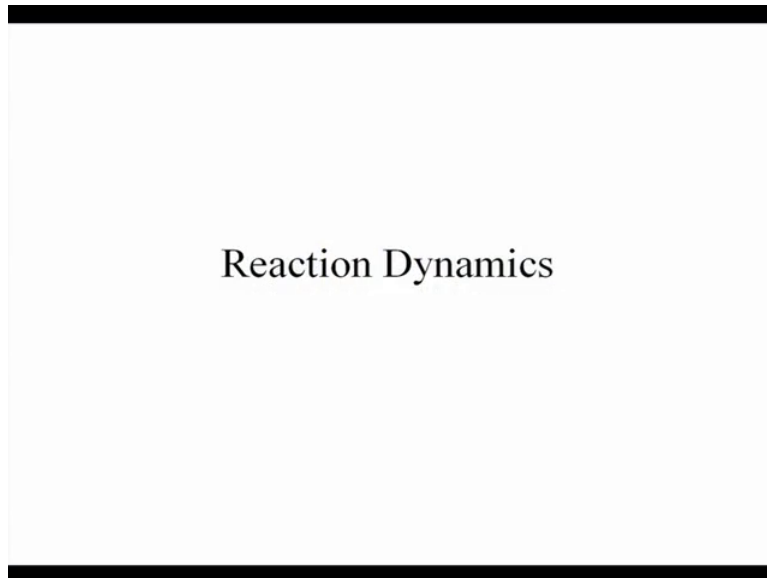**Rate Processes**

Prof. M. Halder

Department of Chemistry

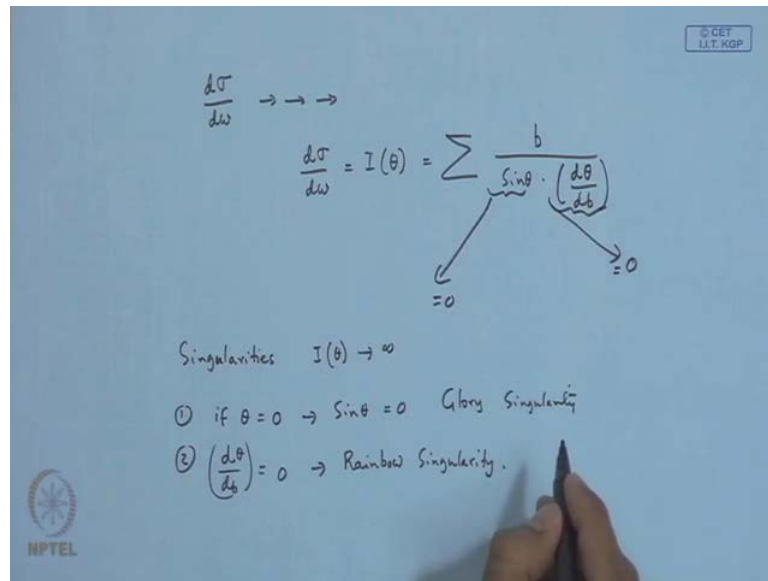**Indian Institute of Technology, Kharagpur**

Module No. # 01

Lecture No. # 35

**Reaction Dynamics: Scattering (contd.)**

(Refer Slide Time: 00:22)

Good morning everybody. We are back with rate processes and we were discussing reaction dynamics and we were in the last lecture here, this scattering process.

(Refer Slide Time: 00:52)

So, in the last lecture we ended, I mean stopped our discussion with this - calculating the differential cross section, that is, d sigma, d omega and from that we arrived at the expression d sigma, d omega which is I theta which is sum over b sin theta into d theta db. We have got two situations: one is if sin theta equals 0, other is if this is equal to 0. So, two singularities, so singularities, that is, I theta tends to infinity. If theta is equal to 0, case 1 if theta is equal to 0 means sin theta is equal to 0 which is called the glory singularity.

(Refer Slide Time: 03:03)
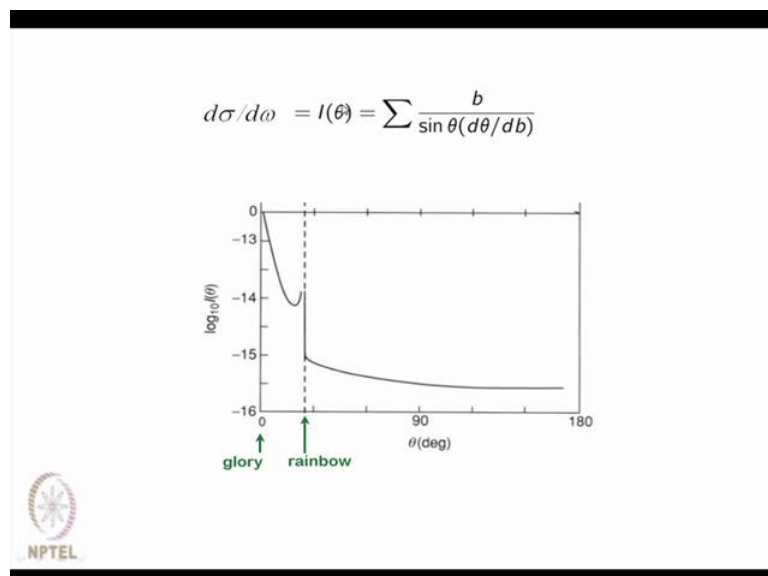
Number 2, the other one if d theta db is equal to 0, it is called the rainbow singularity. So, if we plot this d sigma d omega with theta, then this is the situation b by sin theta d theta db. So, this corresponds to glory singularity and this corresponds to say it goes to infinity, a very high value again. It is this one you see this becomes asymptotic which is called the rainbow scattering, I mean rainbow singularity.

(Refer Slide Time: 04:11)

So, therefore just try to see now what is this meant by. So, definitely from the mathematical perspective this one differential cross section becomes very high under these two situations.

Now, what is this rainbow singularity that at this situation d theta db is 0? Classically, we obtain, it is continuity in the differential cross section as it is here differential cross section. Now, differential cross section at theta r, I mean rainbow angle.

(Refer Slide Time: 04:56)

$$d\sigma/d\omega = I(\theta) = \sum \frac{b}{\sin\theta (d\theta/db)}$$
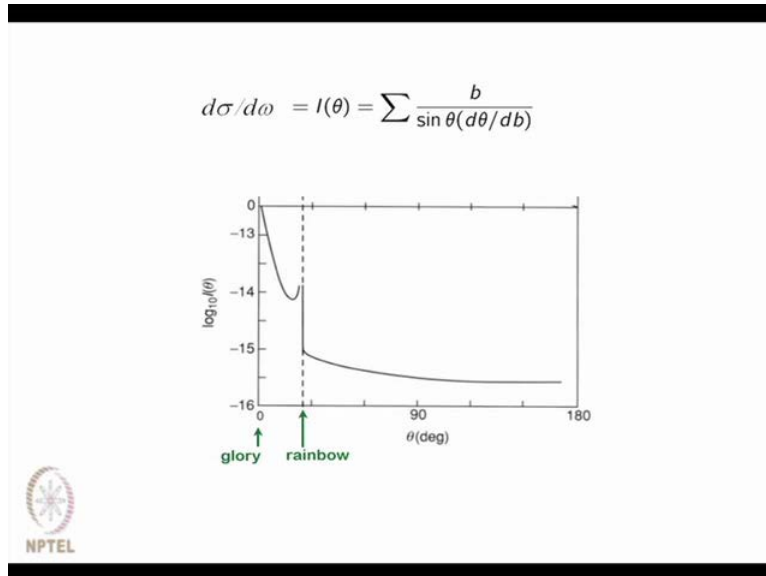
Now, for theta less than theta r, I mean when theta is equal to theta r we obtain this situation. So, we obtain the singularity. Now, for theta less than theta three values of b can lead to deflection through the same scattering angle and leads to interference. It is again a case of interference; I mean which is called a supernumerary rainbow.

(Refer Slide Time: 05:56)

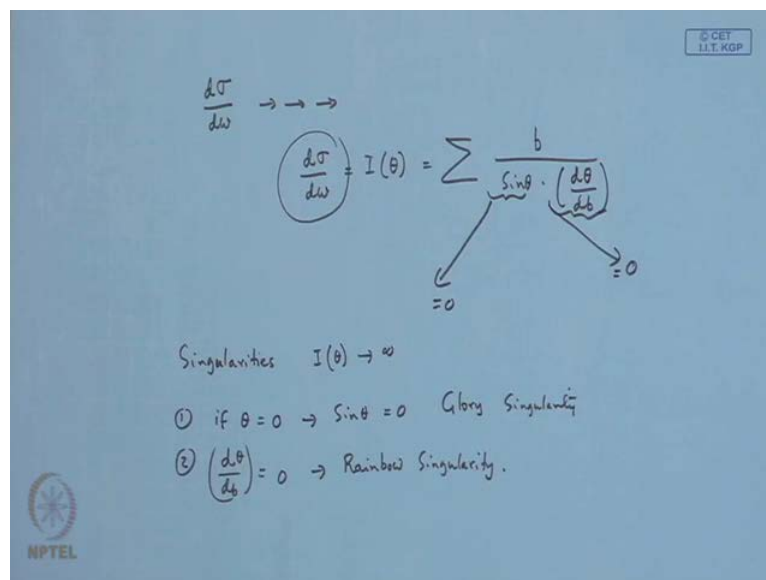Now, basically the features in d sigma, d omega directly related to the nature of the potential energy curve, it is very much related to the nature of the potential energy curve. Also, this theta r that is the rainbow angle, the well depth theta r is sensitive to well depth as well. So, this is very important that it depends on the well depth. Also, I mean the well means this potential well depth.

(Refer Slide Time: 06:37)
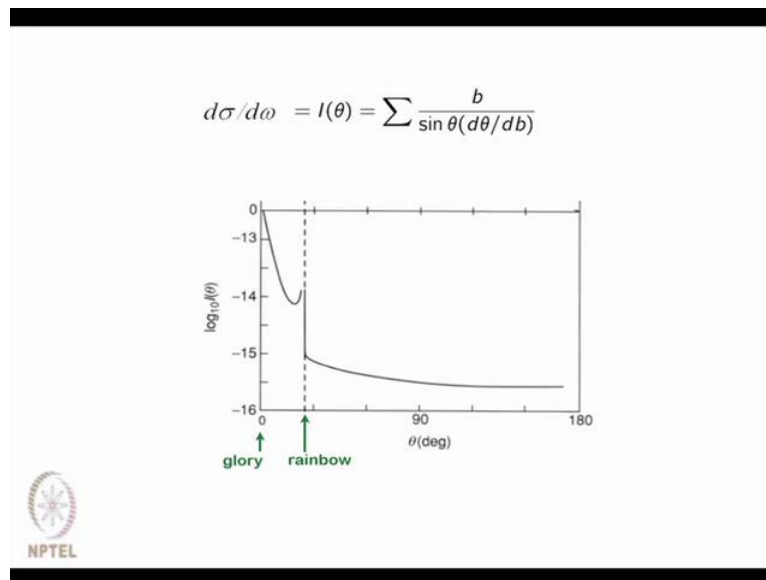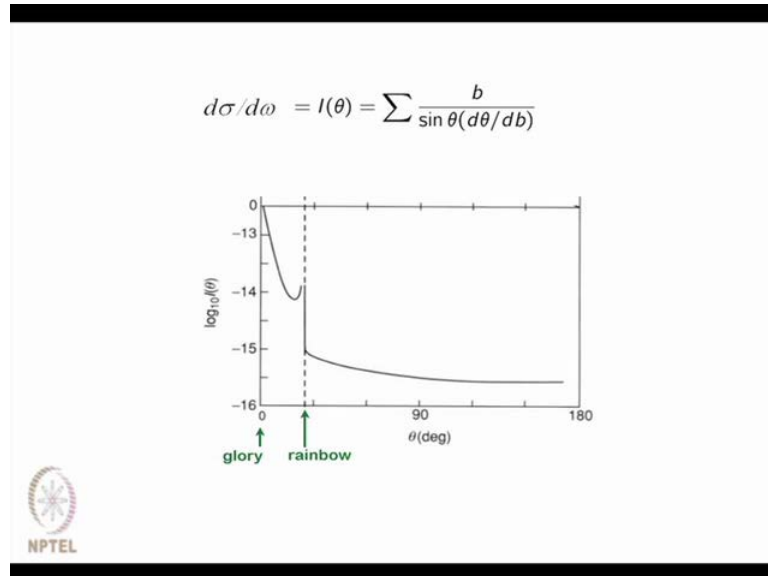

So, these are the two I mean one is glory another is rainbow. These are the two situations on this d sigma, d omega and the physical significance for this rainbow is that we obtain this rainbow when this d theta db becomes 0.

(Refer Slide Time: 06:55)

So, if you want to know in more details, you can consult this text book by Raphael D Levine.

(Refer Slide Time: 07:16)

Now, let us one important point that this as I told you that supernumerary rainbow that is for theta less than theta r that is the less than theta r means rainbow angle three values of b will lead to deflection to the same scattering angle. So, that will as I told you that d sigma d omega is very much related to the nature of the potential energy surface. So, supernumerary rainbow gives us information about the nature, I mean about the range and shape of the potential near the minimum.

This information can be obtained from this supernumerary rainbow when three values of b correspond to same scattering angle which is called the supernumerary rainbow and leads to interference when interference known as that is for three values of b leads to supernumerary rainbow. So, this rainbow is very important in knowing the nature and depth, I mean near the minimum.

(Refer Slide Time: 08:46)
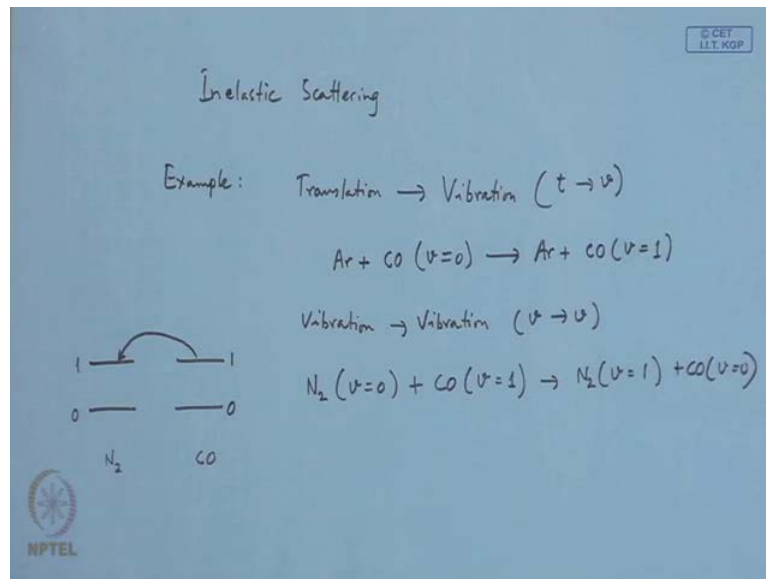
Now, next so we have been talking about this elastic scattering. Now, let us think of inelastic scattering where translational energy is converted, I mean transferred to rotational vibrational internal motion but without any rearrangement of the atomic framework. Example, say translation to vibration t to v, say if it is inelastic scattering, then maybe argon plus carbon monoxide in v equal to 0; it collides argon plus vibrationally excited carbon monoxide. So, the translation energy of argon is given to the vibrational mode and argon <mark>is</mark> gets its energy reduced. Example for vibration to vibration, v to v say nitrogen v equal to 0 plus carbon monoxide v equal to 1 giving rise to nitrogen v equal to 1 plus carbon monoxide v equal to 0.

So, it is basically energy interchange. So, basically you have got, so these are the two vibrational levels say this is for nitrogen and this is for carbon monoxide. So, these are vibrational levels, so 0 1 0 1 so because of collision this energy is given, maybe this excess energy is given to here. Thereby, it is coming down to here, so exchange of this is basically the vibration to vibration energy transfer. You can find plenty of literature on this aspect even it is by scattering.

Maybe, you can think like when a photon collides with an atom, then energy of the atom increases. So, you may think in that way, I mean classically you can think that this photonic energy is transferred and thereby your electronic energy is increased. Although, classically it is difficult to explain this phenomena fully but maybe classically you can start to defend in this manner.

Now, so there are factors whether there is energy mismatch, I mean vibration to vibration is important when there is less mismatch between this and that. If it is highly mismatched, then there is a problem; if they are very close, then usually energy can be transferred. So, there are several aspects, I mean several factors which determine whether this energy transfer vibration to vibration or translation to vibration, translation to rotation these are feasible or not.

(Refer Slide Time: 13:43)
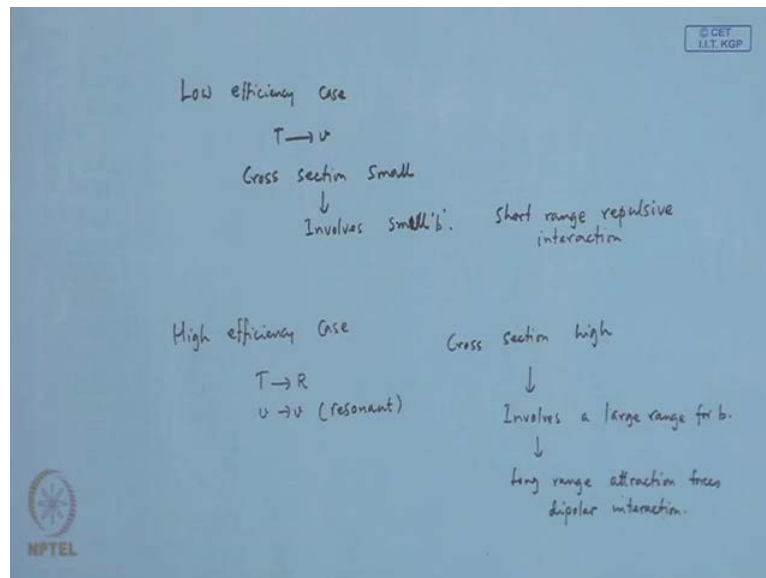
So, controlling factor, one is think of a low efficiency process. So, low efficiency process efficiency case as for example, translation to vibration, the cross section this transfer efficiency. So, cross section will be small and generally, it involves when b factor is small, impact parameter is small. So, usually involves small b and it is controlled by short range repulsive interaction. High efficiency case may be translation to rotation or may be vibration to vibration resonant. Cross section high, large at usually involves a large range for b and it is controlled by long range attraction forces like dipolar interaction.

So, controlling factors for this energy transfer they depends on like if it is a low efficiency case, then short range repulsive interaction. If it is a high efficiency case, so long range attractive forces like dipole interaction is responsible.

(Refer Slide Time: 17:25)
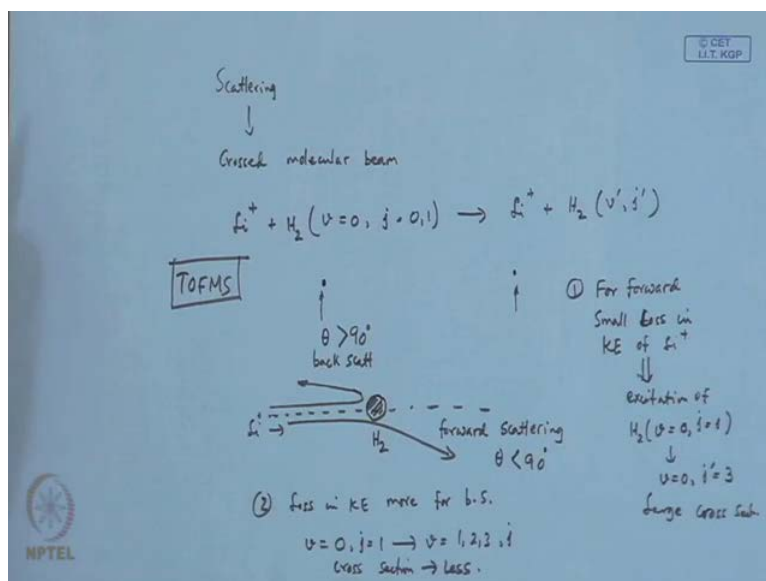
So, let us look into scattering experiment again. So, a crossed molecular beam say for example, lithium ions plus H2 vibrational level equal to 0, rotational level say j is equal to 01 these are populated. So, crossed beam interaction like this giving rise to lithium plus H2, of course v primed j primed some different v and different j. In this case, since energy is transferred from here to here, like so of course the velocity of lithium plus should be altered because of this energy transfer. So, how to look into that?

So, now in this case the energies have been transferred means and of course v becomes v primed, j becomes j primed. So, it is a case of inelastic scattering, so how to look into that? So, if you can detect Li plus means its velocity, if you can plot the contour of velocity in different direction, then you should be able to get some idea and that can be done by time of flight mass spectrometry (TOFMS). In that case, you do the mass spectrometry and of course monitoring the time of flight that is suppose you have got lithium ion over here and you have got same lithium ion over here. So, in by knowing how much time it takes to travel from here to here, you can get idea means you can find out the velocity. So, you detect the lithium over here, you detect lithium plus over here, so using time of flight mass spectrometry.

Now, when it is the case of scattering, there is a provision for head on collision and there is a provision for like sideway the colliding, I mean say v molecule can go like this. So, you have got like H2 over here. Although, it is a direct way but we are showing <mark>as a</mark> just as a ball lithium plus is coming this way. So, what is going to happen that when it directly hits almost head on, it will rebound, I mean backward scattering back scattered.

So, in this case theta will be greater than 90 but may be other situation that forward scattering may take place like this. So, forward scattering, in this case theta will be less than 90 degree. These are the two situations <mark>and then</mark> that you can think of that may be possible two extreme situations. For forward case forward scattering, so kinetic energy loss will be less for lithium plus. So, small loss in kinetic energy of lithium plus and that corresponds to excitation of H2 v equal to 0, j is equal to 1 2, maybe v is equal to 0 2 maybe j is equal to 3 and it has got large cross section.

The second situation that loss in kinetic energy is more for the back scattered, so loss in KE more for back scattered and that corresponds to excitation. Since, it is more loss that corresponds to excitation from b equal to 0 to maybe b primed is equal to 1 2 3. So, v is equal to 0 and j equal to 1 to v is equal to 1 2 3 and j primed and its cross section less. So, these are the two situations that we can think of.

So, definitely back scattering will have lower cross section than the forward scattering because you see probability wise two body collision means head-on collision. Out of many situations, side and side on or sidewise or whatever this situation is perhaps will be lesser in cross section.

(Refer Slide Time: 25:58)
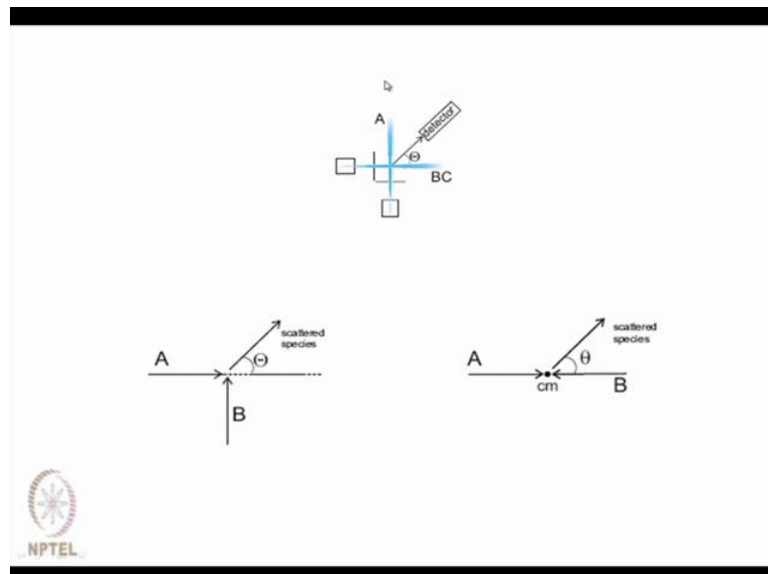
Now, so since there are two options, one is this, another like this. So, two extreme situations so there will be angular distribution in various angles. So, angular distribution you can measure like here, crossed molecular beam experiment. Now, what is done in molecular

beam scattering experiment? It is like that one of the molecular beams is usually chopped, I mean there are two molecular beams chopped or pulsed. Pulsed means not continuous but on then off, on off, on off like that. So, in that case that will help in doing this time of flight mass spectral measurement.

So, in doing the time of flight mass spectrometry, out of two beams one beam can be pulsed. I mean in between two successive pulses, you can measure the time of flight or maybe on beam is on, then keep it off for the time of flight measurement of say lithium plus and then again keep it on I mean make it on.

(Refer Slide Time: 27:33)
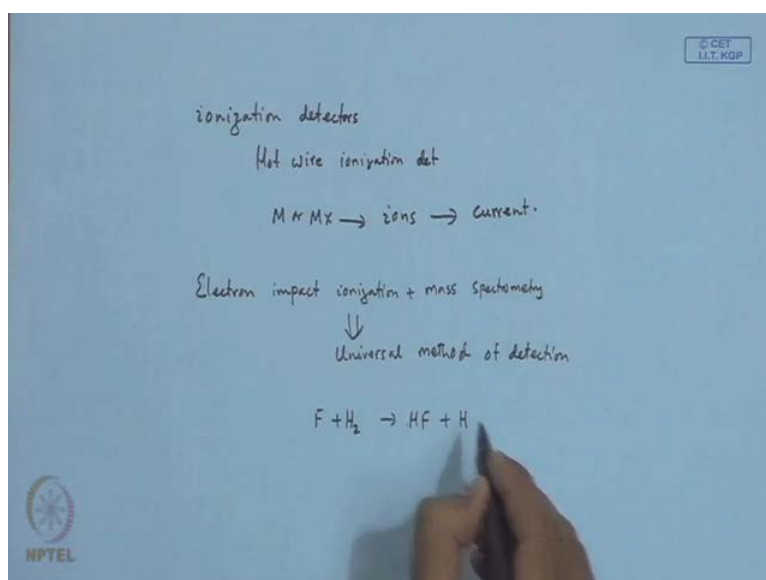
So, how to detect, I mean these scattered entities? So, one maybe ionization detector that is hot wire ionization. So, like what is done is you have got hot ion, I mean hot wire and then when the element or something like M or E the element and or may be its compound say EX when hits, then maybe ionization takes place.

So, maybe M or MX ions, then this ion generates some current. This way you can measure using hot wire ionization but it has got this is having good angular resolution but energy resolution wise it is not that great. Another is electron impact ionization coupled with mass spectrometry. So, it is electron impact ionization coupled with ionization plus mass spectrometry and this is a universal method of detection. So, this is another method and the thing is that rarely it has sensitive to allow product quantum state resolution. So, product quantum state means in one case, it is in vibrationally excited. Another one may be

vibrationally not excited or little less excited like one is v is equal to 2 another is v is equal to 5. So, it is difficult to resolve this quantum states. For example, F plus H2 giving rise to HF plus H. So, this problem is there that is its limitation and for the earlier one, this speed resolution wise this one the hot wire ionization is not that great and like but here quantum state resolution is not possible.

What about other methods? There can be of course, spectroscopic method like laser ionization method or laser induced fluorescence method. Suppose, your species is fluorescing or maybe the moment your reaction product is directed to a direction, then you shine your reaction mixture with laser. Then it will out of many one of the components in the mixture is giving rise to fluorescence, so you can measure it.

So, spectroscopic method is always sensitive and accurate. Therefore, using laser induced fluorescence or maybe laser ionization method, you can do it but it has high energy resolution sensitive. Sensitive in the sense, that if the population of your species that fluoresce if it is significant, then it may be sensitive but if it is very less, then sometime it may means detector may not be able to detect the fluorescence or maybe the ionized things, ionized entities. So, various other detectors are possible with little variation of these basic things.

So, you have to do the time of flight mass spectrometry. While doing this molecular beam to look into their velocity distribution, I mean velocity contour and then you should be able to know whether it is a case of back scattering or it is a case of forward scattering.

(Refer Slide Time: 33:49)
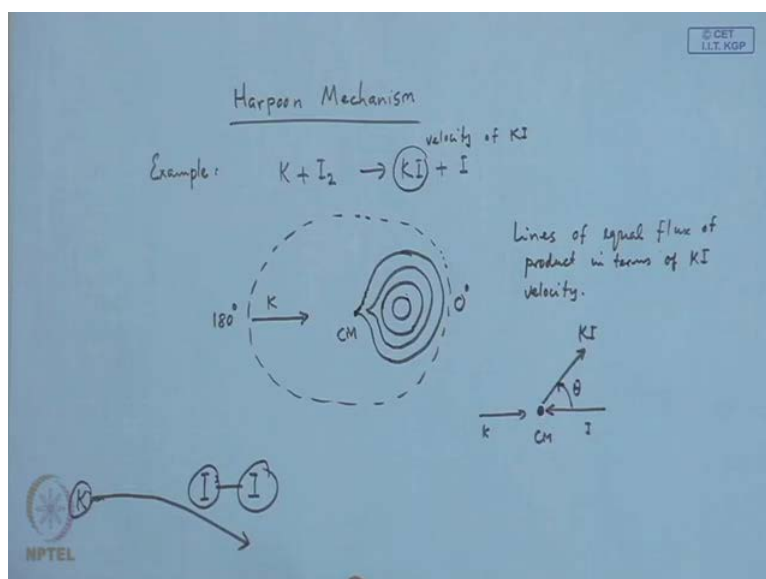
Next is, we will move on to mechanism of the various such processes we have been discussing. So, one is harpoon mechanism. Example, K plus I2 giving rise to KI plus I. Now, let us plot the data in the form of contour plot in the centre of mass system for such that centre of mass is stationary for such a system. So, this your K, this is your centre of mass something like this contour, this side is 0 degree, this side is 180 degree and you have a circle. Although, it is not circle shown, you have to draw a circle and this side is 180 degree.

You see that contour, this is your centre of mass product distribution is in this side. So, at the 0 degree, I mean this side not in the back scattered side that this contour represents lines of equal product flux as a function of KI velocity. We are looking into the velocity of KI, so it is a contour plot in the centre of mass system such that the centre of mass is stationary.

So, this contour represents lines of equal flux of product lines of equal flux that is equal flux lines are joined, equal flux of product in terms of KI velocity, potassium iodide velocity. The circle outside represents the maximum possible product velocity which is said by the energy conservation. So, basically this is your centre of mass and since centre of mass is thought to be stationary I, this is K and your KI. So, you are detecting KI velocity with theta. So, lines of equal flux of product are drawn as a function of KI velocity and in this case, scattering the forward sense we are getting.

Now, when it is the case of rebound? Now, the case of rebound happens when heating head on and in that case, it is strongly back scattering. Now, what is the harpoon mechanism? Now, what is the meaning of this harpoon mechanism? Now, for fairly heavy or heavier reactants, for fairly heavier reactants, what is happening that since, it is a case of forward scattering, so you have got your iodine over here like your K is coming maybe this way. So, the moment it is coming close to this iodine, it plucks it that is it takes away and then follows this path.

So, it plucks the light atom from the other reactant or maybe plucks one atom from the other reactant as it passes and newly formed diatom is forward scattered. So, newly formed diatom means this KI is forward scattered and the other reactant that is the reactant that is acting as a spectator, I mean this cannot do anything as such, so it remains over there. Only thing is that what is happening to it is that it there is a loss of atom.

So, it is basically a spectator that as if it is helpless, it cannot do anything. So, it comes this way, then it plucks this iodine, becomes KI and goes away. So, this is pretty much what is

meant by your harpoon mechanism. It is a harpooning process and since, it is forward scattered, so that is why you get this contour in the forward direction, not in the backward site.

So, what can you talk about this harpoon mechanism? It has got a large cross section for the reaction like many other alkaline halogen reactions. It gives you forward scattered product like this. This is the characteristic low energy release into translation, so translation energy is not that much. So, KI is in highly excited, internally excited not much velocity, I mean low energy release into translation.

(Refer Slide Time: 42:38)
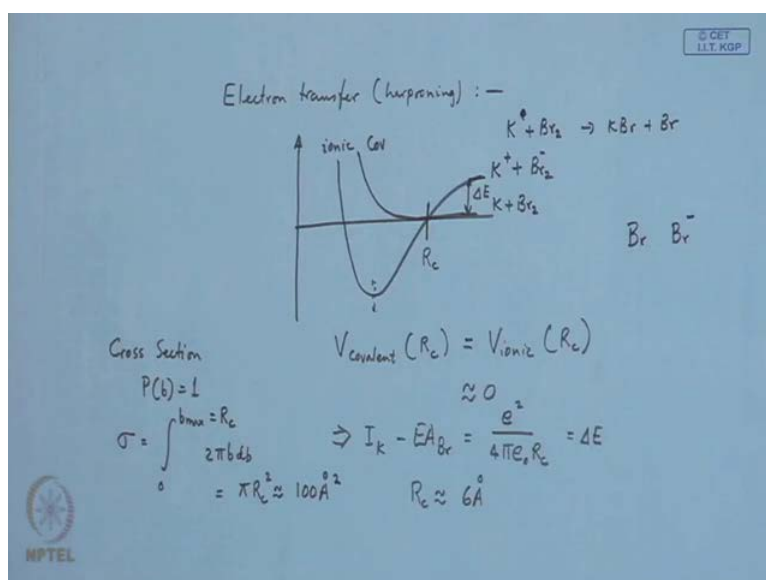
So, the formed KI should be internally excited. Now, this electron transfer harpooning takes place under the condition let us try to look into. So, electron transfer harpooning, this takes place under the situation that let us look into the potential energy diagram say for a reaction that K plus Br2, so giving rise to K Br plus Br. So, this is your covalent surface and this is ionic surface. Ionic surface means it is K plus Br2 minus covalent surface; it is K plus Br2.

So, what is this gap? This gap is means there is a gap in energy, so we look into it. So, V covalent and this is your Rc that is crossing point, V covalent Rc is v ionic at Rc which is almost equal to 0. That is this means IK ionization energy of K minus EA electron affinity of Br2 is equal to e square by 4 pi epsilon 0 Rc.

So, that is delta E, this is your delta E. Now, in this case Rc is of the order of 6 angstrom means further your this true ionic potential energy curve minimum. How to estimate the cross section? So, cross section under this condition, let us try to find out the cross section and also assume Pb equal to 1. So, your sigma is equal to integration from 0 to b max which is equal to Rc, so impact parameter Rc twice pi b db which is equal to pi Rc square is of the order of 100 angstrom square.

So, what is happening here that Br 2 minus is formed with inter-nuclear separation such that there is a little repulsion between Br and Br minus and K plus carries off Br minus in its original direction that is the forward direction. So, Br minus is formed with inter-nuclear separation such that there is little repulsion between Br and Br minus. So, they are at such an inter-nuclear separation that there is rarely a repulsion and K plus carries off this Br minus I mean it takes off because they are nearly, I mean they are not repelling each other. Electron transfer making Br2 minus and then there is basically they are at such a separation that there is no repulsion between them. So, they are loosely as if loosely bound and K plus takes off that Br minus and goes away making KBr.

So, that is an interesting situation for electron transfer harpoon mechanism like happens for many other alkaline and halogen reaction.

(Refer Slide Time: 49:08)
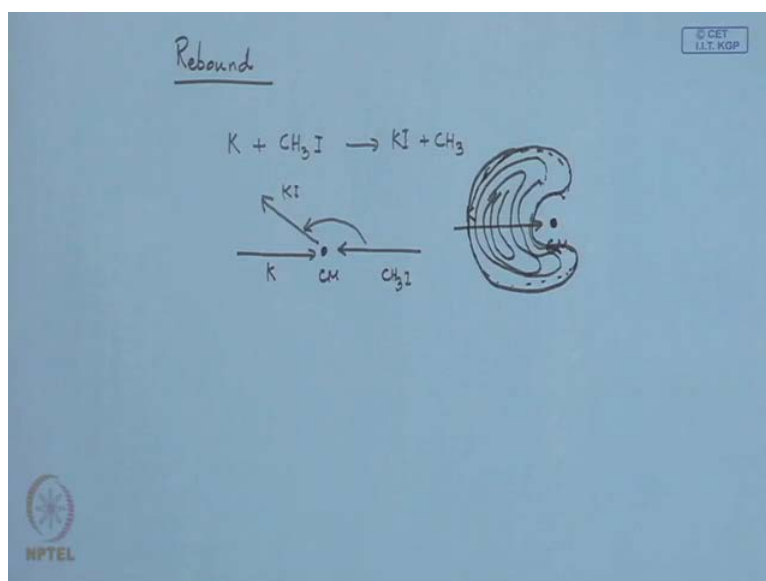
Next, Rebound. What is this Rebound? Think of a reaction like K plus CH 3I giving rise to KI plus CH3, that is the product is rebounding. I mean it is not forward scattered but it is

back scattered. It takes off and then comes back, so this is your species CH3IK reacts and then goes back. So, in centre of mass system can represent CM, you can represent this and this is your scattered KI theta is more. This is your CH3I, this is your K and if you do a contour plot, then you will be seeing this is your CM, stationary CM from this side your K is coming.

So, your contour plot will be something like this. So, it is mostly this side, so if you detect KI, then this will be mostly in this side. So, it is back scattered product, I mean rebound, so that means your product gets rebound this way as per this figure. Therefore, this side your contour shows that the probability is more over here and you have got a small cross section backward scattering, it is that happens with small impact parameter b. It releases high translation energy that means in contrast to harpoon where low release of translation energy and highly excited but here the situation is opposite. It is also a harpoon reaction but electron affinity has got a change in sign, I mean electron affinity it acts in the reverse. I mean EA of CH3I this one is negative in contrast to your electron transfer harpooning. So, this rebound case is also harpoon reaction.

So, I guess I should stop over here and I will just quickly have a recap. What we have done in this piece of lecture? We talked about these singularities for differential cross section. So, differential cross section and then we talked about these rainbows. Then we started with inelastic scattering and then we discussed this harpoon mechanism. It is basically a plucking mechanism, so we discussed, I mean for harpoon mechanism you can have forward scattered as well as back scattered as I talked in terms of rebound.

So, I guess that is all for today. So, in the next piece of lecture, we will again talk about this means a little more on this harpoon mechanism. So, that will be taken up in the next class and after that maybe some other aspects of the observations, I mean some other aspects of chemical reaction dynamics, we will take up in the next pieces of lectures. So, till then thank you.