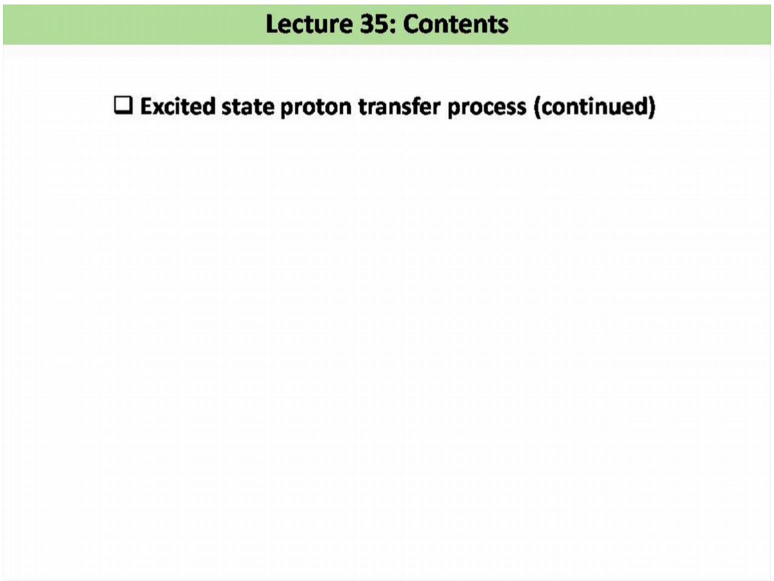
Basics of Fluorescence Spectroscopy
Prof. Pratik Sen
Department of Chemistry
Indian Institute of Technology, Kanpur

Lecture - 35

(Refer Slide Time: 00:14)

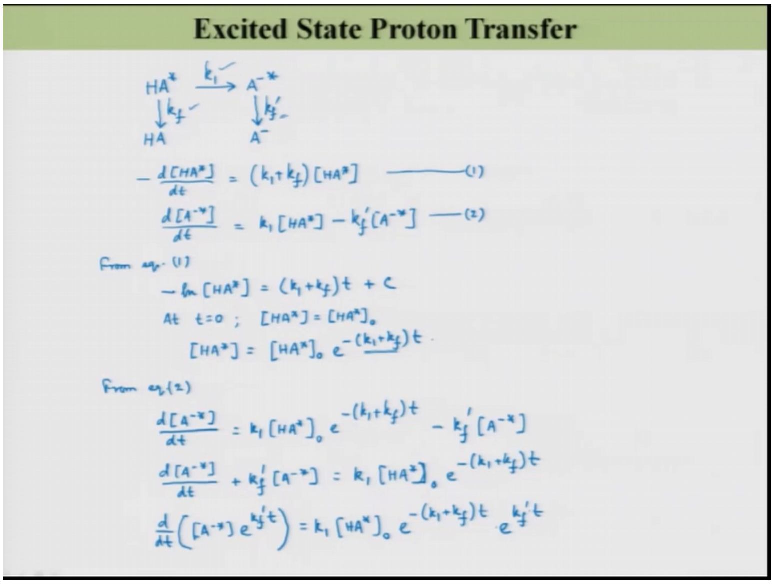


Lecture 35: Contents

☐ Excited state proton transfer process (continued)

Welcome to lecture number 35. So, in the last lecture we were discussing about the excited state proton transfer and today I would like to show you how to find out the rate of this kind of excited state proton transfer process. To start with let me take a very basic model of a two state irreversible proton transfer process.

(Refer Slide Time: 00:44)



Excited State Proton Transfer

$$\begin{tikzcd} HA^* \arrow[r, "k_1"] \arrow[d, "k_f"] & A^{-*} \arrow[d, "k_f'"] \\ HA & A^- \end{tikzcd}$$

$$-\frac{d[HA^*]}{dt} = (k_1+k_f)[HA^*] \quad \text{———} (1)$$

$$\frac{d[A^{-*}]}{dt} = k_1[HA^*] - k_f'[A^{-*}] \quad \text{—} (2)$$

From eq. (1)

$$-\ln[HA^*] = (k_1+k_f)t + c$$

At $t=0$; $[HA^*] = [HA^*]_0$

$$[HA^*] = [HA^*]_0\, e^{-\underline{(k_1+k_f)}t}$$

From eq (2)

$$\frac{d[A^{-*}]}{dt} = k_1[HA^*]_0\, e^{-(k_1+k_f)t} - k_f'[A^{-*}]$$

$$\frac{d[A^{-*}]}{dt} + k_f'[A^{-*}] = k_1[HA^*]_0\, e^{-(k_1+k_f)t}$$

$$\frac{d}{dt}\left([A^{-*}]e^{k_f't}\right) = k_1[HA^*]_0\, e^{-(k_1+k_f)t}\, e^{k_f't}$$

So, let me write it over here, I have this H A star, which is converted to A minus star because of the removal of proton from it. Let me write this rate constant here as K 1, but these you do not forget that this H star has its own radioactive rate constant right. So, or the deactivation rate constant which I all together termed as k f over here, and this one I termed as k f prime. So, then with these rate constant it will form the ground state of the H A, and with these rate constant it will form the ground state of A minus.

So, my whole model for this excited state proton transfer from H A star to A minus star is like this with the three different rate constant k f, k f prime and k 1 right. Now if I write this rate equations over here I can write minus d H star d t is equal to the two path way right one is k 1 another is k f right. So, I will just write k 1 plus k f all are small k do not confused with the capital and small capital k, here is the small k; k 1 plus k f into concentration of H star and I can also write the formation of this A minus star right like that way. So, d A minus star d t, here k 1 is the formation and this k f prime this one is the decay.

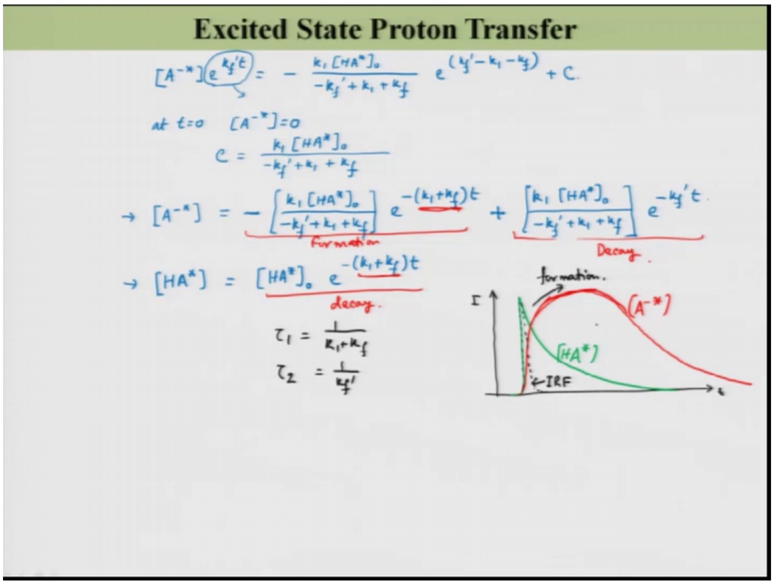
So, k 1 to H A star minus k f prime into A minus star right. So, let me name this as the equation 1 and this let us say equation 2. So, from equation one what I can write is minus l n H A star right is equal to k 1 plus k f to t plus c right. Now I put these boundary conditions over here. So, here the boundary condition is at t equal to 0; that means, just before the starting and just time 0 of the starting of the reaction.

The concentration of H A star is H star 0. So, it is a initial concentration. So, I will write these conditions over here at t equal to 0, H A star is equal to H A star 0. So, I can write this equation as H A star is equal to H A star 0, e to the power minus k 1 plus k f into t. So, you see if you monitor the H star, the concentration of the H star will start from initial value and then it will decay exponentially and the rate constant is k 1 plus k f and the time constant will be inverse of this right time constant will be just inverse of this ok.

Now, let me do one thing, now let me take from the equation 2 and from equation 2 let me write this as d A minus star, d t is equal to k 1 this is my equation 2; k 1 H A star right and this H A star now I will replace with this expression. So, I will just write H A star 0, e to the power minus k 1 plus k f into t right minus k f prime to A minus star that is it. So, I can take this k f prime A minus star in the left hand side, and then I will multiply the both side with e to the power k f prime into t.

Let us do that. So, d A minus star d t plus k f prime A minus star is equal to k 1 H A sorry H A star 0, e to the power minus k 1 plus k f into t and I am multiplying both side with e to the power k f prime into t. So, then this whole differentiation I can write as d d t of A minus star e to the power k f prime into t right is equal to k 1, H A star 0 e to the power minus k 1 plus k f into t into e to the power k f prime into t.

(Refer Slide Time: 07:59)



Excited State Proton Transfer

$$[A^{-*}]\,\underset{\searrow}{\boxed{e^{k_f' t}}} = -\frac{k_1[HA^*]_0}{-k_f'+k_1+k_f}\,e^{(k_f'-k_1-k_f)} + C$$

at $t=0$ $\quad [A^{-*}]=0$

$$C = \frac{k_1[HA^*]_0}{-k_f'+k_1+k_f}$$

$$\rightarrow [A^{-*}] = \underbrace{-\left[\frac{k_1[HA^*]_0}{-k_f'+k_1+k_f}\right] e^{-(k_1+k_f)t}}_{\text{Formation}} + \underbrace{\left[\frac{k_1[HA^*]_0}{-k_f'+k_1+k_f}\right] e^{-k_f' t}}_{\text{Decay}}$$

$$\rightarrow [HA^*] = \underbrace{[HA^*]_0\, e^{-(k_1+k_f)t}}_{\text{decay}}$$

$$\tau_1 = \frac{1}{k_1+k_f}$$

$$\tau_2 = \frac{1}{k_f'}$$

So, from that equation, now I can write A minus star e to the power k f prime t is equal to minus k 1 H A star 0 divided by minus k f prime plus k 1 plus k f e to the power k f prime minus k 1 minus k f plus c right. Now I need to find out this c, I can simply first divide both the side with e to the power k f prime into t and then I will put this condition that at t equal to 0, A minus star is equal to 0 just after dividing both side with this quantity. So, this, this, this, this, I will divide both side and then I will write this one then the equation what we will get is for c is equal to just this one with the positive signs.

So, k 1 is H A star 0 divided by minus k f prime plus k 1, plus k f and then if I put this value of c in that equation, ultimately the equation what we will going to see is A minus star equal to minus in that quantity k 1, H star divided by minus k f prime plus k 1 plus k a f into e to the power minus k 1 plus k f into t, then plus exactly the same quantity will come now k 1 H A star this would be 0 divided by minus k f prime plus k 1 plus k f, e to the power minus k f prime into t.

Earlier what we have seen? Earlier we have seen this H A now H A star, how H A star must decaying with time and we got this formula H A star equal to H A star 0, e to the power minus k 1 plus k f to t. So, this is the how the florescence intensity of H A star is changing with time this one, and this is how the florescence intensity of A minus star is changing with time. Here we can see for H A star only decay because this is a positive right and this is exponential minus rate constant into t 1 over the rate constant is your time constant. So, it will start from initial value and will decay.

But in this case please note here these two are same this quantity and this quantity are same now see this is special case right for the irreversible to state proton transfer, but most interesting thing is that here you have a negative sign and here you have a positive sign, negative signs this exponential means the formation. So, first this A minus star will form and then A minus star will decay. So, here is my formation, here is my this part is my formation and this part is my decay and here is my decay. So, that is why people generally do not want to tell the florescence decay as in general. We want to say the florescence transient right because it may be in some case like these case it is not a decay it is a formation it is a rise right. So, generally we speak as the florescence transient right.

So, now if I plot this florescence transient of H A star and A minus star, how it will going to look like let us plot it quickly to see that. So, let us say this y axis is my intensity and this x axis is my time axis right and this is my florescence intensity, and let me draw this

H A with green colour. So, here H A will looks something like this, this is just a single exponential decay and a single exponential decay.

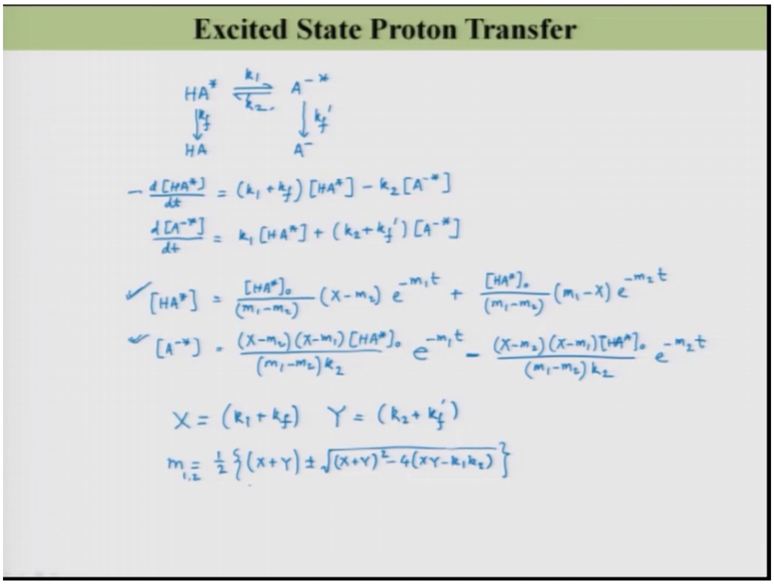
But this A minus will be first there is a growth right and then there is a decay. Now you see for the formation this rate constant and for the decay this rate constant there exactly same right. So, that is why I draw the formation like from here to till over here and then it will start decaying right. So, this is for the A minus star and the other one is for H A star.

So, from your time resolve measurement either by t c a p c, if t c a p c is good enough if this process is slower than 100 picosecond, because your time resolution t c a p c is about 100 picosecond, but in most of the cases like if you do in the water like 2 napthol in water this rate of proton transfer right is in the order of 1 picosecond. So, t c a p c is not suitable for such kind of experiment what you have to do? You have to use a up conversion method because in up conversion the IRF is alone 200 femtosecond 100 femtosecond, right.

So; obviously, here the IRF is over here. So, this is my IRF right and with this IRF it is visible right. So, this formation is visible over is my formation. So, as I told you this one over this is your time constant. So, generally people write this as a time constant. So, we can write the tau 1 is equal to 1 over k 1 plus k f, and tau 2 is equal to 1 over k f prime and we can write all this time constant from this experimental data.

Now, let me just quickly show you that what happens if this is a reversible two state case.

(Refer Slide Time: 16:18)



Excited State Proton Transfer

$$\begin{tikzcd} HA^* \arrow[r, shift left, "k_1"] \arrow[d, "k_f"] & A^{-*} \arrow[l, shift left, "k_2"] \arrow[d, "k_f'"] \\ HA & A^- \end{tikzcd}$$

$$-\frac{d[HA^*]}{dt} = (k_1 + k_f)[HA^*] - k_2[A^{-*}]$$

$$\frac{d[A^{-*}]}{dt} = k_1[HA^*] + (k_2 + k_f')[A^{-*}]$$

$$✓ [HA^*] = \frac{[HA^*]_0}{(m_1 - m_2)}(X - m_2)e^{-m_1 t} + \frac{[HA^*]_0}{(m_1 - m_2)}(m_1 - X)e^{-m_2 t}$$

$$✓ [A^{-*}] = \frac{(X - m_2)(X - m_1)[HA^*]_0}{(m_1 - m_2)k_2}e^{-m_1 t} - \frac{(X - m_2)(X - m_1)[HA^*]_0}{(m_1 - m_2)k_2}e^{-m_2 t}$$

$$X = (k_1 + k_f) \quad Y = (k_2 + k_f')$$

$$m_{1,2} = \frac{1}{2}\left\{(X + Y) \pm \sqrt{(X + Y)^2 - 4(XY - k_1 k_2)}\right\}$$

So, in that case my model is H A star is forming to A minus star and here is k 1 here is my k 2, and this is as usual is k f and this one is k f prime, this is making H A this is making A minus.

Then similarly I should right those equations to start with minus d H A star d t is equal to k 1 plus k f, H A star minus k 2 this is my extra turn which was not present in case of irreversible a two state proton transfer. So, A minus star and I have d A minus star d t is equal to k 1 H A star, plus k 2 plus k f prime into A minus star.

Like similarly what we have done for this irreversible case I can also do this for the reversible case and ultimately this solution will be much more difficult than the previous one and it is out of scope that I will solve in this lecture, but I would like to show you the result. Ultimately if you saw what you will get, you will get the H star, how the H star is changing with time how the A minus star is changing with time. Those you will get like in the previous case and those expressions I will show over here.

So, H star equal to H A star 0 divided it by m 1 minus m 2 to x minus m 2, e to the power minus m 1 t plus H A star 0 divided by m 1 minus m 2 is a complicated one to m 1 minus x, e to the power minus m 2 into t; obviously, I have to tell what is m 1 m 2 that I am telling later and then A minus star will have the form x minus m 2 into x minus m 1, then H A star 0 divided by m 1 minus m 2 and then k 2 this is my k 2 over here, I should have this exponential part e to the power here it will come as minus m 1 t and then I will get this minus. So, the here this minus sign signified the formation right minus x minus m 2 into x minus m 1 like this way, H A star 0 divided by m 1 minus m 2 into k 2 and this is this will be my e to the power minus m 2 t. In this case x is defined as k 1 plus k f and y is equal to k 2 plus k f prime and m 1 2 is defined is 1 and 2 is equal to half x plus y plus minus root over x plus y whole square minus 4 into x y minus k 1, k 2.

So, now as you can see here this is this is going to very complicated equation and, but if you monitor the decay of this H A star or the florescence transients of A minus star, it is possible to evaluate the different rate constants like k 1, k 2, k f and k f prime. So, you see in this case the equation is little complicated right, but by monitoring the time resolve emission one can get such kind of rate constant of the proton transfer, so we will finish.

Thank you for your kind attention.