Rate Processes

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Lecture No. # 36

Reaction Dynamics: Controlling Reagents etc.

Hi, good morning everybody, friends we are back here again with this rate processes. So, we were in reaction dynamics; and we started with this collision processes, and we discussed many other aspects, and last in in our last lecture, we have taken up this mechanism like, one is harpoon mechanism, and we also discussed this rebound dynamics. Now, as a, you know, as a recapitulation, now harpoon mechanism; what is this harpoon mechanism?

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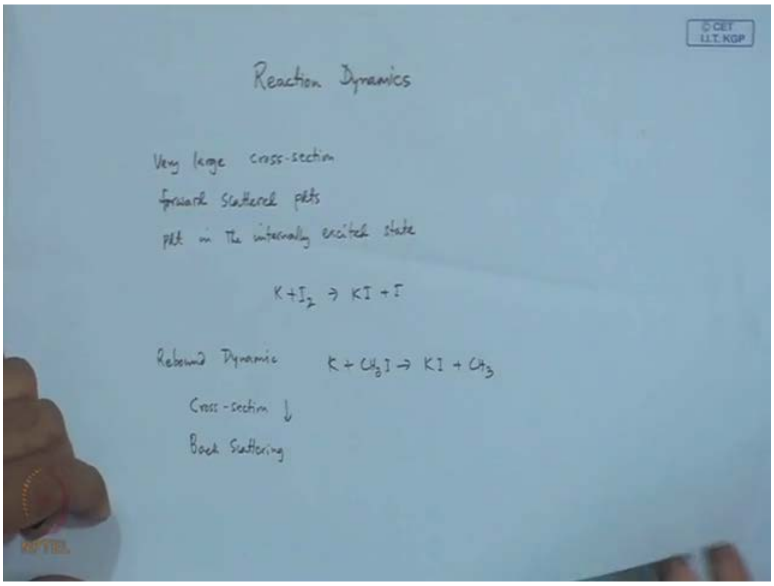

Reaction Dynamics

Very large cross-section
forward scattered pdts
pdt in the internally excited state

$K + I_2 \rightarrow KI + I$

Rebound Dynamic $K + CH_3I \rightarrow KI + CH_3$

Cross-section ↓
Back Scattering

Now, this reaction has got large cross section, very large cross section; cross section and in generally forward scattered products are obtained forward scattered products; and in the translation mode, low energy is released, and generally your product is in internally excited state. So, product in the internally excited form excited state, and it is in this case, what happens that for for this harpoon mechanism, fairly heavy reactants, plucks the light atom from the other reactant, and and a and basically the remaining part is acting as as if it is a spectator, it is it cannot do anything; so and reaction occurs.

So, basically you know, the reaction is like, I have given example of K plus I 2 or maybe K plus b I two giving rise to K I plus I 2 sorry K I plus I, so it plucks iodine from this I 2. And this is one thing, I discussed next, we talked about this rebound dynamics rebound dynamics; and we have taken the example of K plus CH 3 I giving rise to K I plus CH 3, and in this case, in this particular case, cross section is small, so cross section small and back scattering, we we get back scattered product, so back scattering; and the energy is mostly in in translation form. So, that we talked about you can have other examples, like fluorine plus hydrogen giving rise to H F plus H 1, H F is in the vibrationally excited state.

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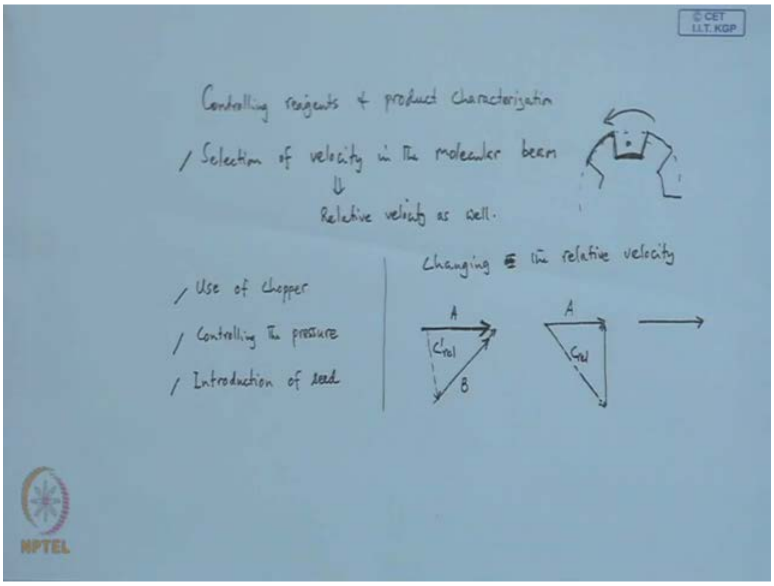

Controlling reagents & product characterization

/ Selection of velocity in the molecular beam

⇓

Relative velocity as well.

/ Use of chopper

/ Controlling the pressure

/ Introduction of seed

Changing the relative velocity

Next, we will start with controlling reagents; controlling reagents reagents and and product characterization; now now how to select means how to select that; so in the molecular beam, you can you can… There is option to to you know, set the velocity, select the velocity, so selection of velocity, so the thing is selection of velocity in the molecular beam - molecular beam.

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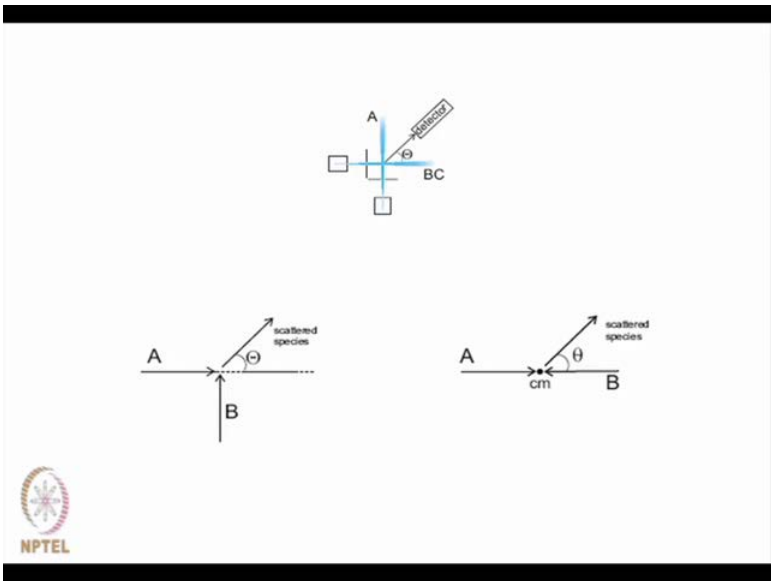

So, basically you know, here you see that your two molecular beams, they are intersecting over here; and they are at 90 degree angle perpendicular, and the detector is you know, oriented somewhere in between. So, it it can move in this way; so, angle - as a function of angle, it can change; so that the detector can detect the product in various angles. Now, the question is do you really means have to keep the the two beams at perpendicular direction at an angle of 90 degree always? So, the thing is that that that I can change actually; now there there are means, now the way is like that, one thing is that how to select the velocity; I mean, this selection of velocity may be it is not the absolute velocity, but it may be a relative velocity, relative velocity as well, relative velocity as well.

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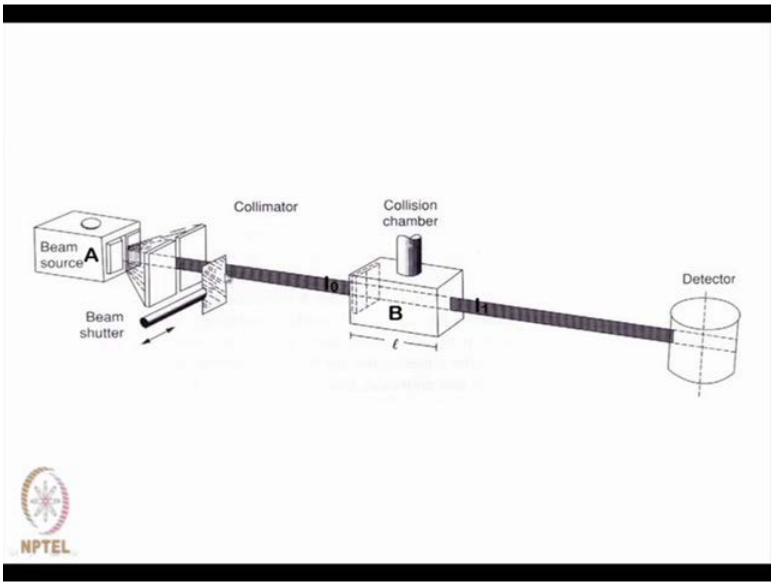

Now how to how to select the speed, I mean velocity; now this can be this can be achieved by chopper like here; you know, like like the beam shutter, you can have a chopper, like chopper blade you know, you know like fan blade, so you can chop you know, certain certain speeds like that; so it is moving - this chopper is moving this way, so, it it selects a specific you know, velocities; like depending on speed speed like, the chopper can be like this; it is a part, I i am showing just a part of that that (No audio from 07:41 to 07:51) so, so when molecular beam is perpendicularly falling on this, this portion is there is no you know block, I mean it is it is open, so molecules can pass through it; next when say this is rotating this way, so next instant maybe maybe for some time, suppose it it has got the speed, some speed, so that I mean and your molecular beam is somewhere over here, so this will continue to keep you know, keep the molecular beam to go to the other side of this page, as long as this block is coming over here.

So, this molecular beam will be will be on for this much of time, I mean the time required for this this part to come to here. So, it will remain on and then off for this much of time, so depending on speed of the the molecules, which are able to come here, can pass through and those which are not able to able to come to this plain of your paper, will not be able to pass to the other side of the paper. So, slower moving slower moving molecules you can select, I mean slower slower moving molecules you can you can stop and you can allow only faster moving or or vice versa depending on your necessity, whether you can… If you are if you are and you know, rotating this this chopper at at some different speed at at some lower speed, then it will allow allow lower speed to pass through, so this way you can select. So, that is one mechanism; so it is it is a kind of you know like this, this is although, it is it is beam is completely blocked by this, but if you can arrange means, if you can replace this with a with a like this chopper, you can select different speeds that is one thing.

Next is, I mean so, so use use of a chopper use of chopper, may be if you if you change the pressure difference, pressure pressure difference between the source and the and you know, target. So, so that will also also change the change the velocity, so controlling pressure, controlling the pressure; and third is introduction of seed, introduction of seed that is it is mixed with some some seed beam, you can you can change it, I mean so there is collision between the seed molecules with with your reactant, and then where the velocity may change. Another, option is that you know, changing of the relative velocity; so changing of the relative relative velocity, relative velocity that is changing the relative velocity, you can changing the relative velocity you can do it.

So, like if you can change the angle between this beam, so this is one one path and suppose this next one is oriented at an angle, which is not exactly 90 degree may be this way, so that means that means in that case suppose this is your A, and so and say this is your this is your this is your originally this was your B, so your relative speed is this, C relative. In other case, say A is remaining like this, like here and your your relative speed is now is now has changed like somewhere here, say if you keep the length fixed, so this is your C primed relative; say this is your A, and say, this is your B, so you can you can change the relative speed by by changing the angle between by changing the angle between between the two two beams; that is that is the intersection angle, the angle of intersection that is the angle originally, it angle was like 90 degree; originally the angle was like 90 degree; as as here 90 degree, but you can change the angle, you can change the angle. So, that will change the relative relative velocity.

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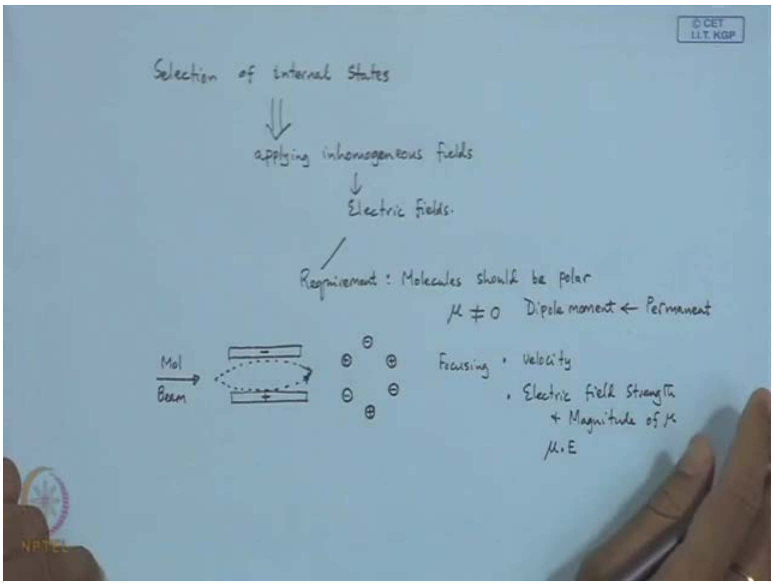

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Selection of internal States

$\Downarrow$

applying inhomogeneous fields

$\downarrow$

Electric fields.

Requirement : Molecules should be polar

$\mu \neq 0$ Dipole moment ← Permanent

Focusing · Velocity

· Electric field Strength + Magnitude of μ

$\mu \cdot E$

Now, next is the question of selection of internal states internal states. So, selection of of internal states, internal states means various quantum states; so you can do that by applying applying inhomogeneous homogeneous fields; that is inhomogeneous electric fields; the thing is that the molecule in that case, molecules I mean, the your your reacting molecules, the requirement is requirement is that your molecule should be your molecule should be molecule should be polar that is dipole moment mu should be should not be equal to 0. So, dipole moment that the that should have permanent dipole permanent dipole moment.

And, what you do is that so you have got say plus or minus plate over here, so these two plates are oppositely charged, and so, what you do is basically, you know say this is your minus plate, say this is your plus plate, so this this is so this from this side your molecular beam is coming; molecular beam containing polar molecules, so what will happen that this cold molecular beam, they will tend to be deflected this way, so if we if we view… This is side view; if we view view from the other side, it will be something like, it is like hexagonal alternate plus minus, plus minus alternate; minus, this is plus, this is minus, this is plus, this is minus, this is plus, so molecules will pass through this inhomogeneous you know, electric field; so you see that it is not homogeneously changing from here, if you go from here to here it is plus; again it is minus. So, and again it is it is plus minus so, it is it is changing constantly with with position. So, it is changing constantly with position.

So, and depending on the internal state of the molecules, internal state means, whether it is you know, like different j state that is rotation on states, so you know, you can select. So, basically you know the velocity with which so, what you have to do? You have to focus like right, so focus is somewhere over here. So, these molecules will be you know, will be attracted, and then again it will go this way. So, basically if the field is not there, they will pass you know, in a linear fashion; the moment it is it is you know, you you apply electric field, it is bulging out. So, it becomes like a concaved kind of convex kind of thing; and then ultimately again it will it will focus over here.

Now, this focusing will depend, means where it will focus? It will depend on the velocity that is this velocity so focusing; so it will depend on velocity and also depend it will depend on the electric field strength strength and magnitude of magnitude of mu; and actually depends on on the on the on mu dot E; basically, mu dot E means, mu E cos theta, so component of dipole moment along the field, so it is a dot product, so component of dipole moment along the field, it will depend.

And, you know separation, I mean, energy change as a result of this this interaction with dipole moment and E is given by mu dot E; so originally energetically degenerated - degenerated pulse are now not degenerate, as a result of this interaction, because of this interaction there are no longer they will no longer remain degenerate, so there will be some separation of energy levels; so energy levels are you know, degeneracy is lifted depending on its on its you know, depending on the interaction of your dipole moment with E. Now, then the thing is that next is you can select; so one option is your inhomogeneous electric field, using inhomogeneous electric field, you can select internal states. Now, you can do that you know, by by also by by Laser excitation, there is another means another means, which is called the Laser excitation method.

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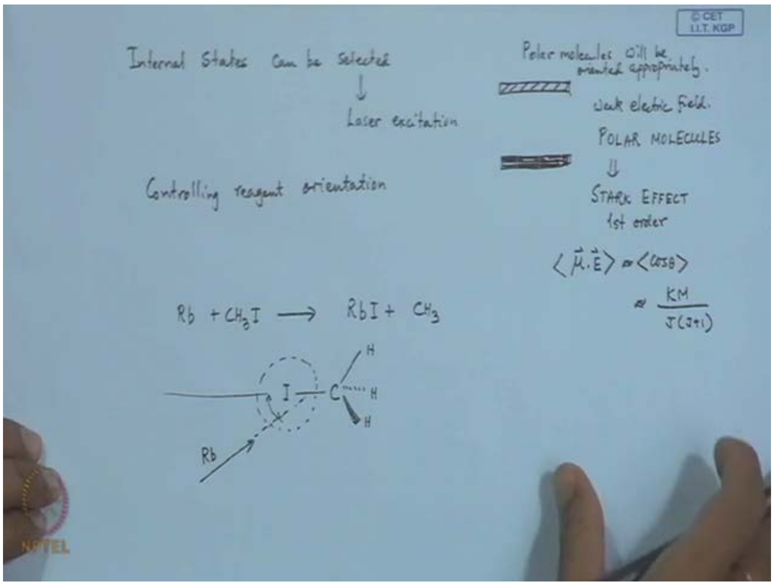

So, internal states can be selected can be selected with the help of Laser excitation; and high number density, that is high population is you know sometime hypo population density of the excited species is sometime difficult in cross molecular beam experiment. So, in that case although you know, we can select, but depending on laser intensity and also frequency, but it is it is possible, internal states can be selected by means of by by using laser excitation. Next is, how to control the reagent orientation; so controlling the reagent orientation controlling reagent orientation.

Now, another option is although, I i talked about this inhomogeneous electric field, where you can depending on the interaction between your your field and between between the dipole and the field; you can you can select the different velocities or you know, different internally excited states. Next, is you can apply a very weak electric field, so weak electric field like you know, say there is a weak electric field, say in between, in between these two parallel plates, and a polar molecule will be oriented in a definite fashion, and it should not be very strong field, it is a weak electric field; so polar molecules will be oriented oriented appropriately.

So, by this way you can you can have the have the orientation of the reagent; another important thing is that, because whenever you do laser excitation, so laser is basically you know, strong electric field. So, the moment this electrical field is passing through your reaction mixture the moment, it is passing through, what is happening that and and also laser is a is a you know, polarized source of radiation; so polarized means its electric vector has got a definite you know definite plane, so this electric vector is oscillating in a definite plane; so the moment it is passing through your mixture, gas mixture, because we are dealing with gaseous reaction and molecular beams; so, the polar molecules will be oriented will be oriented means, the there is a there is a great chance of these those molecules you know getting oriented with respect to the electric field vector of your laser source.

So, this way there is you know there is a chance of orientation, so if you use a weak electric field, then you can then you can so for by weak electric field, you can you can get oriented spaces, the thing is that only important point is that that for polar molecules polar molecules of course, ofcourse, for polar molecules and this orientation you know, is because of the stark effect so and this is because of stark effect; so first order stark effect; and and this average angle between the field and the dipole moment is basically you know, mu dot E cosine theta average, which is you know which goes as like this, so KM divided by J into J plus 1, this way. So, this way you can you can select, you know select rotational states, you know applying your first order stark effect, you can select different different states, depending on depending on how much electric field you are applying. So, depending on electric field, this perturbation is coming accordingly, so they are for your selectively selectively you know, generating the perturbed state.

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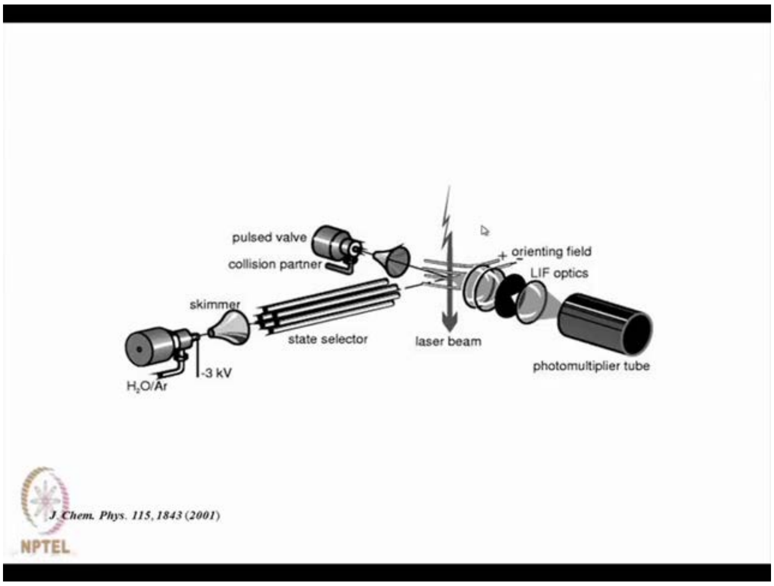

J. Chem. Phys. 115, 1843 (2001)

Next is we will have we will have a you know, an apparatus, which is taken from journal of chemical physics 2001 edition volume 115, where this apparatus you know, gives you the idea of how to you know, do this this collision experiments. So, here you see that you know, it is a reaction between H and carbon monoxide; so it means, it is a collision between H and carbon monoxide, so oriented oriented H. Now you see here you have got H 2 O and argon, they are mixed and then it is passed through a high electric field, electric discharge. So, that this H is generated, then this H through a skimmer and is passed through this you know hexagonally oriented plates, alternatively plus minus, plus minus this way. So, it basically is a selector, it is a selector; and so it generates one partner of course, ofcourse, it is a state selected partner; and then you have got another partner over here. It is also a pulsed valve, and then it is skimmer, and there you have got two beams, and laser beam is here, and this is an orienting field you are applying.

So, what is happening that you are measuring here the light induced fluorescence from your from your products, and there is a photomultiplier tube, which detects the light induced fluorescence with corresponding optics is here, corresponding optical arrangement, so which detects light induced fluorescence; and laser beam which you know excites the sample, and then you accordingly get the laser induced fluorescence. So, so, basically, it is a it is a typical apparatus, by which you can study, so it is schematic and it is taken from chemical physics, journal of chemical physics. So, it is an example of means, how to study and using of course, ofcourse, the laser induced fluorescence as the detection technique.

Next we will move onto next we will move onto you know, is there any stereochemistry? That is whether whether some specific orientation is important for a reaction to take place. So, for this let us take one example that rubidium plus CH 3 I giving rise to rubidium iodide plus C H 3. Now, the point is that you have got the point is here that you have got your CH 3 like this; 3 hydrogen and 1 iodine; and you have got say rubidium, which is coming say from this way; and you want to know you want to know whether whether you are getting any R b I in the backward scattered direction, so to see whether see signal, when iodine of CH 3 I is pointing towards rubidium beam that is important to know, that means that means look for R b I in the backscattered direction, so that is in this in this direction, so it is the backscattered direction.

So, so, basically you know, so if you if you measure that then it should be giving you the idea that whether this geometry or the other geometry is important or not. And, whether there is barrier, I mean if if it is approaching from this side, whether this, you are you are getting your product or it is approaching from this side. So, whether is there any any any means, the reaction faces any barrier with respect to with respect to the angle at which it is attacking your reactant. So, angle of attack is important; so angle of attack means this is your line, so maybe if it is coming this way, this way, so maybe this is your angle of attack. So, whether you know, your your backscattered product is very much dependent on the or the or the extent of your product formation is dependent on on the angle.

So if you want to know more on that you know details on that you can you can go through this Levine's text, so that is the that is the basic idea that maybe maybe this if it is attacking from this side or maybe from this side or maybe this side. So, amount of backscattered product you are you are getting is more or less. So, that will give you the idea, so and not all the reactions display strong Steric effect, because if it is approaching this side, so it cannot access this iodine; so, there is a there is some you know, Steric factor, so the reactions which proceed without any barrier in on the potential energy surface are not generally generally you know, showing showing strong steric effect. Next, is if we would like to if we would like to you know, so here we we have you know, given you the idea of the steric factor, and also told that if it is barrier less then steric factor is less.

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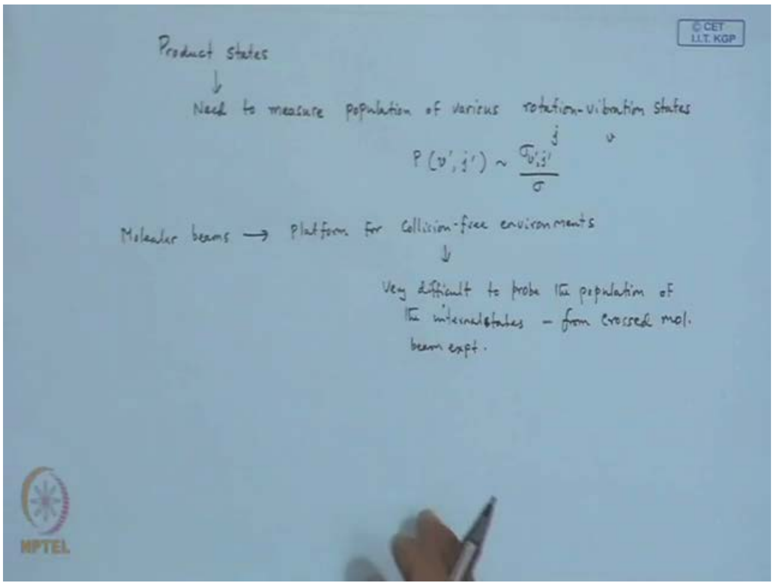

Product states

↓

Need to measure population of various rotation-vibration states

$$P(v', j') \sim \frac{\sigma_{v',j'}}{\sigma}$$

Molecular beams → Platform for Collision-free environments

↓

Very difficult to probe the population of the internal states – from crossed mol. beam expt.

Next is product states product states, so we have to we we would like to you may need to need to measure need to measure measure populations of various rotational vibrational state; rotation vibration states that is characterized by j and v numbers; of course, in the products, and this provides information on the you know, state resolved cross section means, which you know, cross section of specific state resolved reactions, which states are more you know having having more cross section than than the other. And, that is you know quantified by p v primed, j primed, which is like which goes as sigma v primed j primed divided by sigma, where cross section is the sigma; so this sigma is the total cross section, it is provided, it is known, we can we can find out you know, this probability probability factor.

Now if the velocities are not particularly selected, but if if they you know if the velocities are you know thermalized, I mean they are just thermalized, then the population provides information on the state resolved reaction rate constants; and the population provides, this population provides you know the information on the nature of the potential energy surface. So, next is for the measurement; this molecular beam, since molecular beam, molecular beams so it is giving you a platform of collision free environment, so platform for collision free environments; collision free environments.

So that means there is more scrambling of internal states by by energy transfer, that is one good advantage of molecular beam and but it is very difficult you know, very difficult to probe into into difficult to probe the populations of the internal states of the internal states internal internal states from crossed molecular molecular beam experiment. So, it is it is very difficult to find out these things; so, there there requires other techniques by which maybe you should be able to you should be able to find out you should be able to find out this internal state population.

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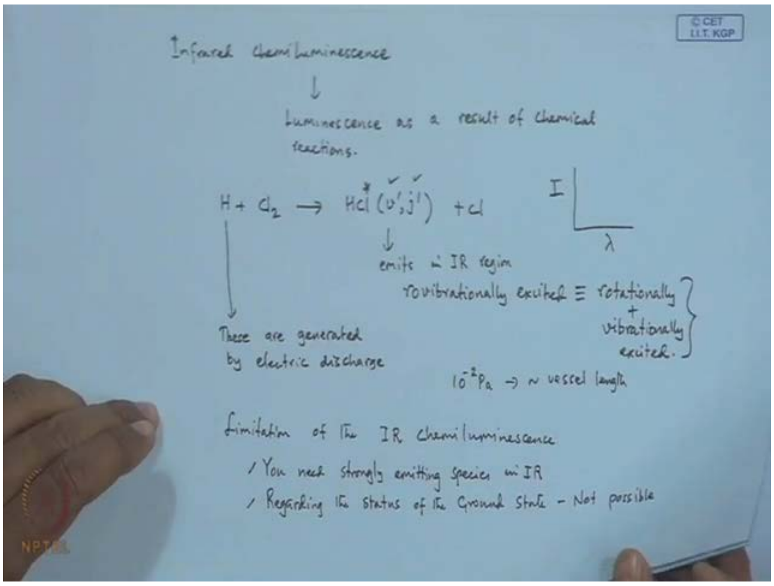

Infrared chemiluminescence

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Luminescence as a result of chemical reactions.

$H + Cl_2 \rightarrow HCl^*(v', j') + Cl$

↓

emits in IR region

rovibrationally excited ≡ rotationally + vibrationally excited.

These are generated by electric discharge

10^{-2} Pa → ~ vessel length

Limitation of the IR chemiluminescence

/ You need strongly emitting species in IR

/ Regarding the status of the Ground State - Not possible

So, other methods are like you know, one is infrared chemiluminescence. Infrared chemiluminescence So, luminescence as a result of luminescence as a result of chemical reaction; luminescence as a result of chemical reactions, so there are plenty of examples you will be finding in any standard physical chemistry text like luminal; so if you if you react with H 2 O 2, so it you know luminous; so it is a cyclic hydrazite, so it will luminesce; so and it is in solution. Now, in gas phase reaction like H plus C l 2 giving rise to giving rise to H C l v primed, j primed plus c l, so this is your you know, rotationally and vibrationally both excited; both rotationally and vibrationally excited; excited you know, system; and it emits it emits emits in the IR region; so it emits in the IR region, so basically what is happening that your hydrogen atoms, these are generated these are generated by by electric discharge electric discharge, and because of this collision, because of this reaction H C l is generated, gas phase H C l is generated in the rovibrationally excited; state rotation vibration both way excited; excited in both sense, So rovibrationally excited meaning rotationally plus vibrationally vibraionally excited; rotationally and vibrationally excited and it luminesce.

So and if you if you can record if you can record the emission spectra, as a function of frequency or as a function of lambda, wavelength you can you can indeed find out the population that is population of the internal states, population of various v and j states; so in this case, what we have to do that you know low pressure, in low pressure case so about 10 to the power minus 2 pascal pressure, and which is low pressure will ensure that

that mean free path is of the order of, which will ensure that mean free path of the of the of mean free path of the process is of the order of vessel length, length and H C l, what is happening that this excited, this is you can write as H C l star; so H C l hits the wall sticks, and then it is deactivated before any secondary collision. So, on IR emission you know, you have to you have to record in in IR emission spectrometer.

So this is one way so you have to you have to ensure that low enough pressure is there, so that this mean free path is about the vessel size, H C l hits the wall, and then sticks and then deactivated before any secondary collision; deactivated means this it is emitting IR photons; so the thing is that it looks like an an interesting piece of experiment, but the problem is that although in this case, it is a nice example nice example that you are getting IR emission, which means when plotted this IR emission, which when plotted as a function of you know you know emission intensity, intensity as a function of lambda will get you important information on the population of various various levels, but the problem is limitation is that not all products, I mean like this are are IR emitters and of course,ofcourse,,,, there should be very strong IR emitter, otherwise it will be a problem, because if it emits but, very but, very weakly then this this will be of not that you know usage.

So, in this case limitation is like limitation of this infrared IR chemiluminescence method, to look into your internal state population; so, it is you know, limitation is like you need you need strongly emitting species emitting species in IR, regarding regarding status the status of of the ground state not possible; so, so we do not get any information about the ground state, so this is another another you know another problem, and first is the species should be strongly emitting in the IR, otherwise otherwise infrared luminescence detector, I mean you know, detector is you know, it will not be very useful. So you need a infrared detector and your species should be strongly emitting in in IR but, the problem is since it is it is emitting from some excited, I mean rovibrational state, so rovibrational excited state; so you do not get any information about the population of the of your ground state.

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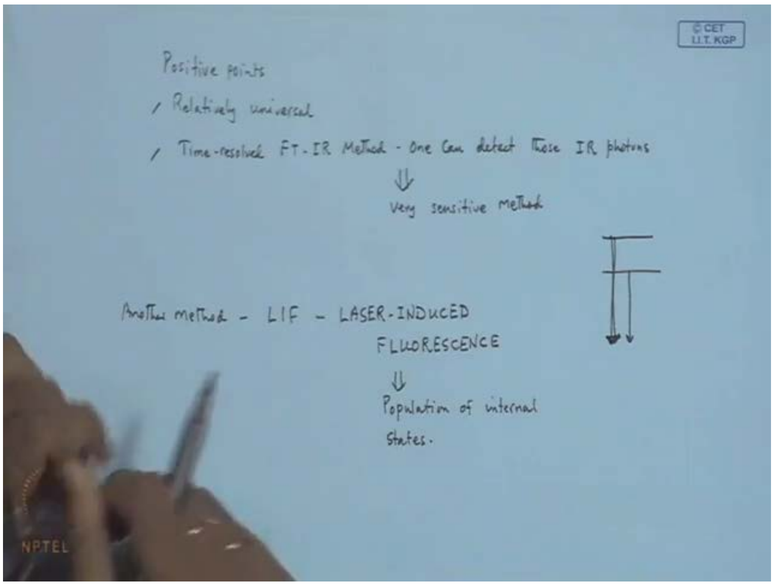

Positive points

✓ Relatively universal

✓ Time-resolved FT-IR Method - One can detect those IR photons

⇓

Very sensitive method

Another method - LIF - LASER-INDUCED FLUORESCENCE

⇓

Population of internal states.

So, what what is happening to the ground state you know, it is difficult to know on that positive points, that one is you know, limitation is a negative negative points. So, positive points it is you know relatively relatively relatively universal, it is universal method. Next, is IR emission can be detected by time resolved FT-IR techniques. So, by means of FT-IR - Time Resolved time resolved FT-IR method, one can detect detect those detect those FT-IR photons IR photons and it is it is it is it is very sensitive very sensitive sensitive method.

Nowadays this FT-IR technique has been has been employed, so so positive you know, of course, ofcourse,,,, it it is very it is a very positive you know, thing that that this method at least give you although not for all reactants, you can get information about this various levels like vibrationally and rotationally excited levels that is a population on that, but still for some reactions like the reaction, I am using over here like H plus C l 2 giving rise to H C l in the rovibrationally excited level, and H C l which is which is formed in the rovibrationally excited level, gives rise to infrared photon, and that gives you information on the on the population of this various levels.

So, that is why, in that respect it is it is a successful thing that using infrared chemiluminescence that is luminescence as a result of chemical reaction, you can find out the information of the various, I mean information of the population of various levels; although it is limited, I mean limited means like H F H C l these are useful, I mean in limited there are there are limited number of infrared emitters, and of course, ofcourse, ground state information you know, it is it is not possible, because we are we are probing the upper level, so from upper level to lower level it is coming and because of this luminescence, we are we can think of I mean we can we can calculate the population with that the upper level, how much it is populated; we can we can you can find out.

So, I mean as a function of wavelength, as a function of wavelength we can if we can record the luminescence spectra, we can get information means, which one is more populated, which one is less populated, I mean higher level, which higher level is more populated, whether this higher level or that higher level is more populated. If this higher level is more populated, so chemiluminescence from this level will be more intense, is intensified compared to maybe this level. So, from that I mean from the intensity distribution you can get the idea of the population of this level.

So, so, that is one one important technique infrared chemiluminescence, we can probe the internal state population although cross from cross molecular beam experiment, it is it is difficult difficult to find out, but from this method we can we can find out, so that is one method. Another method is Laser Induced Fluorescence method, so another method method, which is used which is used is – LIF - Lasar- Induced Fluorescene, Laser Induced Fluorescence to probe into the internal state population for for looking into internal population of the of internal states, so that we will take up in the next piece of lecture.

So, before we conclude today's talk, let us have a quick recap that reagents state, selection in molecular beam, we have talked about and in this case, by using chopper controlling the pressure, source pressure and also introduction of seed can you help in selecting velocity of the of the reactants; and regarding relative speed, relative velocity, you can change the angle between your angle between your two crossed beams, so that you can change so you can change -consederative and you can internal state you can select by introduction of the inhomogeneous magnetic, I mean electric field generally there are six you know, I mean alternatively oriented, hexagonally oriented, plus minus plus minus poles, and by means of laser excitation, you can also select certain you know, internal states.

By the use of your first order stark effect, you can also choose specific rotationally excited level, I have given a example of typical example, I mean example of a typical apparatus by which you can you can study collisions. And, stereochemistry is an important factor for this reaction I mean in certain cases barrier is very much dependent on the angle of collision and looking into the back scattered product, you can see whether this process is is having large barrier or low barrier, and generally when it is low barrier, then steric factor does not play that much of important role.

And, to look into the internal state population, we have discussed one we have discussed in in short in in that you know how you can measure the internal state population that method is you know, infrared looking into the infrared chemiluminescence. So, that will help in, I mean that will give you idea on the population of the of the upper state rather than the lower state that is the ground state. So, that is all for today; so, in the next piece of lecture, we will start with a technique, which is called the laser induced fluorescence technique, so till then have nice time thank you.