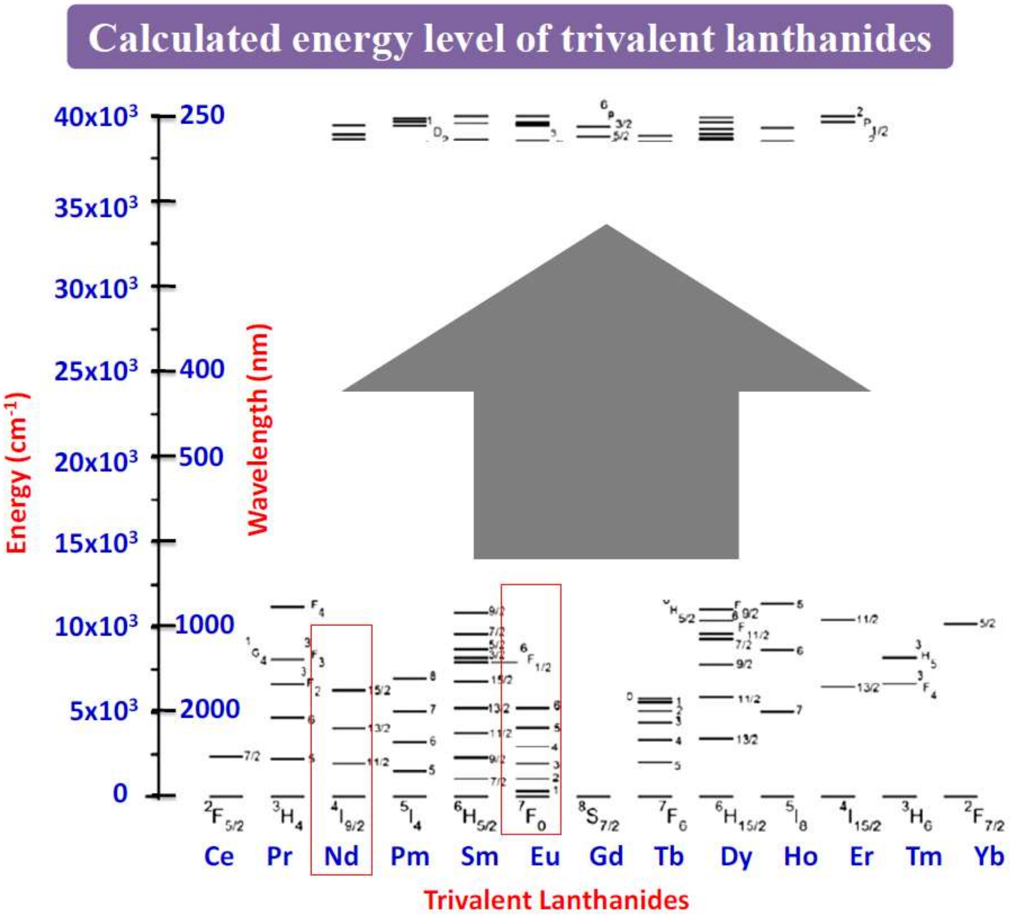
Charge transfer transitions
- ✓ electron is transferred from the ligand to the metal (LMCT)
- ✓Broad
- ✓Intense but less then f-d transition
- ✓ Example : UO_2^{2+}

f-f transitions are forbidden, we see it?
f-f transitions are forbidden by the parity conservation but this selection rule get partially relaxed by the admixture of opposite parity configuration states into the f state wave functions.

Electronic spectra of Lanthanide (Ln)/Actinide (An)
Electronic Spectra of An ions are characterized by narrow bands (compared to transition metal spectra), relatively uninfluenced by ligand field effects, higher intensities (ca. 10 times) than those of lanthanides and complex to interpret.

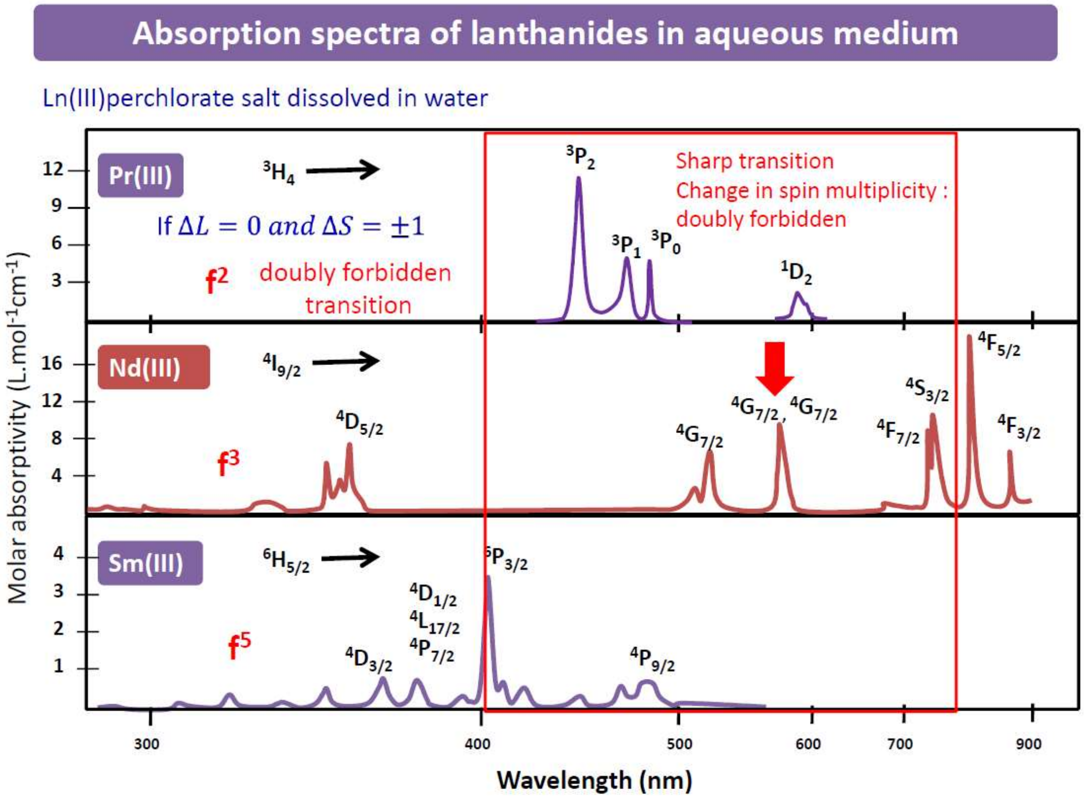
In the last lecture, we discussed the term symbols. We have also discussed, how we measure the UV-visible spectra of any ion, give it a lanthanide or actinide. Later we have seenthat 3 types of electronic transitions are possible in lanthanide, and actinide i.e., intra-configurational transitions, also known as *f-f* transition, inter-configurational transition (also known as *f-d* transition), and the charge transfer (CT) transition. For the metal ions with electronsin the *f*-orbital, inter-configurational, and intra-configurational transition are possible but in the case of metal ions with no f-electrons or f^0 system, whatever transition we observe or whatever color we see in the compounds that mainly arises from the CT transitions.

A very good example of actinide that gives this charge transfer transition is uranyl ion (UO_2^{2+}), an f^0 system. So, if you compare the electronic spectra of lanthanide and actinide, the lanthanides havea bit sharper spectra with a lower epsilon value. whereas, actinide has broader spectra because of the more diffuse nature of the 5f orbital compared to the 4f orbitals. The f-f transitions of actinides have more intensity, and5f orbitals are more participative in any reactions compared to the lanthanide.



Let us see some term symbols that we have alreadycalculated, as you remember we have calculated the term symbol for Eu^{3+} which is an f^6 system, and we have seen that if you just calculate the term symbolforthe f^6 system, you are getting 7F term, and if you just use the coupling L-S couplingyou are getting j value from 0 to 6.Out of these 0 to 6 we have used Hund's ruleto get the stabilized configuration or the ground state configuration, and there we haveseen the ground state is nothing but 7F0 because it is less than half filled, and if you seethis spectrum the ground state is 7F0. So, here in this particular figure the groundstate of all the trivalent lanthanides is given from where the transition will startup to almost 40000 centimeter inverse, and you can see for Europium it is 1, 2, 3, 4, 5, 6, and again you start from the 7F now you reach to the 5D, and then again 5H, and so on.

Similarly, if you just try to get it for neodymium which is Nd3+ which is in the f^3 system youget a state that is $^4I_{9/2}$. I hope you can derive these states, and you can at leastsay that out of the different states that you have derived using this term symbol which oneis the ground state because that is the state from where the transition will start. After all,we are talking about the f-f transitions, and from there, the transition will start, and dependingon the different selection rules that can apply for a given transition we can get differenttransitions like this or this or this. We will just see some of the spectra and how they exactly look when you record this spectrum in the aqueous medium.



So, this is the spectrum of (Lanthanide) perchlorate salt dissolved in acidic solution, and dissolved in the aqueous media. So, you can say that starting fromPraseodymium then neodymium, and then samarium. So, you can see they both have some f-electrons. So, they are mainly having either f-f transition or f-d transition. As you have seen thef-d transition is mainly permanent in cerium, praseodymium, and terbium. These are mainlydominated by the f-f transition.

If you just look carefully at the spectra the first thingyou can always see is the epsilon value is very low. It is less than maybe 10 in manycases. Whether you choose any of the lanthanides, and you see it in the trivalentstate this is very low. This is because these are mainly f-f transitions with the ΔL equal to 0. So, they are parity forbidden. They are not allowed, but because of someadmixture of the different parity with f orbital. You see this transition, but again theyare not allowed. So, they have very weak intensities. Now, one thing if you seevery carefully that these are very sharp transitions, and again the sharpness comes from the deepburied orbitals because we are in the transition is between the fand f orbitals. So, theyare deeply buried anddo not have much influence from the external environment.

The other selectionrule that we know ΔS is equal to 0. That is a spin change or you can say that the spin multiplicitychange should be 0, and you can again see that your initial transition or your bound statehasa spin multiplicity of $2S + 1= 3$.If you see a transitionin which suppose this is not followed, and again as I said this is not allowed.So, if you have this, and both possibilities (ΔL =0, and ΔS= +/- 1) it is a Laporte forbidden, and yourspin (multiplicity Change) is ±1, but not 0. Then it is called doubly forbidden transition, and theirintensities again largely decreased.

I will just repeat it. What I mean tosay is that the spin multiplicity should be the same when you have a transition. If yourspin multiplicity is changing in a transition, their intensity falls drastically because thisis a forbidden transition. So, ideally, your ΔS should be 0 for a transition to be allowed, and here again, you can see your spin multiplicity is 3, and here it is 1. So, here you can saythere is a change.

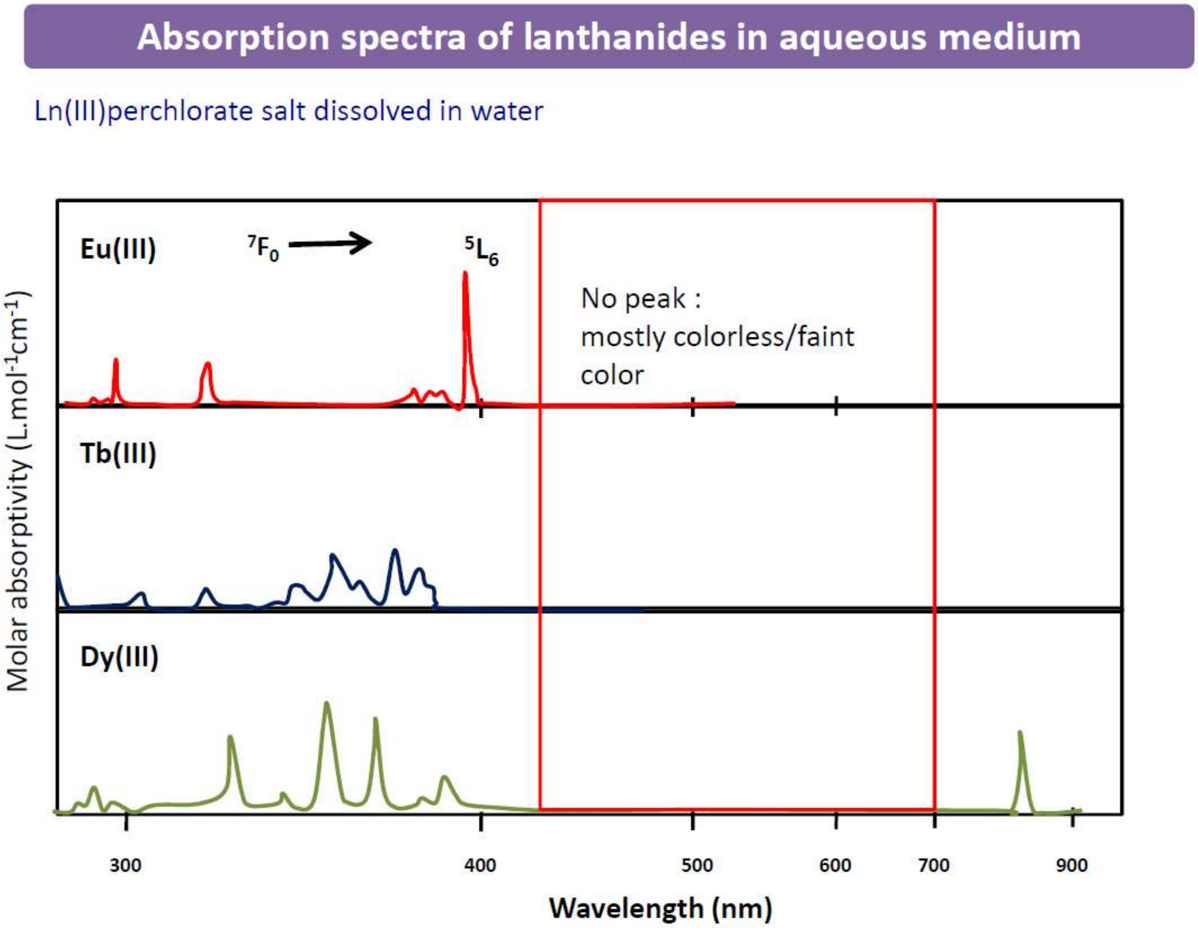
So, this is not allowed. Because of that, the intensity is very weak,but if you compare this with this, these transitions are comparatively more allowed and havea better intensity. If you compare the same multiplicity then again, the overlapbetween the orbitals, and other admixtures comesinto the picture, but generally, if youhave a transition with the same multiplicity, they are more allowed compared to thetransition which is changing both your there is no change in the f-f or ΔL value, and there is change in ΔS. So, these kinds of transition are not allowed. Here again, youcan see, if you just see this spin multiplicity then it is 4, and whatever is with the 4 theyare a bit more allowed compared to the one with the lower numbers.

Here I have marked a peakwith the red color. Some of the transitions are very much affected by the environmentalthough we say that these are the inner orbitals, still they can have some influence onthis kind of transition, and they are known as hypersensitive transitions. This is oneof the hypersensitive transitions that occur in the Neodymiumspectra, and people use thiskind of transition to get information about the change in coordination structure, the metal-ligandcomplex, and the nature of metal-ligand complex around in any phase you can see in solutionsalso.I must again show you the spectra of Samarium, and in a very similar way you can seethe spectra of other ions like Europium, and here you just remember this peak (marked 5L6). It isa very important peak when we talked about luminescence spectroscopy, but just forthat reason I just want to remember that you have a transition from 7F0 to 5L6, and that happens around 394 (nm).

If you see this is around 394 (nm). So, this is one of the most prominentpeaks in the Europium 3 spectrum. Again, you have different prominent peaks. So, ifyou see the use, of one of those use of these transitions, you can see the colorsthat you are getting. You can see in all these we have some transition in the visible region.

When I say visible region, I am talking about maybe 400 to 700 regions in thisregion, and you can see there are certain peaks. So, always in this region, there are some peaks, and as

I have told you in the previous slides when you have some band it willgive you something called spectral color, and when you have some spectral color, the complementary color is visible to you, and since all these have some peaks in the visible region.



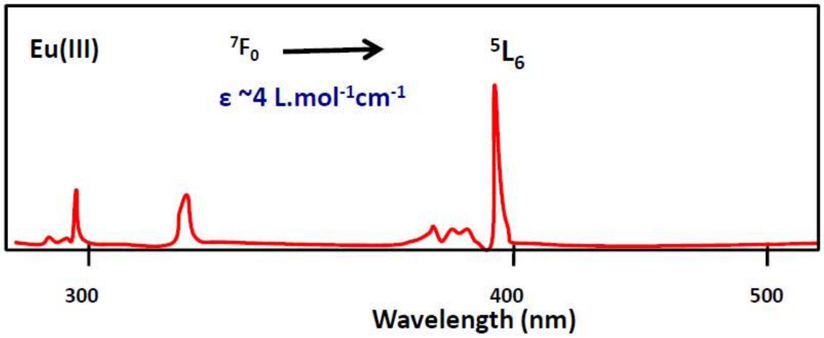
Absorption spectra of lanthanides in aqueous medium

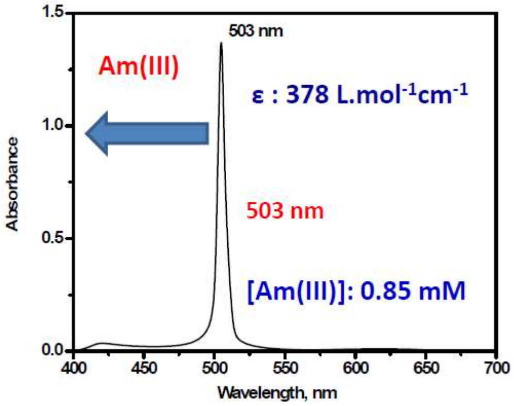
Ln(III)perchlorate salt dissolved in water

No peak : mostly colorless/faint color

If you just draw this 700 nm to 400 nm region, visible region, you can see there is almost no peak or maybe very small in certain cases you can say. So, you see most of the timeif you have Europium salt it is almost time colorless. It is colorless. Similarly,if you have a Terbium salt not a very good color, but if you take the oxide that is Nd2O3 this has a very good blue color whereas most of them are colorless. This too has somecolor because again you can see some transition to the visible region of the spectrum. So, whenever you see the transition in this region you can expect some color when you preparesolutions of this kind of lanthanides, but if you are not able to see any peak in thisregion it should be colorless.

Absorption spectra of lanthanides in aqueous medium

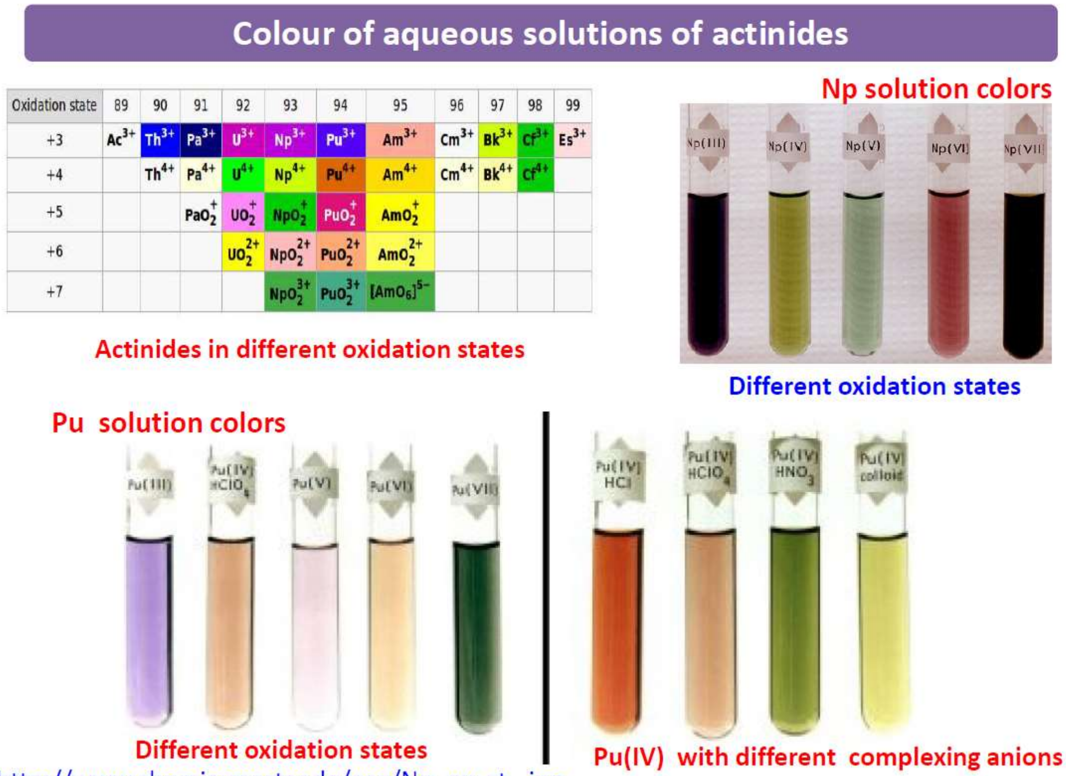




Here, I tried try to compare the spectra of trivalent lanthanidewith trivalent actinide. Here we have taken an example of Europium, and here it is Americium, and we know that it is both are same f6 system. One thing you can directly see fromthe spectra is the epsilon value. See the epsilon value it is less than 4 (for Eu (III)), but hereif you see the epsilon value sorry this is the optical density. So, we must calculatethe epsilon value using the relation A is equal to εCL.

So, absorbance you know fromhere, E you must calculate, and concentration is given. So, you can calculate this for thepath length of 1 centimeter. You can calculate, and we found that the epsilon is very high.So, you can see that they are trivalent ions i.e., Eu^{3+} and Am^{3+}, and since they are being involvedin 4f, and they are being involvedin 5f, and as we have said initially that the 5f is more diffused, and because of that the interactionor you can say that perturbation in 5f is more compared to the 4f. So, these transitionsare more allowed or their epsilon is on the higher side compared to the transition inthe lanthanides.

So, this is one of the examples I have given for the transition of trivalentlanthanide, and actinide where you can directly see that. It is very difficult to talk about the broadness,but in general, the 5f should be broader compared to the 4f, but here since the scalesare very different you may not be able to get it straightforward, but their broadnessshould be on a higher side compared to the broadness that we observe into the lanthanides.So, we have taken care of the trivalent. Let us see what the tetravalent, and the pentavalent look like because in lanthanide we are mainly talking about the trivalent because they aregroup oxidation state is +3, but when you talk about the actinides you can have +2 to +7. So, let us see what the other oxidationstates will look like when you talkabout the actinides.



Colour of aqueous solutions of actinides

Oxidation state	89	90	91	92	93	94	95	96	97	98	99
+3	Ac^{3+}	Th^{3+}	Pa^{3+}	U^{3+}	Np^{3+}	Pu^{3+}	Am^{3+}	Cm^{3+}	Bk^{3+}	Cf^{3+}	Es^{3+}
+4		Th^{4+}	Pa^{4+}	U^{4+}	Np^{4+}	Pu^{4+}	Am^{4+}	Cm^{4+}	Bk^{4+}	Cf^{4+}	
+5			PaO_2^+	UO_2^+	NpO_2^+	PuO_2^+	AmO_2^+				
+6				UO_2^{2+}	NpO_2^{2+}	PuO_2^{2+}	AmO_2^{2+}				
+7					NpO_2^{3+}	PuO_2^{3+}	$[AmO_6]^{5-}$				

Actinides in different oxidation states

Np solution colors

Different oxidation states

Pu solution colors

Different oxidation states

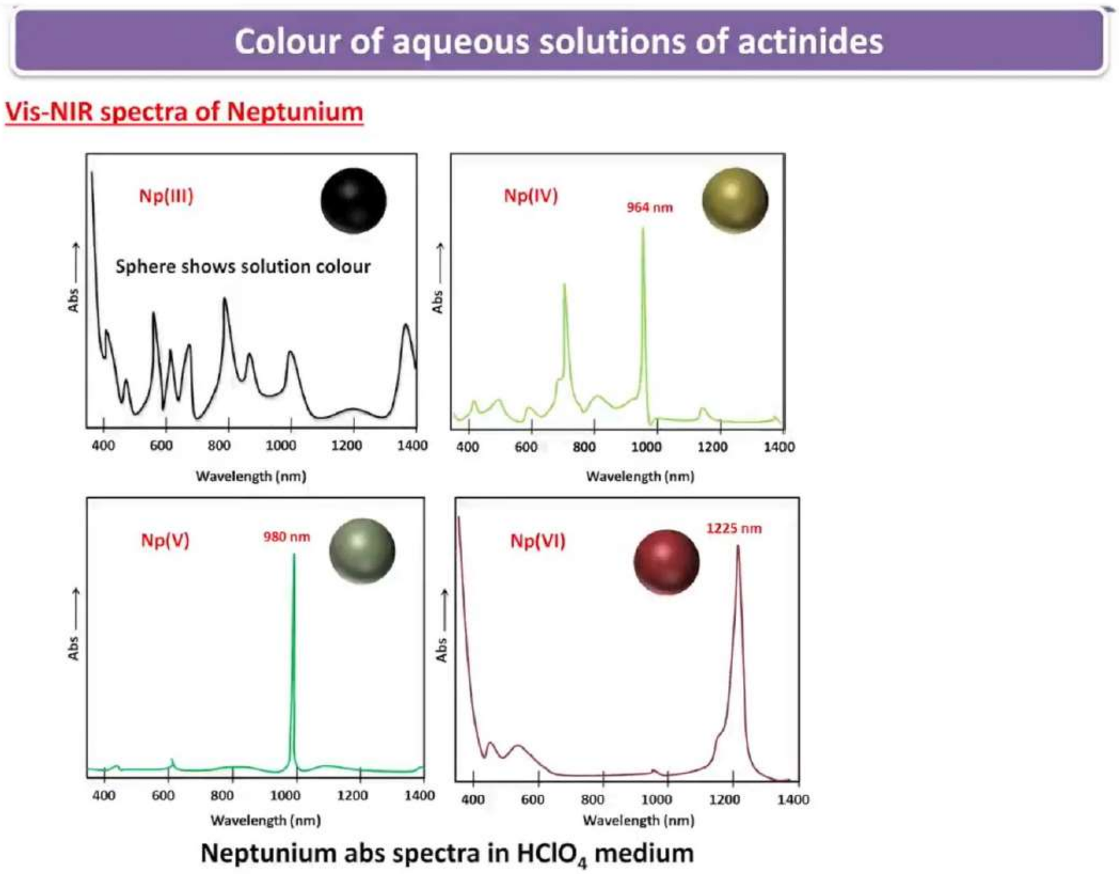
Pu(IV) with different complexing anions

http://www.chemie-master.de/pse/Np_ox_st_.jpg
https://en.wikipedia.org/wiki/File:Plutonium_in_solution.jpg

You see the actinides as I showed you that their oxidation state canbe varied from +2 to +7. You see almost all the oxidation states have some color. Everybodyis giving some beautiful colors and some of the real solutions that they put in the literature.If you see those colors, it is supposed you take the neptunium solution this is neptuniumin a different oxidation state it is like from 3 to 7. So, it is like 3 this is 3 this is4 5 6, and 7.

If you see there is a drastic change in the color when you are moving from3 to 7. Suppose you take the plutonium solution again there is a beautiful color that changesfrom 3 to 7, and the more interesting thing you can see in this diagram. Everybody is plutonium 4, what we are changing? is the media. We start with an HCl media then perchloricacid then nitric acid, and finally, we make some collides which are again in aqueous mediaat a slightly higher pH. So, you can say although everybody's plutonium 4 still their color is different.

Why? Because when we have different kinds of complexing anions in themedia they can very well interact in a very different way with the 5f orbitalsof these plutonium ions, and because of the splitting of those orbitals in the presenceof different kinds of complexing anions they gave very distinct UV spectra, and some ofthe lines are getting maybe allowed, and some of the lines are getting forbidden, and thatcauses a change in the color because now we have a different spectrum different perturbationsdifferent f-orbital splitting in the presence of different kind of anion. So, you can seethat just by changing the anions you can change the colors there, and that shows how stronglythis f-orbital the 5-f orbital has influence or how strongly it can interact with the external environment compared to the lanthanides.



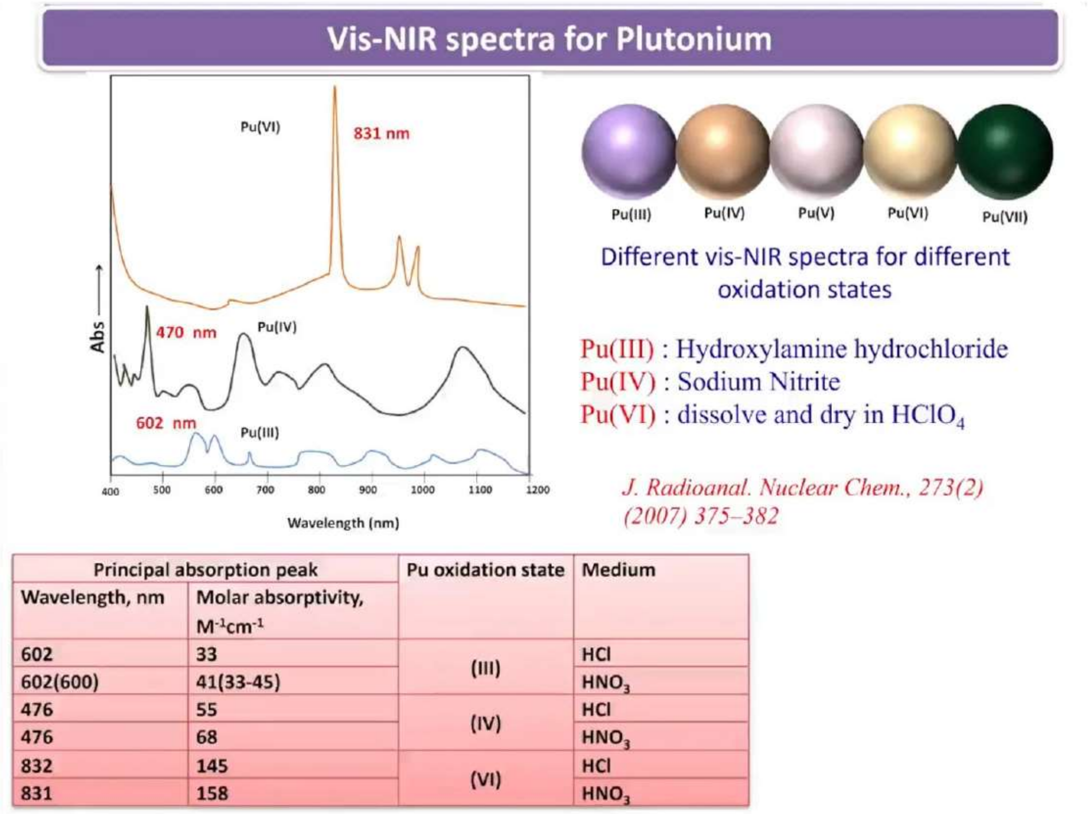
Colour of aqueous solutions of actinides

Vis-NIR spectra of Neptunium

Neptunium abs spectra in $HClO_4$ medium

If you see the spectra neptunium 3 will look like this neptunium 4 again looks very different than neptunium 3 neptunium 5 then neptunium 6.One thing I just want to mention here if you see the spectra everybody looks a bit differentfrom others suppose you see neptunium 4 it has two peaks but if you see neptunium 5 it has only one peak, and if you see neptunium 6 it is having a peak but in the NIR region.The peak position is around 1225 nm in this case it is around neptunium 4 so it is around 964it is around some 715 or so it is around 980. So, you can see that every oxidation state hassome different peak or you can say they have some distinct spectra. So, we will try touse this information when we study the applications of this UV spectroscopy into the lanthanide/actinide chemistry. Do remember that they have very different spectra. Again, we have seen the spectra ofneptunium with different colors, and with different wavelengths, and here again, if you correlateagain with the color, you can see this region may be up to 700 to 750 region you are gettingsome peaks here. Here also you are getting some peaks.

So, here you see although this intensity is very low still it is enough to give you a very good color. So, whenever you have some peaks in this region then definitely you are bound to get somecolor into the solution, and this intensity of the color will depend on the epsilon or the strength of these peaks how strong these peaksare absorbing or strongly they absorb the light. So, depending on that you will getthe corresponding complementary colors.



Vis-NIR spectra for Plutonium

Different vis-NIR spectra for different oxidation states

Pu(III) : Hydroxylamine hydrochloride
Pu(IV) : Sodium Nitrite
Pu(VI) : dissolve and dry in $HClO_4$

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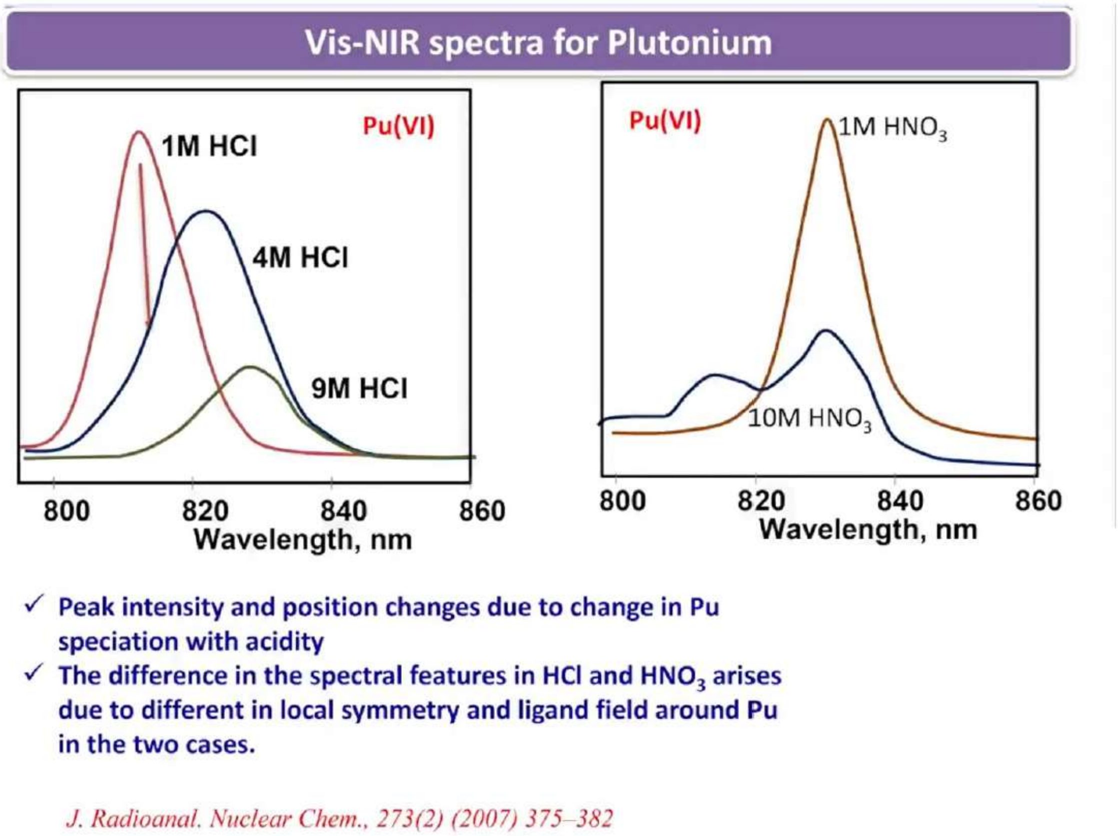
Principal absorption peak		Pu oxidation state	Medium
Wavelength, nm	Molar absorptivity, $M^{-1}cm^{-1}$		
602	33	(III)	HCl
602(600)	41(33-45)		HNO_3
476	55	(IV)	HCl
476	68		HNO_3
832	145	(VI)	HCl
831	158		HNO_3

We will see the UV spectra of the plutonium.Again I have shown you that from 3 to 6 when you go you are getting different colors. If you see the spectra for Pu(III), (V) and (VI), but I have not shown you the spectrum of Pu(V). I hope by the time you can understand that all these 5 whether you are talking aboutplutonium 5 or uranium 5 are very unstable concerning the disproportionation, and because of that the spectra of plutonium 5 are not that straightforward it will getdisproportionate, and in the acidic solutions, and if you are using too much of basic media, chancesof hydrolysis is there. So, because of the disproportionation, we are not giving the spectraof plutonium 5, and all these spectra where plutonium 3, 4, and 6 are not that easyto form. As I told you in the very beginning one of the most stable oxidation states ofplutonium that exist in water is generally +4 in the acidic media, but since theredox potentials are very close to each other. So, in the solution, you will get ideallyall these 3, 4, 5, and 6 everything should be there in the solution, and 5 will again be there, but it will be disproportionate to 4, and 6.

So, we are mainly getting 3, 4, and 6, and then you must stabilize them to get a spectrum because you cannot have amixture of all these things, and you cannot record the spectra. So, you must stabilizethem before decoding the spectra, and these are some of the reagents that are commonlyused for stabilization. For plutonium 3 we generally use hydroxyl and hydrochloride,plutonium 4 is the sodium nitrite, and for preparing plutonium 6 solution we generallyuse an oxidation that is HClO4 itself is acting as an oxidant we use this powder plutoniumoxide or plutonium oxide solution in the solution form. We add perchloric acid we do 2, 3 timesdry, and then we again dry it, and we again add HClO4, we again dry it by the timewe are not getting a spectrum that is characteristic of the plutonium 6. Here I have given youthe different peaks, and their molar absorptivity for the plutonium solution.

Here I just wantto emphasize that if you see you are changing the medium, and there is some change in thepeak position, and molar absorptivity that is because you are changing the ligand, and we have seen also when you are moving from HCl to HNO3 you can see there aresome changes both in molar absorptivity as well as in wavelength, and we will try to seethat since I have shown you that when you have HCl, and this is HCl, and this isHNO3 you can see almost one is you can say orange, and one is green. You can see thatjust by changing from chloride to nitrate the color has been changed, andthe first thingyou just want to notice is that if you are starting from plutonium 3, and going toplutonium 4 there are some spectral changes that I have already shown here when you arestarting with plutonium 3, and plutonium 4 is having some spectral changes, and when plutonium4, and plutonium 6 there is again some spectral changes. So, if you have plutonium 3you can easily identify that yes, it is plutonium 3. So, if you add nitric acid to plutonium3 or HCl to plutonium 3 there is a change in these peaks with increasing acidity thereare some changes, and these changes directly correlate with some interaction between plutonium3, nitric acid in plutonium 3, and chloride ion. So, to understand the kind of interaction, and the nature of species that have been formed in different conditions or different acid strengthswe can use this kind of spectra.



Vis-NIR spectra for Plutonium

- ✓ Peak intensity and position changes due to change in Pu speciation with acidity
- ✓ The difference in the spectral features in HCl and HNO_3 arises due to different in local symmetry and ligand field around Pu in the two cases.

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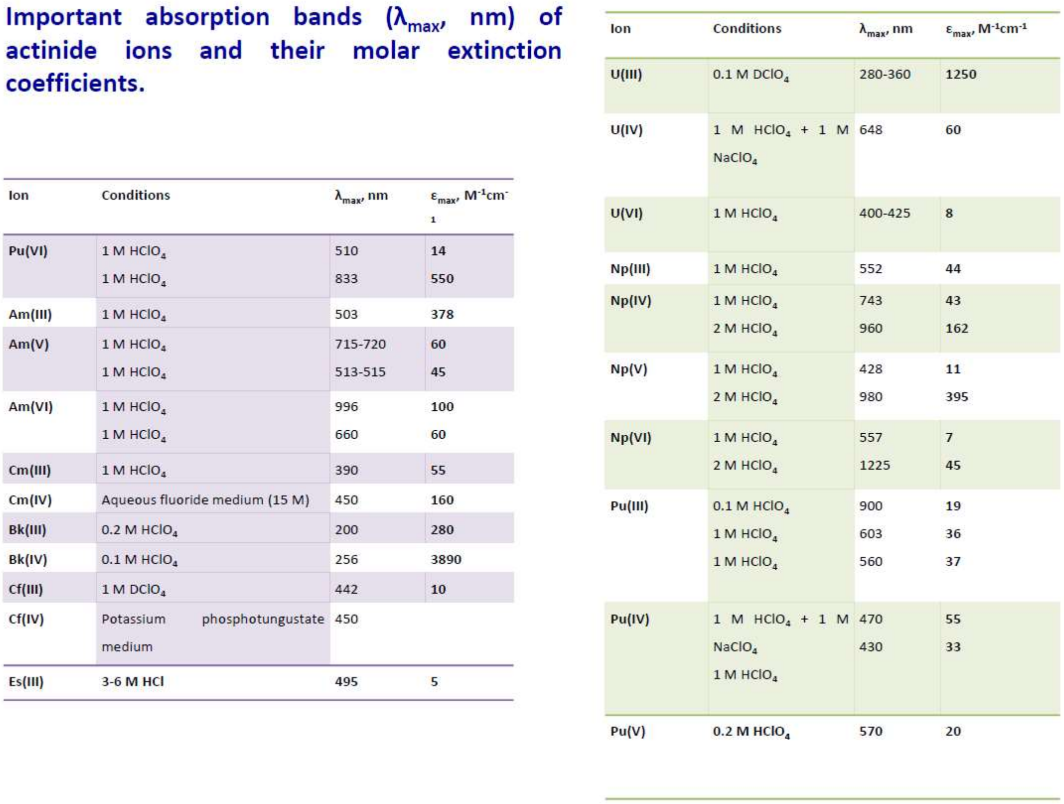
Here again, the same thing is for the plutonium 4. Similarly,you can see for plutonium 6 there is a constant decrease when you are addingHCl because it will lead tothe formation of different species of plutonium in the hexavalent state.So, because of the change in the speciation, there is a change in the spectral intensity.Nitric acid again there are certain changes, and from these changes, you can tellthat yes, the species are different. The species that exist at 1 molar may be very differentfrom the species that exist at higher molarity may be 9 molar HCl in this case, and 10 M HNO_3 in this case.



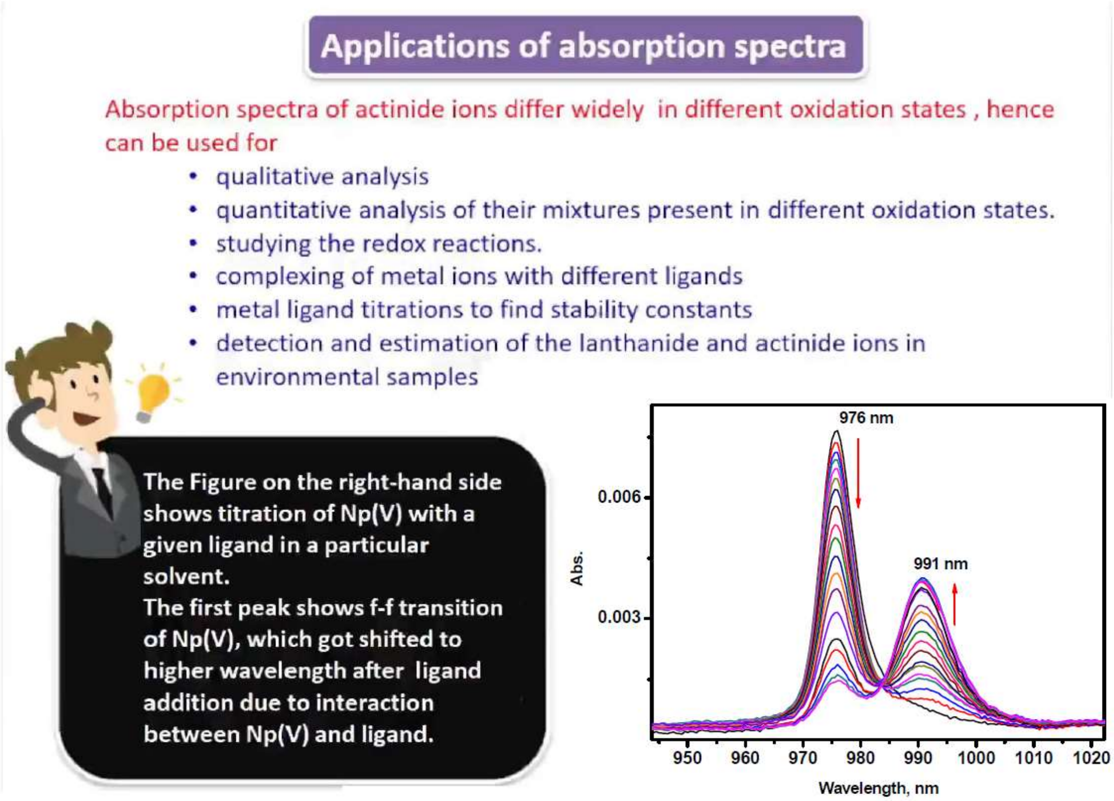
Important absorption bands (λ_{max}, nm) of actinide ions and their molar extinction coefficients.

Ion	Conditions	λ_{max}, nm	ε_{max}, $M^{-1}cm^{-1}$
Pu(VI)	1 M $HClO_4$ 1 M $HClO_4$	510 833	14 550
Am(III)	1 M $HClO_4$	503	378
Am(V)	1 M $HClO_4$ 1 M $HClO_4$	715-720 513-515	60 45
Am(VI)	1 M $HClO_4$ 1 M $HClO_4$	996 660	100 60
Cm(III)	1 M $HClO_4$	390	55
Cm(IV)	Aqueous fluoride medium (15 M)	450	160
Bk(III)	0.2 M $HClO_4$	200	280
Bk(IV)	0.1 M $HClO_4$	256	3890
Cf(III)	1 M $DClO_4$	442	10
Cf(IV)	Potassium phosphotungustate medium	450	
Es(III)	3-6 M HCl	495	5

Ion	Conditions	λ_{max}, nm	ε_{max}, $M^{-1}cm^{-1}$
U(III)	0.1 M $DClO_4$	280-360	1250
U(IV)	1 M $HClO_4$ + 1 M $NaClO_4$	648	60
U(VI)	1 M $HClO_4$	400-425	8
Np(III)	1 M $HClO_4$	552	44
Np(IV)	1 M $HClO_4$ 2 M $HClO_4$	743 960	43 162
Np(V)	1 M $HClO_4$ 2 M $HClO_4$	428 980	11 395
Np(VI)	1 M $HClO_4$ 2 M $HClO_4$	557 1225	7 45
Pu(III)	0.1 M $HClO_4$ 1 M $HClO_4$ 1 M $HClO_4$	900 603 560	19 36 37
Pu(IV)	1 M $HClO_4$ + 1 M $NaClO_4$ 1 M $HClO_4$	470 430	55 33
Pu(V)	0.2 M $HClO_4$	570	20

So in this table, you can find that most of the actinidesthat we generally use for our different kinds of studies that they are like plutoniumamericium or neptunium, and different conditions in which we generally prefer to store themor so the spectra that is in different conditions are given in the previous slide that is innitric acid as well as HCl medium. But here we have just compiled the data in the perchloricacid medium. Why? Because the perchlorate that is $HClO_4$ has anion that is ClO_4^-, and this is kind of a non-complexing anion, and when we recordspectra in this kind of anions, what we assume that whatever spectra we are getting it isthe spectra of the lanthanide or actinide having a very less perturbationinto their coordination sphere because of the presence of perchlorate ion. So, the levelsare not very much split. So, we say that it is something called not exactly freeion but very close to the free ion spectra, and you can see that different ions have differentlambda max and different molar absorptivity constants.

For example, you say that neptunium 5 has to have a major peak around 980 whereas if you see neptunium 6 it has a peakat major peak around 1225. Again neptunium 4 is having a peak at around 960. So just byrecording these spectra, you can see we have information about the different lambdamax. From the table, you can get information about the different lambda max, and their E_{max}, and that is useful when you are trying to identify a proper species or you can say agiven species into a medium.



Applications of absorption spectra

Absorption spectra of actinide ions differ widely in different oxidation states , hence can be used for

- qualitative analysis
- quantitative analysis of their mixtures present in different oxidation states.
- studying the redox reactions.
- complexing of metal ions with different ligands
- metal ligand titrations to find stability constants
- detection and estimation of the lanthanide and actinide ions in environmental samples

The Figure on the right-hand side shows titration of Np(V) with a given ligand in a particular solvent.
The first peak shows f-f transition of Np(V), which got shifted to higher wavelength after ligand addition due to interaction between Np(V) and ligand.

So, these are the applications of the absorption spectra. In general, we use them for we can use them basically for the qualitative analysisthat you have a system suppose you want to understand that okay I have given you somesystem, and you want to understand what the oxidation state is? Suppose Ihave a solution of plutonium or neptunium or any other actinide or lanthanide. The first thing youwant to understand isthe oxidation state of the metal ion in the solution.You can just record the spectrum, and as I have shown you, and you can see from thelist, and you can see from the previous spectra that different oxidation states have differentlines, and just by looking at this spectrum you have an idea that yes in my solution thisis the most prominent oxidation state. You can have a mixture also even in the case of a mixturesuppose I am having a mixture of neptunium 5, and neptunium 4. So if you have amixture of both suppose neptunium 5, and neptunium 4 then we know that neptunium 5 peak is comingaround 980, and neptunium 4 peak is coming around 960. So even if you havea mixtureof oxidation states just by looking at the spectra you can tell yes this is the oxidationstate that is present in my system. So, one of the very crucial pieces of information that you getis the qualitative analysis just by looking at the spectra you can get information yesthis is the ion this is the oxidation state that is present. The second thing is that can we makesome quantitative analysis out of this? The answer is yes. Why? Because here in this table asyou can see we have given you the epsilon values for different metal ions you can see, and we all know that, from the Lambert-Beer Law A is equal to εcl.

Suppose you measure certain spectra again I am just taking an example of neptunium suppose you measure neptuniumspectra neptunium 5. you get a peak like this which is around 980 you get someabsorbance, and what you want to calculate the concentration of the neptuniumion in the solution, and suppose you are getting a pure peak of neptunium 5, and you can justuse this epsilon around 395centimeter inverse absorbance whatever you get from here, and you can calculate the C. So, this can be used for the quantitative estimation as well. Incases even if you have a mixture then depending on the peak positions but supposeyou have a mixture of neptunium 4, and 5 the neptunium 4 is coming somewhere here, and neptunium 5 is coming somewhere here the 4 is around 960 this is around 980 even forthe mixtures if the peaks are well dissolved you can easily get the quantitative informationthat okay how much of the neptunium is present in neptunium 5 how much of the neptunium ispresent in neptunium 4. So, it can also give you information about the quantity so youcan do some quantitative analysis similarly the case of plutonium you can do thequantitative analysis of any other actinides that you want provided you know the epsilonin that media because epsilon does change depending on the media. So to get theknowledge of the quantitative analysis one thing should be always taken care the mediain which you are you want basically to get the quantity you should have the epsilon forthat particular media.

We can study the redox reactions what I mean by the redox reactionwe all know that they are very redox-sensitive both actinides are a little more redox-sensitivebecause lanthanides do have +3 oxidation state most of the time but the actinides arerather very redox-sensitive, and suppose I want to study some reactions. let us assumethat I want to study some disproportionation reaction, take the example of neptuniumonly, so you will have a spectrum like neptunium, and I want to study I have chosen this becauseit contains all the oxidation states of neptunium. If you see this reaction you have neptunium5, neptunium 4,and neptunium 6, and all these 3 oxidation states of neptunium absorb at different wavelengths i.e., Np(V) at 980 nm,Np(IV)around 960, Np(VI)around 1225 in acidic media. All these peaks are well separated fromeach other, and suppose I want to study the redox conditions in which this reaction iscomplete or I want to understand that at what acidity, what is the kinetics of the reaction? and how the reaction is going on. What we can do. we can start with this at a very zerotime in this. you will get only a 980 nmpeak but as time goes on suppose you mustfix the acidity you will start seeing these peaks. So, we can follow the redox reactionwe can follow their kinetics we can also follow many times the mechanism in different kindsof redox reactions using this peak information.since we have shown that they even vary theirpositions, and the epsilons do vary not very much but they do vary depending on theligands you add.

So here I just give you an example of some titrations that how the ligandswill affect the complexation. So here just for example suppose you have a solution inwhich neptunium is coming around 976 nm this is the solution that I have specificallyprepared in some kind of ionic solvents. So, the peak is not at 980 but a little on thelower side but suppose you have some transitions that are coming at certain peaks, and in those solvents, I have added some ligand, and you can see that peak is shifting from976 to 991. So by the shift, you can get some of the neptunium has been complex, and if youkeep on adding the titrant or you keep on adding the ligand you will get a spectrum likethis, and we can use different mathematical equations to get the exact complexation constantbetween this neptunium 5, and that particular ligand and we can also get information aboutthe epsilon of both neptunium 5, and neptunium 5, and whatever L you are going to use. Sothat information we can directly get from the absorption spectra, detection, and estimationof lanthanide, and actinide in the environmental sample.

This is the very important thing that we can dowith this as many times you can see the e-max is very high more than 100 many times yousee. So, what does it mean? It means that when you use an equation, and you have a spectrophotometerthat is quite good enough that you can easily measure 10^2 orders of absorbancein the range of 0.01 I should say absorbance. If you have a spectrophotometer of thiskind that can easily measure 0.01 then if you put this value as 0.01, and suppose yourepsilon for such a species. let us say this is more than 1000. So, you can say it is 1000c into 1. So, you can see easily that c is nothing but 10^{-5} molar.So, you can say even just by simple measurement you can get an idea about the concentration, and that too a very low concentration. Because when we talk about the environmental sample the concentrations are very very low.

Much lower than whatever, I have shown10^{-5}, andin many cases we use some chromophoric ligands such as the Arsenazoto get in very high epsilon for that complex, and for that, we just mix the actinide, and lanthanidethat we want to get the information of the concentration with that chromophore.Then we record, and the beauty is that the epsilon goes to as high as 10 to the power5, and if your epsilon is such a high you can easily go to very low concentrations ofthe lanthanide, and actinide, and you can really see the samples into the environmental media., and this I would just like to end up today's lecture, and we will meet in the next lecture.

Thank you very much

Contact Detail:
Email: mpatra@barc.gov.in
Phone: 022-25594576