Lanthanide/Actinide Luminescence Spectroscopy
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Week – 11
Lecture – 51

Hello everyone, and welcome back to the series of lectures on Actinide Chemistry. In the last lecture, we have left on the absorption studies of lanthanides, and actinides.

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 $HClO_4$	510	14
	1 M $HClO_4$	833	550
Am(III)	1 M $HClO_4$	503	378
Am(V)	1 M $HClO_4$	715-720	60
	1 M $HClO_4$	513-515	45
Am(VI)	1 M $HClO_4$	996	100
	1 M $HClO_4$	660	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 $HClO_4$	743	43
	2 M $HClO_4$	960	162
Np(V)	1 M $HClO_4$	428	11
	2 M $HClO_4$	980	395
Np(VI)	1 M $HClO_4$	557	7
	2 M $HClO_4$	1225	45
Pu(III)	0.1 M $HClO_4$	900	19
	1 M $HClO_4$	603	36
	1 M $HClO_4$	560	37
Pu(IV)	1 M $HClO_4$ + 1 M $NaClO_4$	470	55
	1 M $HClO_4$	430	33
Pu(V)	0.2 M $HClO_4$	570	20

In the Tablein slide, I have given the lambda max as well as the epsilon max which is the molar absorptivity of different actinides in one molar perchloric acid in the table shown in the slide. You can see that many of the actinides have very high epsilon values. What this means is that you can measure even a very small quantity of these actinides using UV spectroscopy. In the application part, we have already discussed what are the kinds of applications you can think of using absorption spectra.

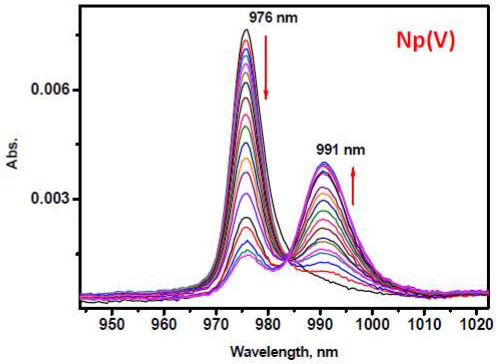
Applications of absorption spectra

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 side shows titration of Np(V) with a 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 of Np(V) with ligand



The first one is qualitative analysis, where we just want to have an idea of the oxidation state. You can also do some quantitative analysis provided the medium in which you want to do the quantitative analysis, you should be having epsilon value of actinide in that medium. So, if you know the epsilon values, you can do quantitative analysis also.

I have given you some examples of the redox reactions also. where, I have shown you that one can study the kinetics of the redox reaction using UV-vis spectroscopy, and the complexation of metal ions using different ligands as we have seen in the previous slides that once these ions make a complex with the different kinds of ligands under a given set of chemical conditions, their absorption spectra will change, and based on that changes, if

you do a titration that I have shown in the figure here in slide. I have shown you that if someone starts with the known concentration of neptunium, and does the titration with a ligand, there is a shift of the peak that occurs at around 976 (nm) for neptunium in given media before titration to 991 (nm)after excess ligand addition. if one does systematic titration and follows the spectral changes, then by fitting the titration data (using certain software based on the Lambert-Beer Law), one can get the step-wise stability constant of the different MLn complexes just using this spectrophotometric titration.

You can also do quantitative estimation of the lanthanide, and actinide that are present in the environmental sample in a very small quantity. In cases where the quantity is so small, then we generally prefer to use chromophoric reagents which make a complex with lanthanide or actinide with a very high epsilon value, and because of their very high epsilon value, you can go to a very low concentration.

Luminescence Spectroscopy

Some Basic Terminologies

Absorption: An absorption spectrum measures wavelengths at which a molecule absorbs light

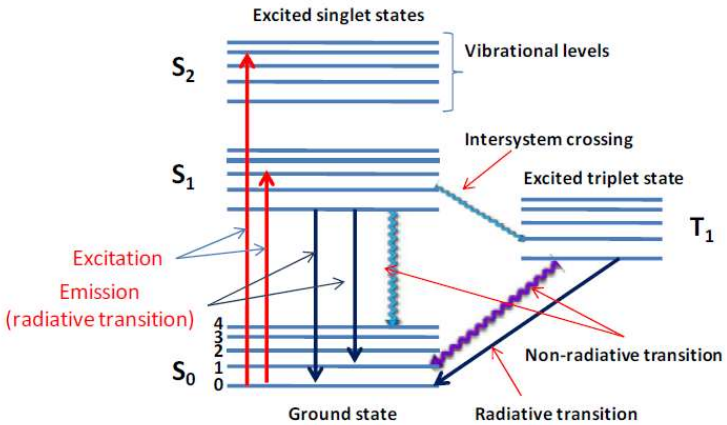
Excitation: An excitation spectrum determines the wavelengths of light necessary to produce emission or fluorescence from the molecule.

Emission : Emission of electromagnetic radiation on **excitation** by an **external source**

"**Luminescence**" a phenomenon of emission of light (**visible region**)

"**Fluorescence** " for very **short period** after excitation

"**Phosphorescence**" for relatively **long period** as compared to fluorescence



With that, we will move to the other spectroscopy which is called emission spectroscopy.

there are certain terms that you may be familiar with, but I will just want to give a brief note on these different terminologies. The first one is absorption which we have already discussed in the previous lectures.

The next term is excitation. So, are the excitation spectra, and the absorption spectra are same? The answer is not exactly. let us assume that you have a species A, with absorption spectra given in slide. In absorption spectra, the complex gets to an excited state with a certain wavelength of light. So, you are getting this kind of spectra, wavelength versus intensity or more specifically absorbance of suppose some species A, but in the excitation spectra, (when we read how to record the excitation spectra, things will get clearer)you will find that whatever peaks are coming for the absorption spectra may or may not be coming exactly same in the excitation spectra that we will see in the coming slides that how the excitation spectra are recorded, and once you know how the excitation spectra are recorded, you can very well understand, and that why there is difference between the absorption spectra, and excitation spectra.

Let's try to understand emission spectra, if you see the simple Jablonski diagram here in slide, we know that absorption starts from the ground state to any one state that can be like some singlet 1, singlet 2, and from there, the photon with the vibronic relaxation comes back to the ground state of the first excited state, and from there, it can either go by intersystem crossing to the triplet or can come back to ground State directly, this kind of coming back directly to the ground state if it is a radiative process, it will emit some radiation which can be recorded, and if these radiations are falling in the visible region, then we say it is a luminescence process, and depending on the time of the decay of excited state, it can be fluorescence which is having a very short period after excitation. Whereas, if the time is comparatively long, basically in those cases, it is going from singlet to triplet or following intersystem crossing, it's known as phosphoresce.

Eu(III) Luminescence

Every configuration has its own energy, means 3003 microstates has3003 energy states (some of them make degenerate e set also)

3003 microstates , but which one is ground state?

The ground states electronic configuration can be understood by using Term Symbol, a Symbolic representation of Energy, angular momentum and spin multiplicity of an atom.

Term symbol representation: $^{2S+1}L_j$; **Spin Multiplicity** : 2S+1

$S= s_1+s_2+....s_n$, for n electrons; j= (L+S) to (L-S)

Terms are denoted by capital letters of the Latin alphabet: S (L = 0), P (L = 1), D (L = 2), F (L = 3), G (L = 4), H(L = 5), etc.

S is the total **spin quantum** number and L is the total **orbital angular** quantum number

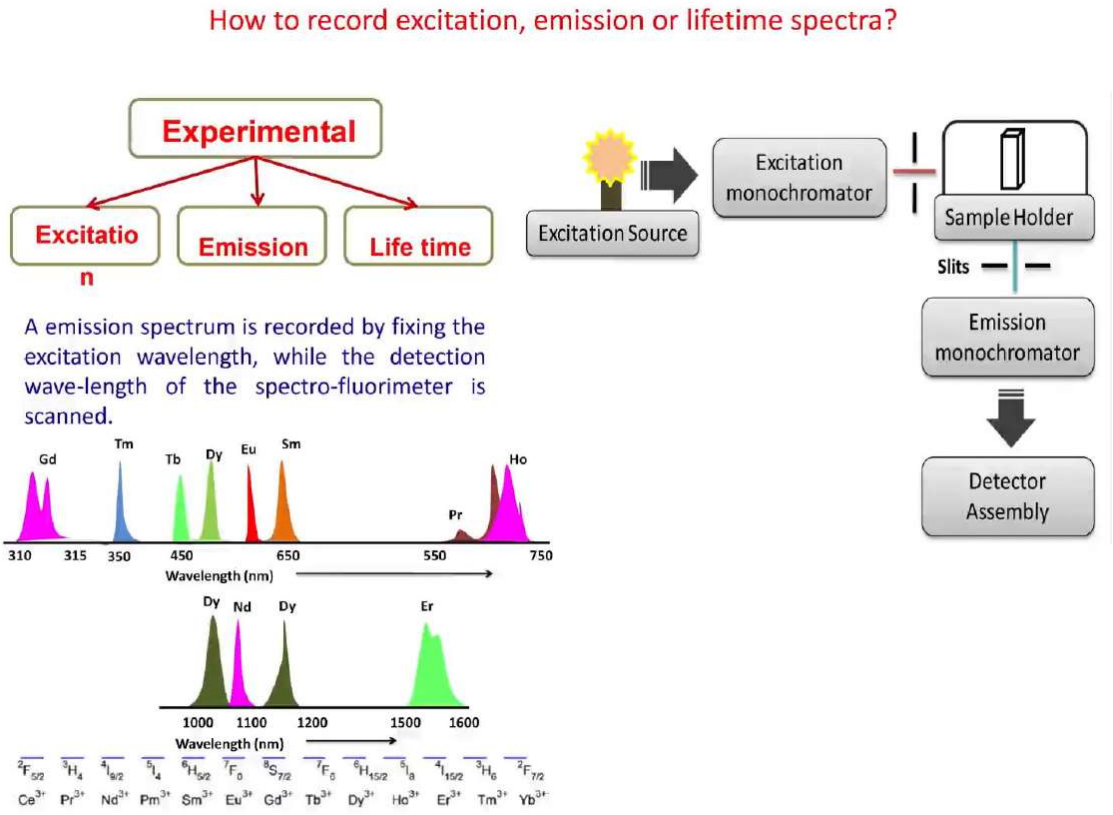
Few Term symbols for f^6 configuration are ^7F, ^5D, ^5P, ^5G, ^3L etc..

What about j value?

Since we know, L and S we can easily calculate j value i.e. j = (L+S) to (L-S). Example: for ^7F Term, L = 3 and S = 3 (as 2S+1 = 7) so j = 6,5,4,3,2,1,0 hence complete term symbol is $^7F_0$,$^7F_1$,$^7F_2$.....$^7F_6$ or ^7F_j (j = 1-6).

Let's more further, and have a look at the states that Europium does have as we have discussed with the f^6 configuration of Eu^{3+}, we have a ^7F state, and in the ^7F state, we have certain J levels, and those levels are j=1-6, giving $^7F_0$ to $^7F6$ states, and we have also seen thatout of these states or term symbols, which is the ground state, and the excited states. For Eu^{3+}, $^7F_0$ is the ground state, and $^7F_{2\text{-}6}$ is the excited state at this ^7F level.

Before proceeding ahead to study Eu^{3+} emission or excitation spectra, let us understand, how one can record the excitation spectra or the emission spectra.



So, here in the slide, I have given you some of the emission spectra of different lanthanides, and you can see that many of the lanthanides emit in the visible region. some lanthanide does emit in the NIR region also. So, most of the colored compounds of lanthanides are generally emitting in the visible region as you can see here in the slide also. The europium complex generally looks reddish under UV lamps. So, that is coming from its emission, many terbium compounds are green due to its emission in the green region.

So, how do we record this kind of spectra?

firstly, you should have a source, since we are doing a photoluminescence, our source is a xenon lamp in this case, and then depending on the metal ion, we can choose the excitation wavelength. Suppose I am using europium, we put the monochromator, and you choose a certain excitation wavelength. So, for europium, we choose a wavelength at 394 nm. If you remember the absorption spectra of europium, I have shown you there that this transition at 394 nm starts from $^7F_0$, and goes to $^5L_6$. So, this is the transition that is taking place at 394 (nm).

So, we are using this transition at 394 nm for Eu^{3+} excitation, and once you excite, then there are some emission spectra. So, what we are doing to record these emission spectra?

we want to record the emission spectra, and what we are doing, we are first fixing the excitation wavelength. In this case, I fix at 394 nm, and then after excitation, I scan the emission monochromator to get emission spectra to get specific lines for the metal ion or its complex. So, this is the intensity, and this is the emission lines we get. So, remember, to record the emission spectra, we are fixing the excitation wavelength.

Similarly, if I want to record the excitation spectra, here I will also try to explain the difference between excitation, and absorption spectra. So, suppose I want to record an excitation spectrum, I want to scan the excitation wavelength at a fixed emission wavelength. For the Eu^{3+}complex, we have fixed it at a certain value, let's say 612 nm. Now, what will happen, we have fixed this path (see slide). What does it mean that suppose, the metal complex gets excited by a certain wavelength, you can only see peaks in the excitation spectra only when you are seeing corresponding emission in the detector.

Suppose, I have 3 peaks in for a Eu^{3+}ligandcomplex in the UV-vis absorption spectra. But even after excitation using this absorption peak, I do not have any emission at 612 (nm). I will not see this in the excitation spectra. Now, I will try to excite at some different wavelength. Suppose, you are excited in the 394 nm region, and you can get some peak, then you will see that peak in the excitation spectrum.

So, only those peaks are visible in the excitation spectra which give photoluminescence at a given or fixed emission wavelength. So, in absorption spectra, you may get several lines, but it does not mean that all those lines are giving you the emission profile. So, by fixing the emission at a given wavelength, when we use the excitation monochromator, we are getting excitation spectra. Now, we have excitation spectra, and we have an emission spectrum.

So, let us say we have recorded both the emission spectrum and excitation spectrum of some Eu^{3+} complex. In the excitation spectra, we are getting peak maxima at 394 nm, and the corresponding emission spectra give peak maxima at 612 nm. So, now I have an emission peak maximum and an excitation peak maximum.

What I will do, I will choose the peak maximum, whatever is getting in the emission spectra, and the peak maximum whatever I am getting in the excitation spectrum, and these two positions I am using to find out the decay lifetime of the Eu^{3+}-complex.

So, to get the lifetime data, I amusing excitation maxima at 394 (nm), and emission line at 612 (nm), and both I am fixing before recording the decay lifetime of the Eu^{3+}-complex.

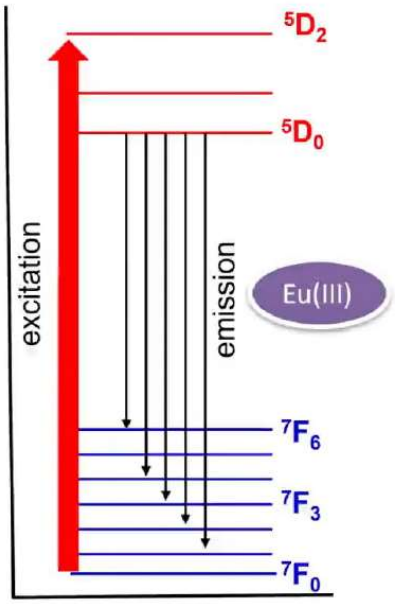
So, this is the way we record these three kinds of spectra that is the excitation spectrum, the emission spectrum, and the lifetime spectrum. Once recorded, what are the kinds of information that we can get from these spectra, we will discuss them in the next slide, and here I have just shown you the different ground state term symbols that you have derived using the term symbol method learned in the previous lectures. So, you can easily follow that, and you can try to derive the term symbol of different lanthanides in the trivalent states.

Eu(III) Luminescence

The convention to describe a transition between two $^{2S+1}L_J$ levels is to write the high energy state at the left hand side and the low energy state at the right hand side.

The arrow points from the initial to the final state. For instance, the transition from the $^5D_0$ excited state to the $^7F_1$ state in the luminescence spectrum is writ-ten as $^5D_0 \rightarrow {}^7F_1$.

The same convention is used for the absorption spectra. The transition from the $^7F_1$ state to the $^5D_0$ state is written as $^5D_0 \leftarrow {}^7F_1$ (NOT $^7F_1 \rightarrow {}^5D_0$).



Plotting the Spectra, wave number or wavelength scale

$$\tilde{\nu}\ (\mathrm{cm}^{-1}) = \frac{10^7}{\lambda\ (\mathrm{nm})}$$

It is recommended to plot spectrum in wavenumber scale with the highest wavenumber at the left and lowest at right side of the spectrum

Since I told you previously, that we will discuss the Eu^{3+} spectrum in a bit of detail, but before going into the discussion, let us see certain basic but important things that one should be able to understand before plotting or recording any kind of emission, excitation or absorption spectra.

The first thing is you should know the different kinds of levels, you should know that what is the ground state, what is the first state, and what is the second state. This we get from the term symbol.

With this information when you are exciting any Ln complex then before the excitation the first question comes at what wavelength, we should excite it, because if you have given a sample, you do not know what is the wavelength at which I must excite that, then what to do?

You can take the help of absorption spectroscopy, and as I have shown you in your absorption spectroscopy you may have more than one peak you must try at different peaks,

use them as different excitation wavelengths, and record the emission profile. At whatever excitation wavelength you are getting good emission you can say this is the excitation wavelength for this metal ion or metal ion complex.

Now, how to write a particular emission or excitation transition?

Suppose, we have excitedEu^{3+} from $^7F_0$, this is my ground state that is $^7F_0$, and after exciting it goes to $^5L_6$ or any other excited state it's going.

So, how to write this excitation transition? So there is a way to write that.

We have two options like $^7F_0 \rightarrow {}^5L_6$ or we can also write $^5L_6 \leftarrow {}^7F_0$

So, what is the right way of writing? How do we represent this transition that this is my excitation transition, and this is my emission transition?

The rule is that whenever you want to write either you want to write an excitation transition or an emission transition you should always take care that your high energy state is always on the left-hand side, and your low energy state is on the right-hand side. what it means that if you see this notation

$^7F_0 \rightarrow {}^5L_6$ is the wrong representation as the high energy state is on the right-hand side, and the right representation is $^5L_6 \leftarrow {}^7F_0$ with a low energy state on the right-hand side.

So, what we must do? we have to always keep this in mind that whenever we are writing my low energy state should be on the right-hand side.

So, what is my low-energy state here? My low energy state here is supposing $^7F_0$. So, this should be on the right-hand side, and my high energy state supposes I am using excitation transition to some $^5D_0$ this $^5D_0$ should be on the left-hand side.

so this transition I need to write like this $^5D_0 \leftarrow {}^7F_0$. Suppose I want to write about the emission transitions, here also you have to write like this only that your low energy state is on the right side but since you are talking about emission you have to write like this

$^5D_0 \rightarrow {}^7F_0$. So, only the arrow direction will change the initial, and the final state positions will not change.

So, even in the recent literature, I have seen lots of people not follow this notation strictly but I think it is a good habit that if you start following this habit that whenever you are writing you should be cautious that always your low energy state should be on the right-hand side.

One more thing is that many times whenever we are plotting any spectrum, we use either wave number or sometimes wavelength but in general convention one should plot always in wave number scale with the highest wave number on the left-hand side, and the lowest wave number on the right-hand side of the spectrum.

This is an atypical spectrum of the europium that I have given here. If you see that it has several lines that arise from the transition from $^5D_0$ to different lower states that $^7F_0$ to $^7F_1$, $^7F_2{}^7F_2$. So, you can see from this diagram very well you have exited from $^7F_0$ to $^5L_6$.

Now there is thermal or non-radiative relaxation to reach up to $^5D_0$, and further emission is taking place from $^5D_0$. So, when they are emitting you are getting a peak that is from $^5D_0$ to $^7F_0$. For quick representation, we can write this as 0-0 peak, i.e., in j-j terms. Then transition to $^7F_1$, $^7F_2$, etc. Since they start from $^5D_0$, we can write them as 0-1, 0-2, etc.

Eu(III) Luminescence

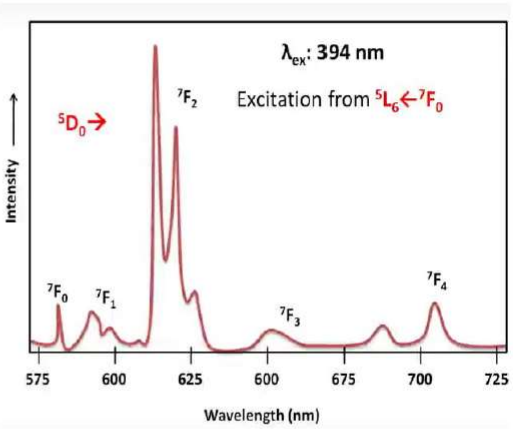
The distance between a J and the J+1 line increases with increasing J value ,i.e. The $^5D_0 \rightarrow {}^7F_1$ transition is very close to the $^5D_0 \rightarrow {}^7F_0$ transition, but the $^5D_0 \rightarrow {}^7F_6$ transition is lying more than 50 nm further to the infrared than the $^5D_0 \rightarrow {}^7F_5$ transition.

Landé interval rule: the interval between successive energy levels is proportional to the larger of their total angular momentum values J (i.e. the splitting increases with increasing J values).

The majority of the transitions observed in the luminescence spectrum are induced electric dipole transitions (ED transitions), arising from, the interaction of the lanthanide ion with the electric field vector through an electric dipole.

Intraconfigurational electric dipole transitions (e.g. s–s, p–p, d–d,or f–f transitions) are forbidden by the **Laporte selection rule**.

Magnetic dipole transitions (MD transitions) are allowed by the **Laporte selection rule**, but their intensities are weak and comparable to those of the induced electric dipole transitions.



MD transitions are largely independent of the environment and can be considered to be constant

"Internal reference"

In the Eu^{3+} emission spectrum, we'll be getting all these peaks that are $^5D_0 \rightarrow {}^7F_0$, $^7F_1$, $^7F_2$. we are getting several peaks in the emission spectrum but what information we can derive from this? First, since we know that these peaks are due to the f-f transitions, we can have some idea about the differences in the energy levels of the metal ion of the atom you are probing. You can also see that when we are moving from the $^7F_0$ to $^7F4$ states you can see the distance between the J's, and J+1 line increases. If you see the distance between F_0 and F_1 lines they are very close to each other, but the moment you go for higher j values. you can see that the distance between the two J lines is increasing. This is coming from the Lande interval rule that the interval is increasing as we are going from the left-hand side to the right-hand side in the Eu^{3+} spectrum or you can say the extent of j-j splitting has increased when we are moving towards the higher J values. The transitions that we are getting in the photoluminescence are mainly known as induced electric dipole transitions, and their origin is mainly due to the interaction of the lanthanide with the electric field vector through the electric dipoles of the electromagnetic radiations. These f-f transitions are Laporte forbidden.

So, their intensity is also not very good, but still, you get the emission lines because of the intermixing of the different states, and they are no longer pure f-f transitions. Since these are Laporte forbidden, and they are very weak. So, this is called induced electric dipole transition, but one more type of transition that you can see in the emission spectrum of Eu^{3+} is called magnetic dipole transition. These transitions are largely independent of the environment of the lanthanide ion, and sometimes they are also used in internal reference when comparing different spectra. The table in the slide shows the selection rule that is given for electric dipole, magnetic dipole as well as induced electric dipole transitions.

Eu(III) Luminescence

Various transitions observed in the Eu(III) emission spectrum

Transition from $^5D_0$	Dipole character	Range
$^5D_0 \rightarrow {}^7F_0$	Electric dipole	570-585
$^5D_0 \rightarrow {}^7F_1$	Magnetic dipole	585-600
$^5D_0 \rightarrow {}^7F_2$	Electric dipole	610-630
$^5D_0 \rightarrow {}^7F_3$	Electric dipole	640-660
$^5D_0 \rightarrow {}^7F_4$	Electric dipole	680-710
$^5D_0 \rightarrow {}^7F_5$	Electric dipole	740-770

Selection Rules for various types of transitions

Type of transition	Transition	SLJ selection rule
Electric dipole (parity change)	$4f^n \rightarrow 4f^{n-1}5d$	$\Delta S=0$, $\lvert\Delta L\rvert \leq 1$, $\lvert\Delta j\rvert \leq 1$, $J=0 \leftrightarrow J'=0$ and $L=0 \leftrightarrow L'=0$ are forbidden
Induced Electric dipole (Judd forced) (no change parity change)	$4f^n \rightarrow 4f^n$	$\Delta S=0$, $\lvert\Delta L\rvert \leq 6$, if $L=0$ or $L'=0$; $\lvert\Delta L\rvert = 2,4,6\ 6$; $\lvert\Delta J\rvert \leq 6$; if $J=0$ or $J'=0$; $\lvert\Delta J\rvert = 2,4,6$; This implies that $J=0 \leftrightarrow J'=0$ and $L=0 \leftrightarrow L'=0$ are forbidden
Magnetic dipole	$4f^n \rightarrow 4f^n$	$\Delta S=0$, $\lvert\Delta L\rvert = 0$, $\lvert\Delta J\rvert \leq 1$; $J=0 \leftrightarrow J'=0$ is forbidden

And as I showed you all these transitions are of not the same nature. Some of them are electric dipoles, and some of them are magnetic dipoles, and here I have just given you the list. So, if you see the emission line from $^5D_0$ to $^7F_0$ this is an electric dipole, but the second one is a $^5D_0$ to $^7F_1$ is a magnetic dipole transition. When I say magnetic dipole transitions

it means that their intensity does not have very much variation when we are changing the ligand field, and the rest you can see are electric dipole transitions.

So, many times this transition that is $^5D_0$ to $^7F_1$is used as an internal standard when we are trying to compare different systems of the same metal ion, and we will try to understand what the ligand strength how the ligand is splitting, and the nature of splitting? So, sometimes we use this kind of magnetic dipole transition to understand the ligands or the symmetry around the metal ion. These are some of the selection rules that generally come from the quantum mechanical calculation of what kind of transitions are allowed, and what kind of transitions are forbidden using this set of rules that is called selection rules, and depending on the selection rules those transitions follow the selection rule they are intense whereas those transitions who do not follow the selection rule they are either they do not happen or if there is some intermixing between the different f states they have a certain probability of happening, and because of that they get some intensity, but again it is a very poor intensity.

Eu(III) Luminescence

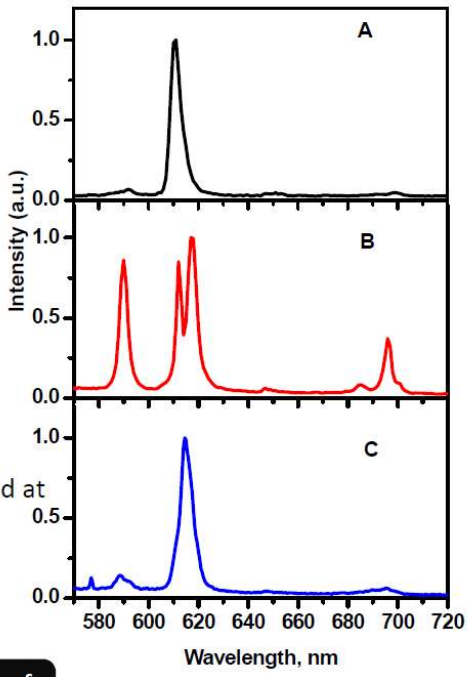
Applications of emission spectra

- complexing of metal ions with different ligands
- metal ligand titrations to find stability constants
- Detection of the lanthanide and actinide ions in environmental samples

Emission spectrum can be used to tell the symmetry around the Eu^{3+} in the complex.

An important parameter that can be derived form the emission spectra is the asymmetry ratio, it is the ratio of the $^5D_0 \rightarrow {}^7F_2$ transition peak area to $^5D_0 \rightarrow {}^7F_1$ transition peak area & is >1 for asymmetric system.

Number of emission peaks (recorded at low Temperature)
Symmetric system: less peaks
Un-symmetric system: more peaks (splitting of j terms in 2j+1 states).



A, B and C shows Luminescence spectra of Eu^{3+} in different ligand environments.

Typical emission spectrum of Eu^{3+}

We'll now discuss the application of emission spectra. Once you have the emissions spectra recorded what is the kind of information that you can draw from the emission spectra?

The first information you can easily draw is whether you have different complexes or the same complexes. When I say different complex or the same complex my metal center is the same. When I say different, I mean the symmetry around the metal ion. Suppose you have a complex let us say Europium with three different ligands that are L1, L2, and L3, what you can see directly from this figure is that although they have Europium in the center, the peak intensities and the splitting pattern is quite different from each other. So, just by looking at this spectrum what information you can directly derive is that the symmetry around the Europium ion in the three systems is different. So, this is the direct information we can get.

Suppose you want to have information about the stability then you can take any system, and as we are doing titration in the absorption spectroscopy, you can do some sort of titration here also, and from the titration data you will get the stability constant of that complex. So, this can also be used for the determination of the stability constant. You can also use this kind of spectroscopy for the detection of lanthanide and actinide in the environmental sample. The detection of uranium in various kinds of environment samples using a laser fluorometer which is a kind of emission technology technique is very common. So, this is also used for the understanding of local symmetry as well as for the quantification of the metal ion into the environmental samples.

As I said earlier you can say the symmetry is different, but what is the symmetry? You can tell using the emission spectra that will come in the next slide. But before that, as I told you you have certain peaks, and out of those peaks the peak at $^7F_1$ is magnetic dipole, rest others are electric dipole. So, if take the ratio, if you take the ratio of the magnetic dipole transition to the electric dipole transition you will get some value, that is called as asymmetry ratio. This asymmetry ratio is very important when you want to understand the symmetry around the Europium ion. It so happens that this ratio is generally high when the symmetry is very low, and the ratio is low when the symmetry is higher. For example, in water where the local symmetry around Eu^{3+} is high, this ratio is around 0.5 to 0.6. This asymmetry ratio can be used to say at least whether the symmetry is high or the symmetry is low, but what is the exact symmetry?

Eu(III) Luminescence

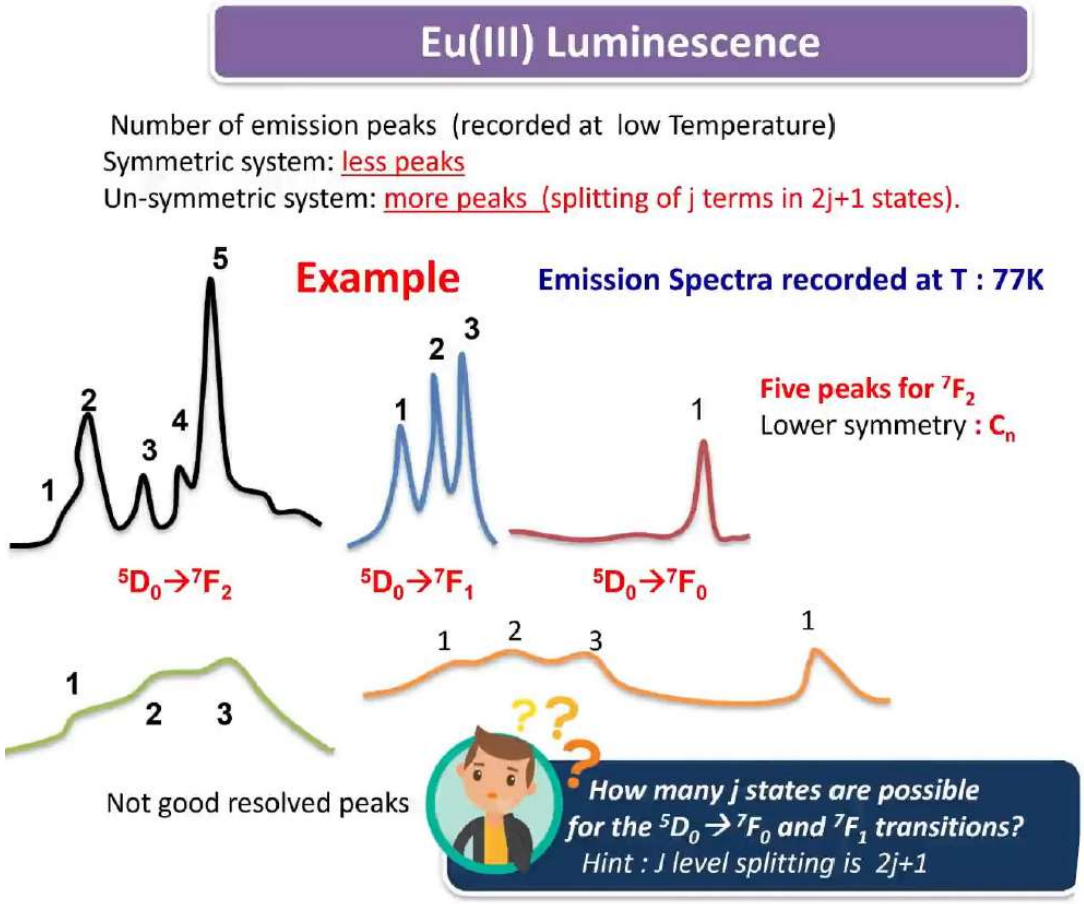
Symmetry class	J=0	J=1	J=2	J=3	J=4	J=5	J=6
Icosahedral	1	1	1	2	2	3	4
Cubic	1	1	2	3	4	4	6
Octagonal	1	2	3	4	6	7	8
Hexagonal	1	2	3	5	6	7	9
Pentagonal	1	2	3	4	5	7	8
Tetragonal	1	2	4	5	7	8	10
Trigonal	1	2	3	5	6	7	9
Orthorhombic	1	2	5	7	9	11	13
Monoclinic	1	2	5	7	9	11	13
Triclinic	1	2	5	7	9	11	13

- 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.

To get that information we must look at this table. So, as we have seen, when we have somestates let us say $^7F_0$ or $^7F_1$ or $^7F_2$etc., arises because of the L-S coupling scheme. theses ^{7}Fj states further get split because of the j-j coupling, and total j-j splitting for a given j state is 2J+1. So, you can say the $^7F_1$ can split into 2J+1 means 3 more states. So, that is ^{7}F(+1, 0,-1). So, you can say that all the J states can further split depending on the ligand field around them depending on the electric field around them. So, from this splitting pattern that we get in the J splitting, we can understand what is the exact symmetry class around that particular metal ion.

One thing you have to take care of is that you can just tell about the symmetry class. you may not be able to tell about the exact point group, because for a given point group the splitting pattern is identical. So, you may not be able to get exactly whether it is D4h, D4, or C4v, but you can certainly say that when we have certain splitting suppose you are having this splitting that the first peak is not split, and this is 2, and this is 4 (see table in the slide). So, you are having 1, 2, 4, 5, 7, etc., this kind of splitting pattern for j, you can

tell yes the europium is having a tetragonal environment, but exactly the D_4 hand C_{4v} it is not that easy to tell, but people try to tell that using other combination studies at low temperature, but that requires a lot of experience, and it is not that straightforward, but you can at least have an idea about the symmetry class just by looking at the splitting pattern of the J level. So, in the next slide, I have given some examples that how the splitting pattern for different symmetry will look like. So, for the ^{7}F2 level, the maximum j splitting is 5, and to get the maximum you should have symmetry in the triclinic region where you can say that 7 F2 should be 5 (see table in the slide).



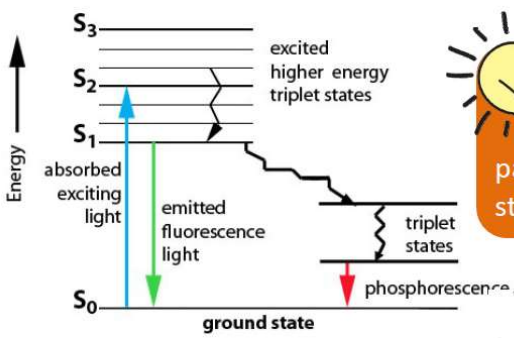
So, the more unsymmetric the environment more the J-J splitting. So, the triclinic is the most asymmetric. So, we are getting 5 peaks here, and you can say 7 F1 which has a maximum J-J splitting of 3, you are getting 3 peaks. So, if you are doing studies at a very low temperature you can get this fine splitting pattern, and from this number of fine splitting of different J levels, you can get information about the symmetry class of

Europium ion and what the symmetry around the Europium ion in this particular complexes.

We have also studied the hydration of Europium ion, and there we have seen that the luminescence spectra can also be used to find out the number of water molecules in the primary hydration sphere, and for that one needs to measure something called decay lifetime, and I have shown you that for measuring this decay half-life or decay time you have to excite at a certain wavelength and then you have to measure emission at a certain wavelength and that should be done at a fixed excitation wavelength at given emission wavelength.

Excitation spectrum - Similar to (but not exactly as) Absorption spectra

Absorbance spectrum shows the attenuation of incident light by all inter band transitions that occur at that wavelength.
Excitation Spectrum : The relative efficiencies of different wavelengths of incident light to excite the species is determined as the excitation spectrum.

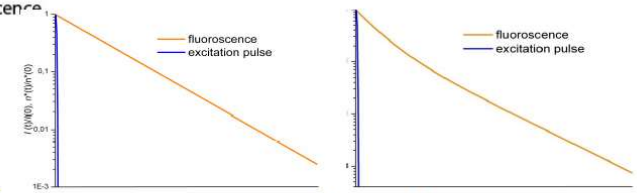


Decay time or Lifetime ?

The decay time (life time) of a particular species is time taken for the excited state population to become 1/e of the initial.

Information from the decay or life time spectra

The number of H_2O molecules in the primary coordination sphere of a metal ion ($N(H_2O)$) can be calculated from the observed life time values (τ) by the following empirical relations



Typical life time (decay curves)

$N(H_2O) \pm 0.5 = (1.07/\tau) - 0.62$ for Eu (III)
$= (0.65/\tau) - 0.88$ for Cm (III) / Am (III)
Where, τ = observed life time values in 'ms'

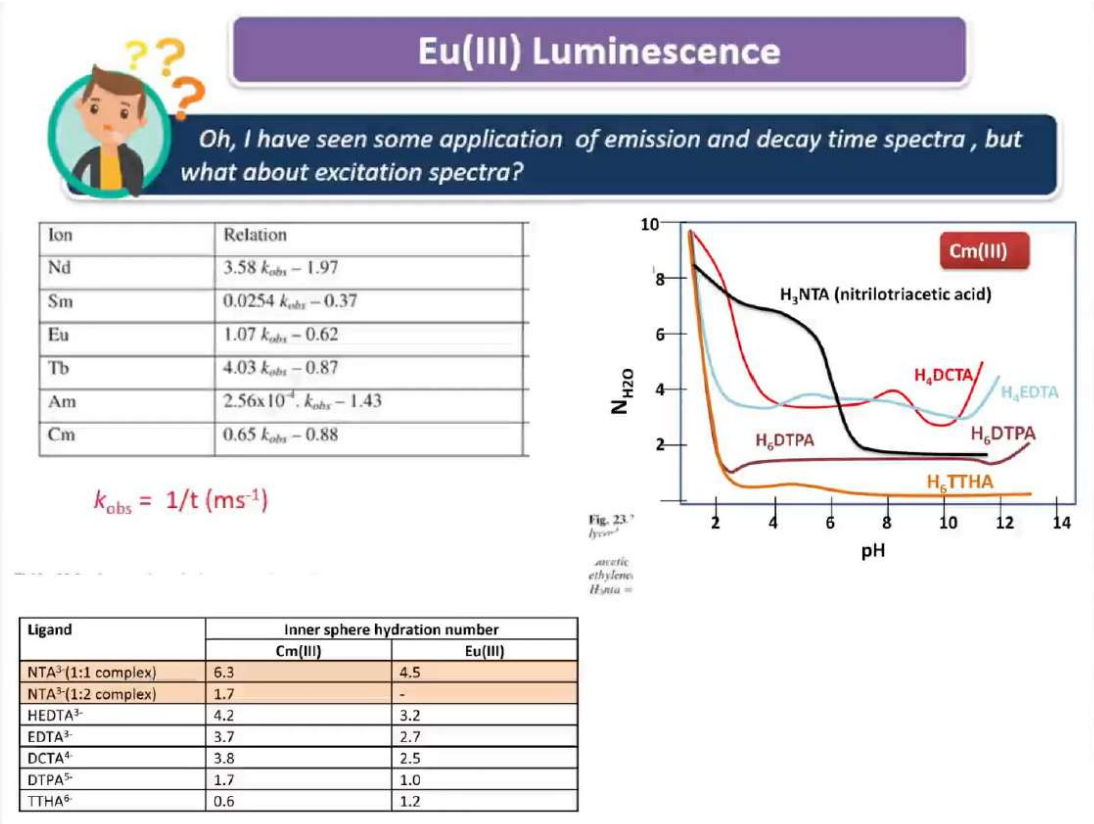
So, once you have a certain wavelength let us say for Europium the excitation at around 394(nm), and the emission at 612(nm) you will get this kind of curve as shown in the slide when you follow the decay of Eu^{3+}withtime. Once you get this kind of curve, we have to just fit this curve using a mono, bi, or tri exponential decay equations to get the decay lifetime.

So, with the decay curve with intensity on the Y-axis, and time (in milli-, micro, or nano-second) on X-axis. The decay equation is given by

$$I(y) = A.\exp(-t(x)x k_{obs})$$

So, in this equation, A in the preexponential term,t is the time on the x-axis into your decay constant, and k_{obs} is the observed decay constant.

The above equation is for the mono-exponential similarly we can write for the bi-exponential or tri-exponential, and from there you can get information about k_{obs}, and from this observed decay constant you can have an idea about the number of water molecules in the primary sphere.



How we can get an idea about the number of water molecules? because we have certain linear relationships. So, suppose we take Europium as an example, we have a direct relationship between the number of water molecules in the primary hydration sphere ($N(H_2O)$), and the observed decay constant(k_{obs}).

$N(H_2O) = 1.07k_{obs} - 0.62$

$k_{obs} = 1/t$

Here you must take care that the decay lifetime (t) is given in milliseconds.

So, suppose you have a lifetime of 100 microseconds, and as I said before using this equation you have to convert this 100 microsecond lifetime to millisecond. dousing the value of decay lifetime or observed decay constant to the above equation, the value of N(H2O) is around 8 to 9. So, directly using the above relationship with the measured decay constant you can get the idea about the number of water molecules in the primary hydration sphere. The graph in the slide shows variations in the number of water molecules in the primary hydration sphere with the pH. Here the metal ion iscurium. Suppose you have curium, and you have added some ligand into the system, and now you are varying the pH. What will happen when you vary the pH of the metal ion + ligand system?

As pH increases the ligand gets deprotonated. Let's assume, initially, curium has 8 water molecules around it, the ligand is deprotonated, and it has 2 binding sides (a bidentate ligand). So, now it can attach to the metal ion, and it can remove 2 water molecules, and since it is removing 2 water molecules. So, we are left with only 6 water molecules around the curium ion at some pH. So, depending on the nature of the ligand that can happen at different pH. For example, in the first 2 ligands, you can see that even at pH 2 the complex is strong enough to remove all the water molecules, whereas for certain other complexes such as nitrilotrilacetic acids (NTAs), this is not that straightforward. So, it is a stepwise removal of the water molecule. So, just by doing the lifetime spectroscopy, you will get this kind of information in changing the number of primary water molecules using different ligands in a set of pH conditions, and this table also shows you that for a given ligand depending on the stoichiometry of the metal-ligand complex how many water molecules are possible. So, suppose I give you a ligand that is again nitriloacetic acid, and I assume that it has a stoichiometry of 1:1.

So, if you have a stoichiometry of 1:1 how many water molecules should be there in the primary sphere, you can just follow the equation that is given in the Table. From this, you

can always get information about the number of primary water molecules in the metal-ligand sphere. So, with that, I would like to end.

Thank you. Thank you very much for listening.Thank you.

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