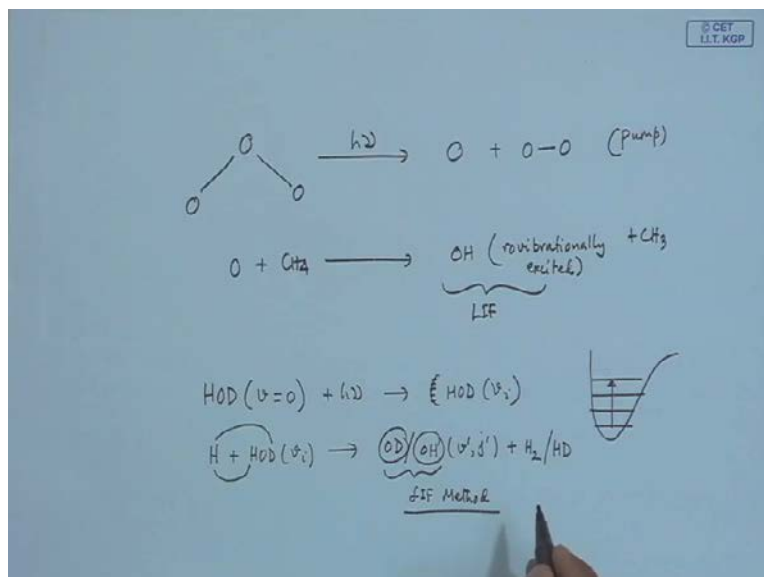


Rate Processes
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Lecture No. #38
Reaction Dynamics: Controlling Reagents etc. (contd...)

Hi friends. We are back with Reaction Dynamics. So, in the last lecture, we have been discussing this, you know, how to know the population of various j and v states of your nascent product; I mean nascent reactant, I mean reaction product. That is, nascent **rovibrationally** excited species means, what is the, you know, population pattern, how to probe that. So, we discussed this, you know, nothing in detail, but we just can give you an outline of the technique, that is very useful, is your Pump-probe technique.

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In this case, you use two lasers, you know; I mean two photons; one is for, you know, pumping and next is for probing. So, so basically, you know, basically we have used this example of ozone reaction. With $h\nu$, you generate O and O_2 ; and then, so, this is a pump, and then O plus CH_4 giving rise to OH rovibrationally excited, rovibrationally excited, plus CH_3 . So, you use, LIF for this, laser-induced fluorescence.

And, there are certain points that one should look into; that means, there should not be much delay between pump and probe. Especially, you know, when the lifetime of your, this nascent species, I mean lifetime of the species which are trying to probe. So, nascent rovibrational this, you know, state; if it is less, then it is a problem that sometimes you will miss it. So, that is why pump-probe gap should be, time gap should be less.

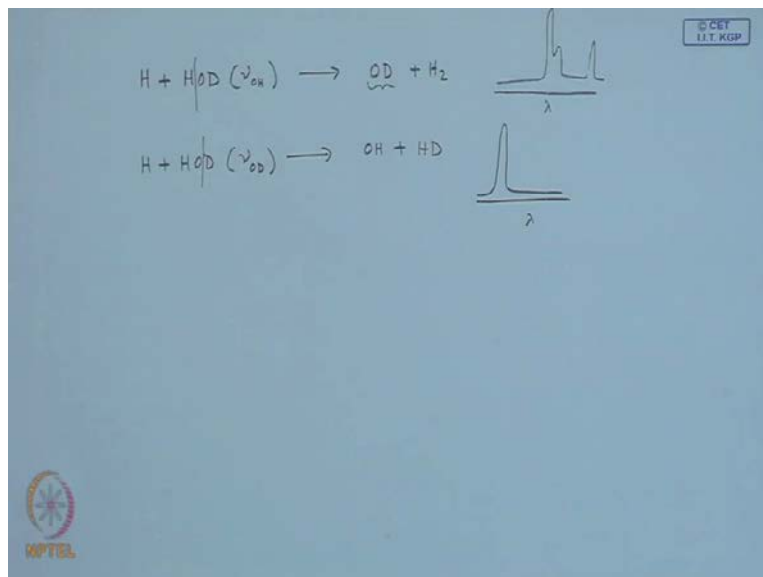
Now, the thing is that, regarding the, regarding reagents, you know, molecular beams are very good, you know, for cooling molecules, because it is a directed; they are not, you know, random, because temperature is a measure of a mean random translational kinetic; and so, more the randomness, you know, more is that, more is the temperature. So, if they are more directed, collision is less; then, you know, there, you know, translational temperature is less. In some cases, rotational states can also be selected with the help of your, you know, pump-probe method. But the point is vibration level is very difficult to pick up, you know; selectively exciting the vibration level, but we can take the help of pump-probe method to selectively, you know, selectively excite certain levels.

So, as an example, let us have like this HOD; so, deuterated, mono-deuterated water in the vibrationally least level V , is equal to $0 + h\nu$. So, you generate HOD, we generate HOD in the i th vibration level. So, i th vibration level means, you know, it is vibrationally excited; and 0 means, it is having a 0 point energy, little residual this motion, but when you excite with $h\nu$, it goes to somewhere, about here may be, like this. So, here, so, it is doing like this, some motions, like this may be, you know, translation, may be, I mean, may be your, I mean, symmetric or may be antisymmetric; I mean, this vibration could be of different types depending on which mode you are losing into. So, this HOD, V is equal to $0 + h\nu$ giving raise to HOD $V + i$. Then, you know, using a microbe discharge, if you can generate hydrogen, I mean, nascent hydrogen. So, microbe discharge generating nascent hydrogen $h +$, then plus HOD $h +$ plus HOD $V + i$. So, that will give rise to, you know; possibility is OD or OH; I mean, may be like this reaction will take place or may be this reaction will take place; so, that is why, like, if this happens, then this happens, then it will generate OH; if this happens, it will generate OD, and of course, $v' + j' + H_2$ or HD.

So, these can have two, it can have two options; either it will approach from side of hydrogen or it will approach from side of deuterium to give rise to these two products. Now what to do as, means, as I told means, as I have given you the, you know, example

of laser-induced process, you can probe this using laser-induced fluorescence technique; that is, these two can be probed by laser-induced fluorescence method LIF method, and you can do mode-selective reaction.

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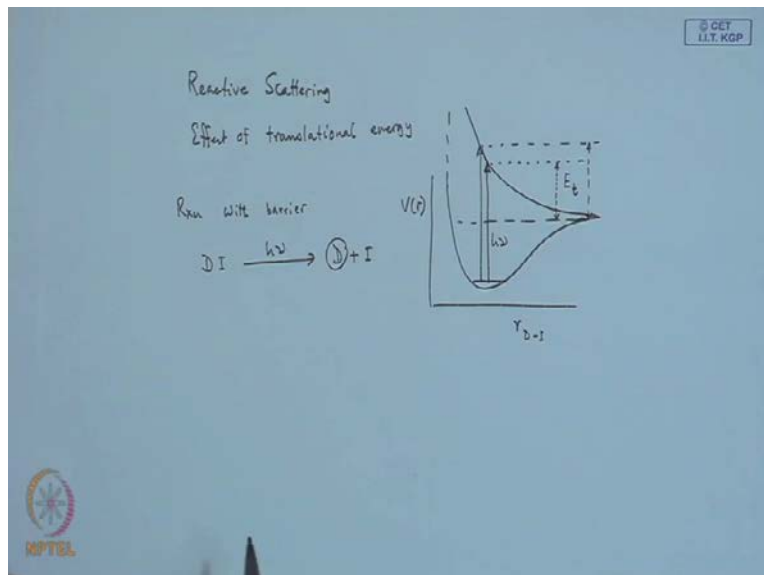


You can selectively excite a particular vibration mode with the, **with the** help of, you know, with the help of your laser. So, therefore, in that case, if it is a mode-selective reaction, then H plus HOD with ν_{OH} ; that is fourth with ν_{OH} , then you will be getting OD plus H₂ or if you do other mode-selective options like H plus HOD ν_{OD} , then you will have OH plus HD. So, then if you, **if you** probe your, this OH or OD, you will be, you will be, you know, you will be seeing different laser-induced fluorescence pattern; like for this, here you may get like something like, as a function of wavelength λ for here, may be I am not designating the, you know, exact which one is which, but this is one pattern you will be getting. But, if you do the other one, I mean the mode-selective one, may be here, for this one, you may be getting something like this; this is a λ sign. So, so mode-selective reaction will, you know, give rise to, you know different reactivity.

So, you can selectively, you know, break the bond; I mean, you can selectively excite the particular bond; I mean, this is ν_{OH} , so that means you can you can selectively, you can break this bond. So, ν_{OD} means, you selectively excite this bond, therefore, this will be ruptured here; you selectively excite this, and of course, with the help of specific

frequency, may be IR frequency, I mean, IR laser, you can do that; you can do this mode-selective reaction. So, selectively break the vibrationally excited bond.

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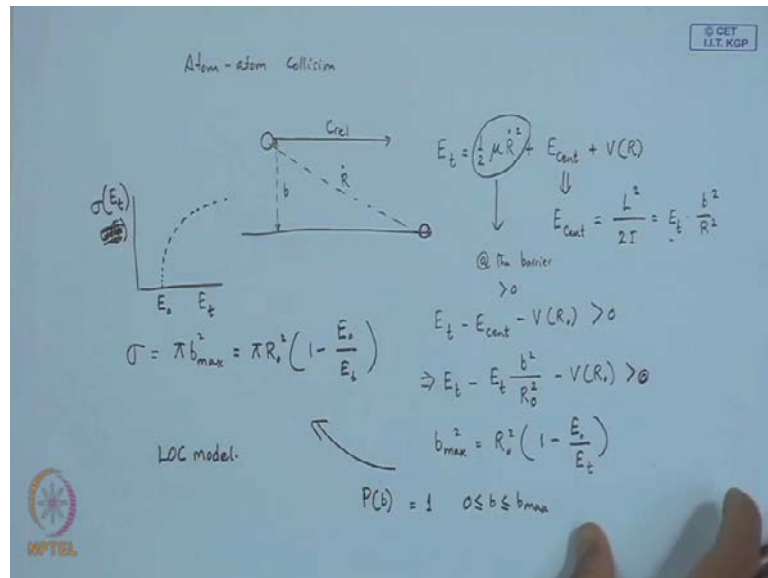
Next, we will move on to, **move on to** reactive scattering, **reactive scattering**. So, models for, you know, reactive scattering and the effect of translational energy reactive scattering, rule of translational energy effect of translational energy. Now, consider a reaction with a barrier reaction, with a barrier such that, I mean, you know, say deuterium iodide reaction with barrier. So, $DI + h\nu$ giving rise to $D + I$; so, **it is** disassociation. What is, what is the, you know, what is going on? Now, in this case, this is what this disassociates.

The kinetic energy goes to the, goes to the lighter d atom so conservation of energy and momentum is taking place. So, if you plot this like this; so, this is your ground state, this is excited state, so, this is a repulsive; this one is repulsive and this one is attractive, so, $V(r)$ versus r $V(r)$ versus r ; so, you excite from here to here. So, basically, this excess amount of energy, this much, so, this is your r DI . So, this excess energy, I mean, this much is the E translation. So, this excess energy is going to your going to your lighter the atom. So, you can also vary, you know, by changing the frequency by changing ν ; so, this is $h\nu$. So, if you change this frequency, may be here, then, this one will be more.

So, if your, if your, you know, E_0 , that is the, that is the, you know, minimum energy, that is the, surmount the potential energy barrier; I mean, there is a potential energy

barrier. So, if your energy is just sufficient to surmount the potential barrier, may be that is not sufficient, because there is a centrifugal barrier. So, in that case, only reaction is possible at low b now. Considering atom-atom collision reaction, so, in that case, no structure basically hard sphere; so hard sphere model atom-atom collision basically hard sphere model.

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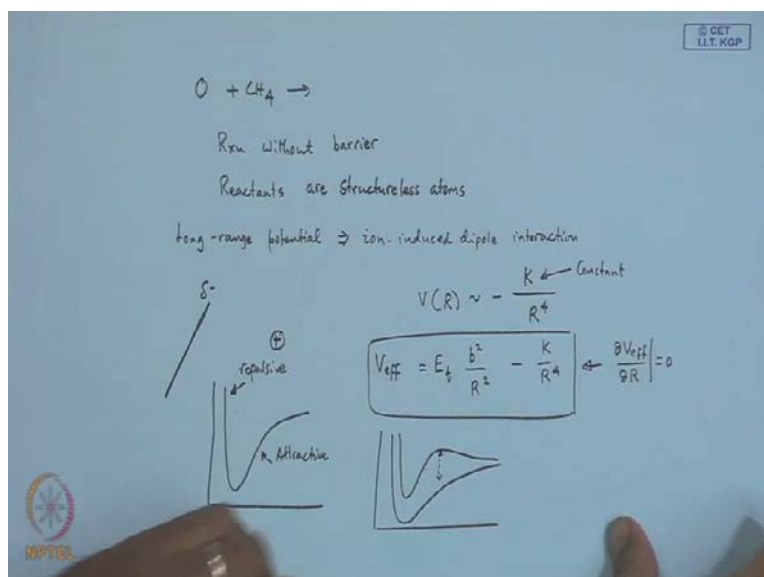
Now, in that case, so, you have got you're here, atom-1; and you have got your b over here. So, impact parameter b is this and **this is your...** It is changing with time, because it is moving this way. So, this is your r dot; and, say, this is your c relative, **relative**. So, translational energy E_t can be written as half-reduced mass into r dot square plus your centrifugal energy centrifugal energy.

If you want to know more, you can consult this Any Standard Classical Mechanics text book by Herbert Goldstein. And, V r per centrifugal energy is a square by twice $i E_{cent}$. It is basically a square by twice; I mean it is related to your rotational, I mean total angular momentum by twice i and it can be shown to be equal to E_t into b square by r square reaction. Now, the reaction can occur if your radial kinetic energy, radial kinetic energy at the barrier is greater than 0. So, this is your radial kinetic energy. So, if it is at the barrier, at the barrier if it is greater than 0, then reaction can occur. So, that means you can write your, in this way, from this you can write; so basically, this one. So, E_t

minus e cent minus $V R 0$; why $R 0$? That is at the barrier. So, which is, which has to be greater than 0.

So, that means, putting all the possible, you know, ingredients E_t minus E_t into b square divided by $r b$ square by b square by $R 0$ square from here minus $V r$ which is greater than 0. So, from this, we can write the maximum value of b . So, b_{max} can be calculated to be 0 square divided by 1 minus $E 0$ by E_t . Now, if you assume that $p b$, this is your opacity function, which is equal to 1 when 0 is less than equal to b is less than equal to b_{max} . So, this is your consideration. Then cross section for the reaction σ can be written as... So, from the σ can be written as σ is equal to πb^2_{max} , which is equal to $\pi R 0^2$ into 1 minus $E 0$ by E_t . So, basically, if you plot, you know, you know, σ , σE_t ; sorry E_t . This is, I should write it again; σE_t versus E_t , you can write like this, you know; it is like this. So, this is your $E 0$, so, this is your line of center model for the cross section LOC model, for you know, calculating the, you know, cross section. Next, so, this is, with a, with a, with a barrier so, atom-atom collision with a barrier.

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Next, look into this reaction. Say, O plus CH_4 ; that is the insertion reaction. So, ion molecule reaction, often do not have barriers. So, so, reaction without a barrier, without barrier in this case, although sometimes the reactants are complicated; but let us think

that these are structure-less atoms, so, reactants are **reactants are** structure-less atoms. That is, like a, they are like a, you know, hard spheres.

So, so what is happening in that case? In that case, if it is the ion molecule reaction, **if it is ion molecule reaction**, what is the interaction energy? I mean, what is the interaction that is happening? So, it is the long range potential. So, long range potential long range **potential for**... So, long range potential. So, in this case, we have to assume this ion-induced dipole interaction and which is happening **happening** at a long distance.

So, what is happening? That is, you have got an ion; say, this is an ion and this is an ion. So, this is, this is **another another...** So, this ion may be inducing dipole; may be like, if it is coming close. So, if it is a negatively charged one, what will happen? That may be, it will tend to induce a positive charge over here. So, so what is happening? That, that, you have got your, may be, may be your ion over here; so, plus charge, which is inducing. So, a dipole is induced; I mean this side becomes delta minus. So, naturally, may be other side will become, say, less; it is not negative, less negative. So, it will act as an induced dipole. So, induced-dipole ion interaction, and it is a long range interaction. And, generally, it is written as that is r to the power 4.

So, V_r goes as some like, something like minus something k divided by r to the power 4. So, this is r to the power 4 law, where this is a constant. So, it is a negative value, as this value increases, this value decreases; so, fourth power. So, although there is no potential barrier, there is no real potential barrier for the reaction to occur, but may be, **may be maybe** there is, there will be still, there will be centrifugal barrier, **centrifugal barrier**; I mean your V_{ff^2} can be written as your E_t into b^2 by r^2 minus k by r to the power 4. So, this is, this is the type of, you know, barrier, you know, may you, may be may be looking at. So, let us see the, if it is a presentation, I mean we can represent the type of the barrier, I mean let us see. So, you know, normally what is happening is that, if you, **if you** have your, **if you have your** potential barrier of the form.

So, generally your, you know, as I earlier told you, that this part is your, you know, repulsive one and this is your attractive one **attractive one**. This one is attractive and the other one is repulsive. So, so the thing is, there are, you know, different types of barriers **that...** I mean, let us see if you have that particular representation. **So, you know, you may be**. So, barrier will be like, it will be like this; may be somewhere it will be like this.

So, this is the additional barrier. So, this is because of the centrifugal force that is operative. So, that is, you know, referred to here as your, you know, centrifugal barrier. So, even if there is no potential barrier, but centrifugal barrier must be there. So, that is why this expression. So, effective v effective will be like this. And next, what you have to do?

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$$R_0 = \sqrt{\frac{2K}{E_t b^2}}$$

@ the centrifugal barrier
 for rxn to occur $\frac{1}{2} \mu \dot{r}^2 > 0$
 \Downarrow
 $b_{max} = \left(\frac{4K}{E_t}\right)^{1/2}$
 $\sigma = \pi b_{max}^2 = \pi \left(\frac{4K}{E_t}\right)$

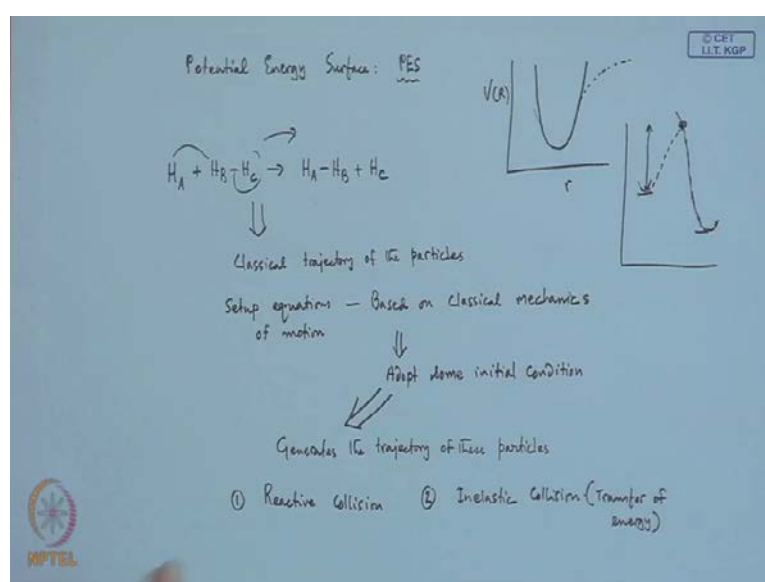
$\sigma(E_t)$
 E_0 E_t
 Langevin Model

We have to del v effective del r ; that we have to put to be equal to 0, that is to find out the location of the centrifugal barrier. And, if you do that, then del v del r effective will be will be giving you, will be giving you, like R_0 ; that is the location of your centrifugal barrier. R_0 to be like $2K$ divided by E_t into b square whole to the power half.

So, during the same procedure as we did for the earlier case of the centrifugal barrier, we require. So, at the centrifugal barrier, we require at the centrifugal barrier, we require that half $\mu r \dot{r}^2$ will become greater than 0 for the reaction to occur. So, for reaction to occur, to occur, so, and you get the, using this condition, we get the get the value of b_{max} impact parameter. So, plugging in this information as we have done for the earlier case with a barrier, we get, we get the expression for b_{max} square; and the cross-section can be, can be, I mean, b_{max} square becomes, b_{max} square becomes $4K$ by E_t to the power half, and so, σ is equal to πb_{max} square, which is equal to π into $4K$ divided by E_t whole square.

Now, if you plot $\sigma(E_t)$ versus E_t , this plot is different. So, earlier case, the plot was like this; with a barrier, the plot was like, I mean, it is different that is $\sigma(E_t)$ versus E_t plot, it is an E_0 minimum energy just cross, crossed the barrier. But since there was a centrifugal barrier, so, you know, there was centrifugal barrier. So, you know that minimum energy will not be sufficient. So, so, you have to do that; in that case, it has to surmount this centrifugal barrier. So, for the earlier case, you know, only reaction will take place at low, you know, b . So, and this is called your, this one is called the last one which, you know, reaction without a barrier is termed as the Langevin model; the earlier one was line LOC model and this is your Langevin, **Langevin**, **Langevin** model.

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Next, you know, we have to start with, you know, what is known as the potential energy, surface potential energy, surface PES? Because, you know, to look into the details of the potential energy surface, you know, we have adopted various experimental techniques; the various experimental techniques to, I have the details of this population of various rovibrational levels, that is population of various nascent rovibrational levels. So, this will, this will give us, you know, the nature of the potential energy surface that is involved in the reaction. So, for, means in **in in** the last two places of discussion we had, we have talked about this; what is happening with **the, with the, with, with** a reaction having a barrier or a reaction without a barrier and, you know, you know, cross-section reaction; cross section, when you plot with respect to E_t , **that is**, that is the translational energy.

So, then I mean translational energy, means when disassociation takes place, this excess energy, you know, because of the energy conservation, **so**, it is this translational energy is, you know, gained by the generally by the lighter component. So, if you plot this as a, I mean, sigma as a function of translational energy, then you get two different plots. That is, for the cross-section. And, when there is a barrier, then **it is**, it is different than when there is no barrier; but anyway, even if there is no barrier, the reaction has to do in order that the reaction should proceed, and it should cross the centrifugal barrier.

So, if **we**, a potential energy surface means, we all of, we, you know, most of the cases, you know, often use this potential energy diagram. Say, for the diatomic system, V versus r , ideally it is like a, **like a** parabola, but for, you know, explaining the disassociation of a diatomic system, you know, this nodes function **has been**, has been introduced to take into account of the, you know, a dissociation level; because, if the, if this is the true potential and the diagram for a diatomic system, then you will never, you will never reach, you know, you, you will never disassociate a diatomic system. But, it happens. That is why there must be a mechanism by which this does.

Now, generally, what we do for a, **for a**, chemical reaction, this is your, say reactant, this is a product side and generally, this is one potential energy diagram, and this is another potential energy diagram. So, maybe, they may be intersecting; and this point, this point is the highest point, it is called the activation energy for the forward process. So, the reaction proceeds and it goes to the active rested; and then it moves to another potential energy surface, giving rise to, maybe, disassociated product.

So, let us consider, you know, reaction in a collinear fashion; that is, $HA + HB \rightarrow HC + H_2$ reaction, giving rise to $HA + HB + HC$. So, we would like to find out the classical trajectory particle. So, classical trajectory of the particles involved in such reactions. So, what you have to do? And since, you know, as I mentioned earlier, that for Langevin system, quantum mechanical, you know, calculations are difficult, and since it is a, you know, hard sphere collision model, you can nicely apply, you know, classical laws of motion **for a** for a state of initial few initial conditions.

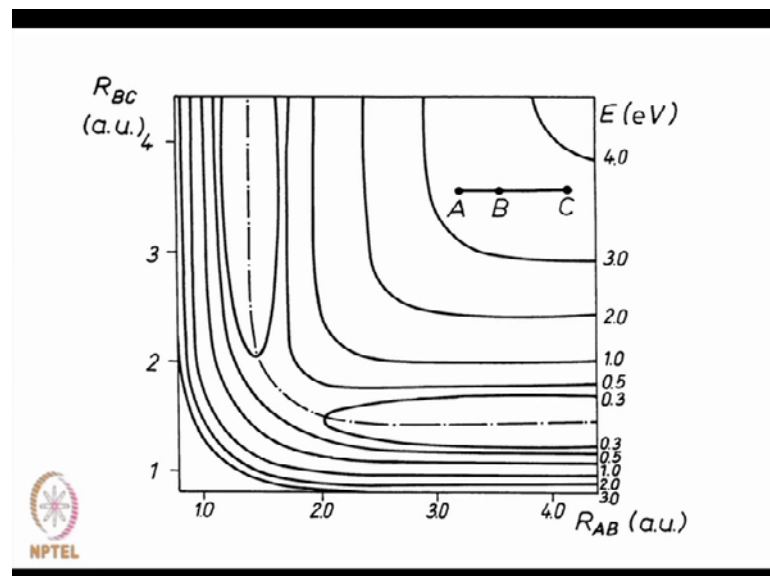
So, you setup classical equation of motion. So, setup equations based on classical laws, based on classical setup equations of motion of various particles, based on classical mechanic and adopt some initial condition, **adopt some initial condition** which leads to,

which gives rise to trajectory of these particles during reaction, during a course of reaction. So, generate the trajectory of particle.

Now, in one case, you may have two options; one is reactive collision, another is inelastic collision elastic; I mean, I mean inelastic one case you will have means, that trajectory is correspond to, you know, may be reactive collision that will lead to the chemical reaction or may be, **may be**, inelastic collision; other situations will be inelastic collision, elastic collision and inelastic collision. So, so, inelastic collision means transfer **of energy** of energy.

So, what is, you know, happening? That you say this is simple case, that HAI mean, hydrogen atom reacts with hydrogen molecule dehydrogenate, **basically to...** So, this is basically an atom exchange reaction and it is expelled, this one is expelled. So, so classically, you have to solve the equation. So, classically, you have to solve the equation means, we have to setup equation of motion for individual particles with based on classical mechanics. We have to adopt some initial condition; initial conditions could be like initially, they were in this bonded distance, and this distance was larger, then gradually will reduce the distance, so that, this bond is firmly, it is increasing.

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So, we generate trajectory of particles and the two situations could be your, you know, one situation could be your reactive collision that leads to reaction, other situation could be your inelastic collision; this is a representation of your three atom system like HA HB

and HC. This side is your energy, so, it is your this line joining the same energy contour. So, this is your RAB, this is RBC. So, AB, RAB between A and B and RBC. So, this is a contour. So, energy contour, and you see it is value is, this is your 0.3, this is 1; it is increasing. So, this is the, **this is the** minimum energy, I mean, joining minimum energy line here; it is more, it is still more. So, it is basically a valley, **it is basically a valley**. Of course, you know; this along this diagonal. So, it will, this portion, this is called the highest energy, you know; this is the highest energy state, maybe it is the top of the potential energy barrier, **which is called the...** So, what is happening? That here, AB and BC, **so, so** maybe it is proceeding from here to here, the reaction is going on.

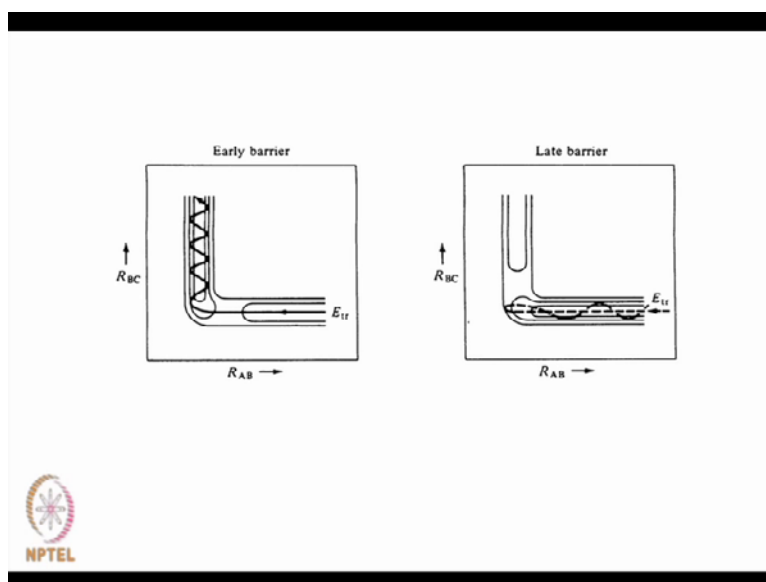
So, fall for the reaction to occur, maybe this is your progress of reaction; this is the progress of reaction may be this way. So, what you, what we are doing here in the potential energy diagram? The potential energy surface shows equal energy lines are joined together. So, this is your 0.3. So, this is joined together, this is another same energy value. So, this corresponds to your 0.5, this line corresponds to your 1, this is 2, this corresponds to 3. So, energy is increasing high and high; and here, is energy is increasing so high then lowering; this is minimum; then again it is going up.

So, thereby, you know, **so**, you join the equal energy lines with equal energy points with lines to generate your contour; and these contour, say, and this contour; I mean this is a, you know, cross-sectional wave. This contour is called the, you know, potential energy surface, this is called the potential energy surface and **it is a**, it is a three dimensional one, because, you will have another, you know; this way access, you know, projecting, you know, towards you. So, so, what is going on here? That, **so**, this way, you can, **you can, you can** generate the potential energy surface for various, you know, various reactions. The example which we have used over here is the, **is the** simplest example of hydrogen exchange, it is a hydrogen exchange reaction.

Next situation is, you know, let us have situation that early barrier this is your early barrier the barrier is over here. So, the barrier could be somewhere over here; in the earlier keys, the barrier is here. So, it is going this way, then again it is going on top; I mean here, in this region. The energy is again increasing from here, next is still more energy, still more energy, like that energy is increasing.

So, ultimately, here somewhere over here, along the, **along the** diagonal somewhere over here, it is, you know, it is, I think the highest energy and then again it is reducing. So, when reaction process may be this way, to that way or may be that way to this way; so, it passes through a maxima and then again minima.

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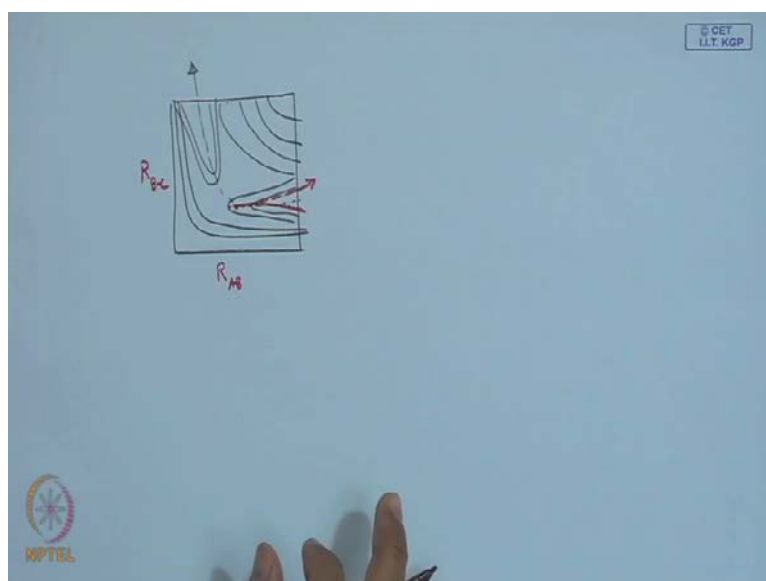


So, that corresponds to the barrier of the process; but the situation could be, that barrier could be earlier, which is called the attractive release. Earlier, over here, originally, in the earlier picture, it was somewhere over here, but it is here. So, barrier, in the entrance channel and this is your translational energy. So, one means, actually, if you think of your absolute reaction rate theory, that one of the vibration nodes is converted to a, **to a** translational mode, and that is responsible for the passage of your reactant to passage from reactant to the product.

So, barrier is somewhere over here means, it is early; it has been, you know, it is somewhere means, over here means, earlier than this point. So, barrier is in the entrance channel. So, exo-thermicity released before it, reaches equilibrium position. So, this is one situation you know. So, it crosses the barrier and then it crosses this part; basically, maybe fragmented products. Maybe this corresponds to the reaction per unit, you know, this represents a reaction. But the other situation could be, you know, if the barrier is somewhere at later point, **so**, what will happen in that case? In that case, it is a repulsive release and barrier in the exit channel. So, this is called your attractive release.

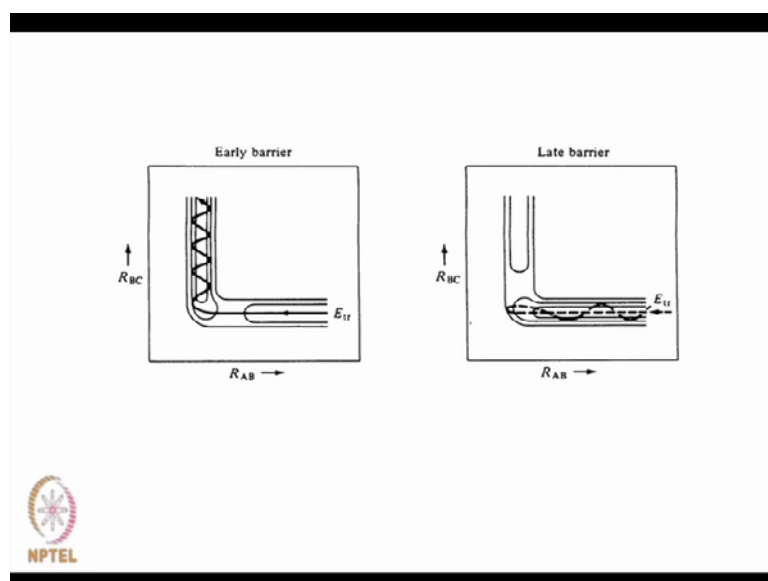
So, barrier is here at the earlier point, but if it is at later point, then this will tend to, maybe this will, you know, tend to be repelled. So, it is called the repulsive release and exo-thermicity released as BC extends. So, if this extends, exo-thermicity is released; preferential release of exo-thermicity into products product translation. So, anyway, so, these are the two possible situations; but another point is that, if it is, you know, inelastic collision means, for a reactive collision maybe for a reactive collision, your potential energy surface.

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I mean, let us draw it over here, maybe like this; they may be here, so, it proceeds this way. But when it is inelastic collision; that is energy transfer; then what is happening? It is like, of course, this is RAB, RBC, so, in that case, it goes this way, then it goes back. I mean, it returns, and of course, in a, in a different direction. So, this is a situation for your reactive collision. So, what you got is that, we have given her a brief introduction of the potential energy surface, that it is based on the classical trajectory analysis, and that gives you an idea of, you know, whether, it means, it gives you the idea on the location, of the, of the barrier and also, whether it is the case of an earlier barrier or it is the, it is the, case of a late, late barrier.

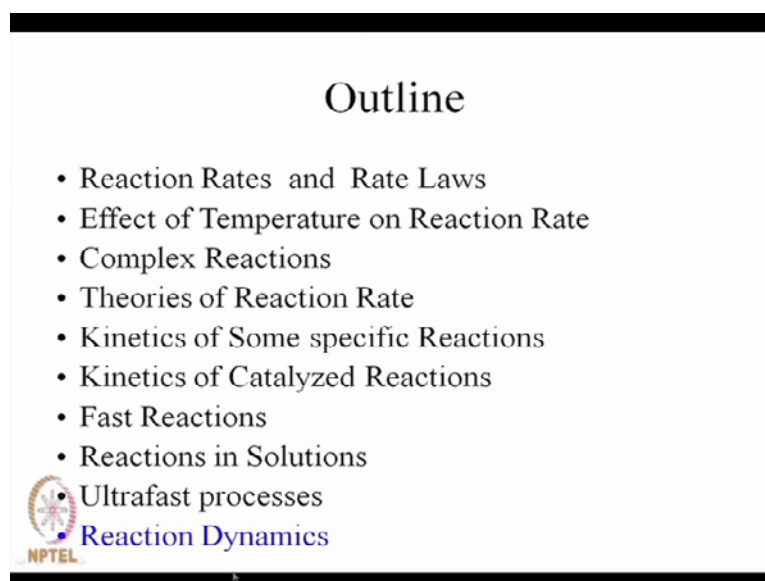
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And of course, when it is the case of earlier barrier, it is **your**, called the attractive release; and the latter barrier, it is called the repulsive, you know, repulsive release. Anyway, that is just giving you a brief idea of the potential energy surface, which is a three dimensional description and other things that we, **that we**, already have talked; it is, you know, opacity function means, measuring opacity function, you know. You can take help of this laser-induced fluorescence method to find out the opacity function experimentally from the distribution of the product. You can, in principle, **find out**, find out the opacity function; because opacity function, **is a**, is a very important, it is a probability function. So, it is, **it is**, an important quantity that while, you know, **you know**, starting this reaction dynamics, it is an important thing.

We already have talked about Fenton chemistry that deals with, you know, that deals with, you know, **you know**, different potential and a crossing; and crossing of different potential energy diagrams; and how sodium iodide decomposes; and decomposed to sodium and iodine; and how, you know, this equivalent and electro, you know, ionic potential energy diagram, you know, crossing each other; and how to explain, I mean, we have explained why there is a there is an oscillation in your, in the, **in the, in the**, absorbed, I mean, time spectra. So, that is also that already has been discussed. So, anyway; so, that covers most of the, you know, major portions of the of reaction dynamics.

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So, we almost have covered the portions; that is, let us go back what are the, what we should have, you know, like let us look into the portions that we have talked about. That is, that is, we already have talked about ultrafast processes. Under that, you know, I mean, some of the portions are come into Reaction Dynamics, like second reaction dynamics; that is the time evolution of the processes; and that, we already have discussed.

So, anyway, some of the portions that we are still to, I mean very little portion that we have not talked about is corrosion; that is, what is happening in corrosion, what are the events, I mean, events that is going on in corrosion. So, maybe we will talk a little about, you know, this femto-chemistry, again, in connection with this potential energy diagram, up in the next lecture. Once, I mean, it is relevance with, you know, reaction dynamics and how or maybe, you know, some other like other reactions like, using use of photoelectron spectroscopy or other techniques, how to look into the transition state of a reaction.

So, may be some of the portions which is still to be, you know, covered, that, we will, we will discuss, may be under the heading of, under the heading of, under the heading of this molecular reaction dynamics. And, may be a little introduction of collision, I mean, corrosion will be will be dealt within the next lecture. So, till then, have nice time.

Thank you.