Rate Processes

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Lecture No. #37

Reaction Dynamics: Controlling Reagents etc (contd.)

Hello friends. We are back with Reaction Dynamics. And, we are almost towards the end of these rate processes. So, last lecture, in our last lecture, we discussed this, discussed how to, I mean, how to find out the population of various states. So, we discussed infra-red chemi-luminescence.

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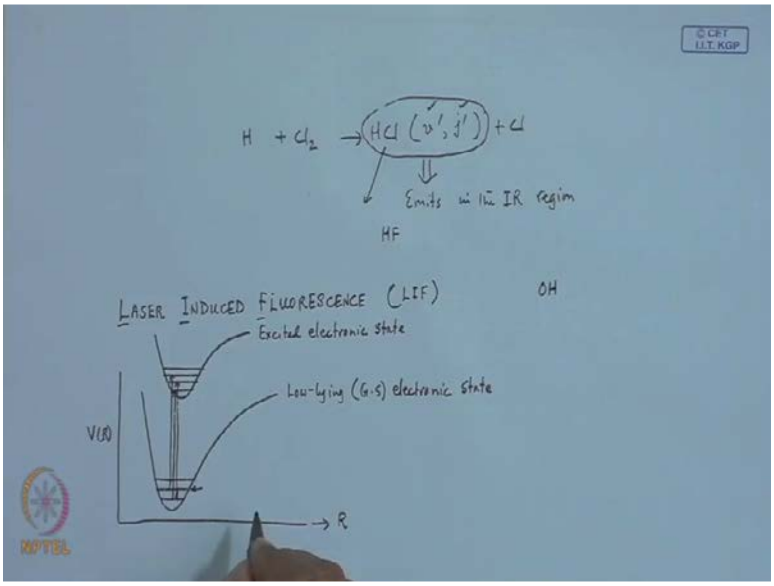

So, infrared chemi-luminescence, and we have taken the example of, I mean, gas-phase reaction. That is, you know, like diatomic halogen; H plus Cl 2 giving rise to HCL. Say, it is v primed j primed plus Cl. So, this one, this guy is vibrationally and rotationally excited. So, what is happening is that, this emits in the infrared region; and, if we monitor this infrared emission spectra, infrared emission spectra as a function of wavelength, then you should be able to find out information of this, on the, on the, about the population of this various these levels, this v primed and j primed levels. But the only problem is that we do not have any idea on this, on the population of ground state, what is the population pattern in the ground state. Whether lowest v level is most populated or intermediate or lowest vibration or intermediate vibrational levels; I mean, exactly it is not possible to find out that. Because, everything we are getting, I mean, whatever information it is from, the excited state vibrationally and rotationally excited state; but it is a good method, good technique in probing this population of various j and v levels. But, although it is selective like for HCl or maybe for HF, you can apply this; that means, your species should have capability of emitting in the optical spectroscopic region; maybe visible may be higher, but here we talked about this higher chemi-luminescence.

Next is, another method is called the laser induced fluorescence laser induced fluorescence; laser induced fluorescence, LIF. So, thing is that, if you have a species, which when excited by specific laser frequency, then it goes to the excited state; and then, from the excited state you can you can get fluorescence. So, this fluorescence is induced by lasers; that is why it is called the laser induced fluorescence. And, the species like, you know, that species may be your like fragments; I mean, like which may be something else which is not like, you know, like stable chemical species that has to be there, but maybe other species of this sort may be, may be useful, that it will it will give you laser induced fluorescence. So, by monitoring, by monitoring, you know, the fluorescence which is which we are getting, we can get a lot of information on the on the population of various levels. So, what is the basic principle for this laser induced fluorescence?

So, the thing is that, since we are doing excitation, laser induced means, first you have to do laser excitation and followed by, you know, looking into your emission. So, VR, it is the potential energy function as a function of r; say, this is the lower potential energy surface and say this is your upper potential energy surface. I will have rather potential energy diagram; not the surface because, it is a intersection, I mean, I mean a cross section of a three dimensional or multidimensional potential energy surface. So, these are the various vibration levels, vibration ladders. This is your excited electronic state, this is your, maybe, lower electronic state; that is, maybe this not the excited one, but it is the lower line, lower line, maybe ground state low line electronic state.

So, what you do? You excite with laser; and depending on the frequency of the laser, maybe it will reach over here, maybe it will reach somewhere over here also, maybe it will originate from here; go to here, this way. So, depending on your excitation frequency, excitation energy, you know; this gap means, when this gap matches with the initial and final, then transition will take place. And, if the population of this state say is more than the other one or maybe this one is more populated; say, this one is more populated compared to other, then the absorption cross section will be more, therefore corresponding, you know, correspondingly upper state population will be more, so, intensity of your emitted intensity of your emitted light will be more.

So, basically, we observe; this means, if you do this one then do this excitation, then possibility is that maybe one or more level gets involved. So, in that case you may observe unresolved, you know, emission. So, in one case like if you excite this way, then all possible levels are excited, but the thing is that when they will emit, their emission, they will emit at a particular frequency. So, from that emission frequency, you will be able to get the idea of the status of the initial population. So, this is laser induced fluorescence, but the point is that maybe you can monitor the total process like you can do another way; that is, you keep your excitation beam excitation beam fixed at a wavelength and you monitor the total fluorescence; that you can do.

So, in that way, what you do is, this is your, this is your excitation beam. So, you keep on changing this excitation beam frequency and you monitor, you monitor the total emitted light. So, this way also you would be able to know about the population population information; and using the standard formulae, you should be able to gain information on what is exactly going on. I mean, what is exactly there in this, I mean with respect to the population of various levels. So, that means you excite different quantum states to an upper electronic state by wherein lambda, I mean this, this one and find out the, I mean, you know, collect the total fluorescence.

And, this is like the absorbance spectra, but in case of absorption, you know, it is not that sensitive; but it has this laser induced fluorescence that is LIF, has the higher sensitivity. So, that is, that is, you know, you know, in one respect, it is advantageous. So, that is laser based absorption methods; and, you know, nowadays, this laser based absorption methods, you know, are also developed, which are also, you know, very much sensitive. Unlike simple absorbance spectroscopy, it is not that sensitive. But fluorescence, since fluorescence is a very sensitive one, you know, depending on the fluorescence quantum yield of the substance or the quantum yield of the species that you are looking at. So, you may get huge fluorescence or you may get a little less fluorescence. So, all these, you know, are to be considered while, you know, while using this LIF technique. Like, let us take one example; that is, reaction of HI with barium.

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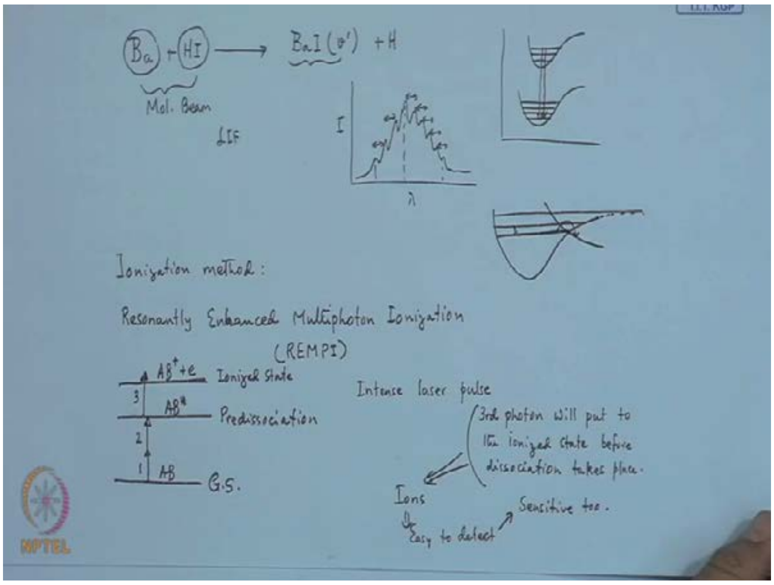

$Ba + HI \longrightarrow BaI(v') + H$

Mol. Beam

LIF

Ionization method :

Resonantly Enhanced Multiphoton Ionization
(REMPI)

Intense laser pulse

3rd photon will put to the ionized state before dissociation takes place.

Ions

Easy to detect

Sensitive too.

So, Bs plus HI giving rise to BaI, in some at some vibrational level v primed plus H. So, here, this Ba and this H, these are, you know, these are in the form of molecular beam; so, molecular beam. And, using this LIF technique, laser induced fluorescence technique, we can, since it is a very sensitive technique, we can detect these products like BaI or maybe some other.

So, typical, you know, spectra, that we may be getting for BaI, it is just like something like this. So, that will give you, that is, your lambda and this is your intensity. So, that will give you the idea of, you know, fluorescence intensity and from that you can gain information like this one is most intense this one is lesser and there is you see there is a progression that mean there is a gap, you know, you see.

So, these are typical, you know, gap corresponding to various levels. So, we can get in gain information of the levels present over there. Only thing is that, only requirement, what is the basic requirement? That, since you are you are probing into, you know; this is your lower level and this is your upper level, so this should fluoresce, I mean, radiative; radiative de-excitation should take place from here to here so that you get emission. This should be radiative. So, if there is no radiative emission, then, you know, this method will not be successful.

So, so why do we need to need to gain information on the population of various levels? That will give you the idea of the levels, I mean, I mean the inner levels; inner levels means electronic associated vibrational and rotational levels and their population, how these levels are populated? So, that will help in gaining, you know, information on the on the on the potential energy diagram for the species concerned. And, that potential energy diagram is very important in determining, you know, the nature of the process.

So, that is why people are interested in finding out this population of various levels. Like one method I talked on this chemi-luminescence, infrared chemi-luminescence; like that this is another method which is your laser induced fluorescence method. Another important point is that many excited electronic state; so, excited electronic state may, means, if the species, you know, gets excited to an excited electronic level then maybe, you know, photo-dissociation result. So, when photo-dissociation occurs, then like suppose this is your excited, excited level; say, there is another level which is a dissociated level.

Suppose you are, you excite your sample over here or maybe you excite over here, and then, you know, vibrational relaxation, the system gets transferred to here, where there is a there is a curve crossing. So, what happens? The system gets transferred from here to here leading to its dissociation, like I discussed this femto-chemistry; sodium iodide decomposition there is, you know, you know, curve crossing; one is dissociate, another is attractive potential energy surface. So, what happens to the system? This is transferred from the bound state to an unbound state and then it dissociates. And of course, in the time scale of emission, that is the emission, emission, I mean, time required for the emission to occur, I mean in the within the lifetime of the of the excited state. Within the lifetime of the excited state means, suppose you your excited ensemble is here. Let us say it is your excited state; and lifetime is basically the time required for the excited ensemble to decay to one (()) of its initial population. One (()) means, e is like close to one third; I mean, it is basically one (()) means one third, like log base e; that e I am talking about. So, that means, the time required to go to one e-th of its initial population, that is the time is called, it is called your lifetime. So, within the lifetime of the excited state if this state dissociates; that is like you have like such a curve crossing. Then it is a problem; you would not get any fluorescence.

Fluorescence quantum yield is rapidly, you know, I mean it is largely reduced. So, your fluorescence will be less, therefore, that we may not be able to able to detect the fluorescence. So, these are the problems, I mean associated problems one may encounter while, you know, doing this laser induced fluorescence. Otherwise, otherwise this laser induced fluorescence is a very, you know, very sensitive technique. And, of course, this laser induced fluorescence, I mean this part of the apparatus, I mean, you can attach such an arrangement with, you know, molecular beam arrangement. That is where the reaction is taking place; that reaction, you know, where these beams are, you know, interacting; I mean crossing. So, there actually you shine with a laser and of course you change the frequency, because you scan the frequency and collect the total fluorescence maybe. So, you scan the frequency and collect the, collect the, you know, emission and then record. That will give you the idea of, you know, this population.

So, this is one technique. Another technique could be ionization method, ionization methods. So, resonant enhanced, I mean resonantly enhanced; it is called the resonant enhanced multi-photon ionization; it is called REMPI, rempi. Excite, what you do you? Excite to an upper electronic state. So, you have got the ground state; say, you have you say pre-dissociation state; pre-dissociation means before; I mean here. Your true dissociation limit may be somewhere over here, here and above; it is called your true dissociation limit. But before you reach true dissociation, if a curved crossing of this short is there, then maybe you get pre-dissociation.

So, so, you know, you do not get since the product gets dissociated so you do not get any emission. So, so, characteristic spectra vanishes as pre-dissociation occurs. So, so it is your pre-dissociative state. So, pre-dissociation is okay. So, this is your ground state, this is your pre-dissociation state. So, maybe say AB, say this is AB star, and another state from pre-dissociation to another. So, it is basically two photons or multiple photons are required; at least two photons or multiple photons are required, multi-photon ionization.

So, basically, this one is pre-dissociative state, and if you from this pre-dissociation if you add another photon, then you go to AB say, plus, plus electron. So, basically this is an ionized state. So, this is your ionization limit. So, beyond this, if you can cross, sorry at least if we can reach you will get ionized, ionized products. So, in this case, what you need, since you require a multi-photon iodization; I mean a multi-photon process, then you need to have a high photon density. So, high photon density means, I mean bi-photonic process or maybe multi-photonic process will be enhanced; that is the, that is, if your field strength, I mean, laser electric field is very high, then the non-linear processes will take place and your multiple, I mean multi-photon absorption followed by ionization will take place.

So, in this case you have to use intense laser pulse, intense laser pulse; and so, you need intense, intense lasers, laser pulse. And of course, and so that means this intense laser pulse will provide the photon, which may be, which may be, you know, which may be giving you to the, giving you to this ionized state. Maybe in some cases it may not be a single; I mean this pre-dissociation step, I mean, level is such a height that maybe one photon will may not be sufficient. So, you may need two photons over here; two photons are required to, I mean, it is a bi-photonic absorption to pre-dissociation, and when the pre-dissociation state is reached, then because of your intense laser pulse, third photon; so, this is first photon, this is your second and this is the third photon, is used to put the put the system to your to the ionized state. And the thing is that, since ions are generated because of this ionization, because of this multi-photonic absorption process. So, intense laser pulse maybe third photon; third photon will put, will put to the ionized state, ionized state before dissociation takes place, before dissociation takes place. And the thing is that, since ions are generated from this, you get ions. So, you can detect ions and ions are easy to detect; and it is a very efficient and sensitive technique. So, ions, so easy to detect, to detect, easy to detect and it is sensitive, sensitive too. So, this way, I mean, using resonantly enhanced multi-photon ionization, you can, you can also, you know, find out it is, it is a way; it is another way. And now, next is, quantum state populations can be measured from, you know, transition intensities. So, different quantum state populations, you know, you can you can find out using, you know, intensity of the transition; I mean the level which is more populated will have, you know, higher intensity of transition compared to the one which is of lower population. Another thing is, you know, velocities, I mean, when, you know, when you are plotting the velocity contour, then velocities can also be probed by Doppler broadening of the spectral lines. Because, if there is a relative motion between your detector and your ion. So, the observed frequency is different compared to the actual frequency like, like when you hear the whistle of a train which is coming to you, and maybe which is going away from you. Suppose that you are moving, you are riding a, you know, you know, bicycle and one train is coming to you in one case; and in another case, say, it is going away from you. So, in both cases, what is happening is that, because of this relative motion of these two, between these two, you know, you see, you experience a different frequency. So, that is called your Doppler shifting. So, what happens is that, you know, velocities can be measured by observing the Doppler broadening of the spectral lines.

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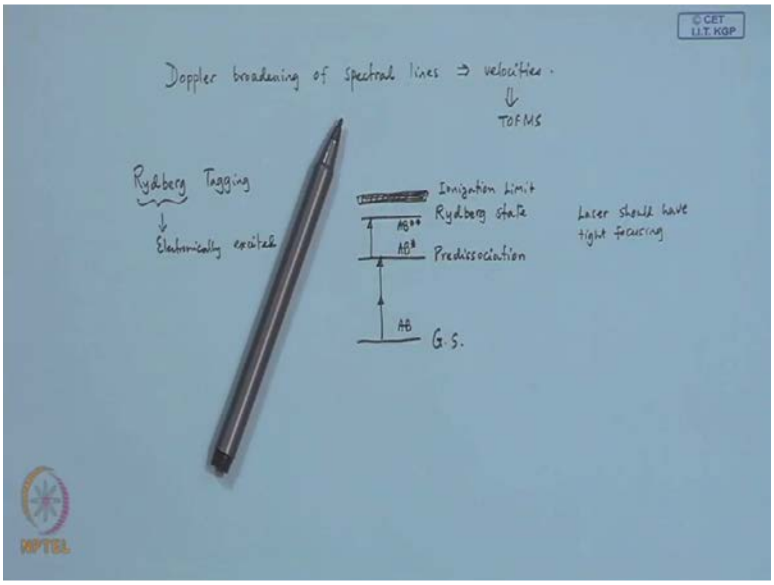
Doppler broadening of spectral lines ⇒ velocities.
⇓
TOFMS

Rydberg Tagging
↓
Electronically excited

Laser should have tight focusing

So, maybe Doppler, see, looking into the Doppler broadening, broadening of spectral lines, we can also look into this velocities. And so, these are, this is another thing; and maybe like that or maybe velocities you can find out by time of flight mass spectrometry; that is time required to fly from one, say, point to another, and that will depend on the mass as well. So, these are the things that one may be using.

Another is, another method is your Rydberg tagging, Rydberg tagging. Now, what is this Rydberg state? Now, Rydberg state is basically, Rydberg state is basically a state that is state of an atom and these are electronically excited states. So, Rydberg state is a state of an atom which is electronically excited with energies following the Rydberg's formula. And also, and they will, and Rydberg formula, as they converge on an ionic state with an ionization energy; means, when you provide ionization energy, it will, it will converge to an ionic state. So, it is a, it is a basically, you know, it is a high highly excited state. So, you know, Rydberg state is basically very close to close to the ionization state; but may be if you, if you, you know, give the ionization energy, then it will easily, you know, converge to an ionic state. So, these are, these are very close not, not much far. So, this diagram is basically, like you have got your ground state, then pre-dissociative state pre-dissociation stage, then you have got your Rydberg state, Rydberg stage, and then is your ionization limit maybe. So, this is your ionization limit, ionization limit. So, what you do is by, maybe by photonic absorption, of course, with intense laser, this is your AB star, this is your AB ground state, then you're AB double star, highly excited another photon. So, it is electronically excited state with energies, following the Rydberg's formula, as they converge to an ionic state with ionization energy. So, so they will, you know, they will be very close to, you know, ionization limit.

So, it is a variant of resonance, resonantly enhanced multi-photon ionization in which the species in the, species of interest is excited to a very high line Rydberg state. So, very high line means, they are very close to ionization; and it is, you know, lying very close to, you know, sufficiently close to the ionization limit. And, if you, you know, under this condition, means, if you do a Rydberg tagging, then if you can have a, you know, sufficiently, sufficiently, you know, it is Rydberg state, which is sufficiently close to the ionization limit, then with the help of a very little electric field, if you apply very weak electric field, then what will happen? That is, this high line, this Rydberg state will lose an electron or maybe it will just simply ionize with the help of, you know, you know weak electric field. So, that is why, you know, you know, Rydberg state is a state of an, I mean, state of an atom which is electronically, electronically, excited state; and generally highly excited state with energies and that is, you know, that follows the Rydberg's formula and they converge to an ionic state. I mean, they will ultimately converge to an ionic state by supplying a little amount of ionization energy.

So, that is why small electric field, small electric field will be, you know, sufficient; electric field will be sufficient to do the, do the thing, to ionize it. So, it is another form of ionization method; although resonance enhanced multi, resonantly enhanced multi-photon ionization, it directly, you know, transfers the pre-dissociative state to the, to the ionization limit. But here, what is, what is done is, you know, it goes via the Rydberg's state; I mean, I mean, high line Rydberg's state.

So, it will have a high velocity resolution unlike your resonance resonantly enhanced multi-photon ionization; because there is no coulomb repulsion between the excited neutral species that is created with the help, you know, I mean with the help of laser. Of course, in this case, laser has to be focused very tightly. So, laser should be should have tight focusing; tight focusing tight focusing means, you know, photon density is very high; photon density is very high means, your photon density high means, a possibility, I mean, probability of transition to a Rydberg's state is more. So, so it is, it is advantageous compared to compared to REMPI, because it will have high velocity resolution, because there is no coulomb repulsion between excited neutral species that is created in the in the laser pulse; I mean laser focus.

Next is Ion Imaging. Ion imaging is another method. So, this provides a direct picture of the velocity distribution. Say, you have got, you have say A plus, say, B 2, giving rise to AB v primed j primed plus B.

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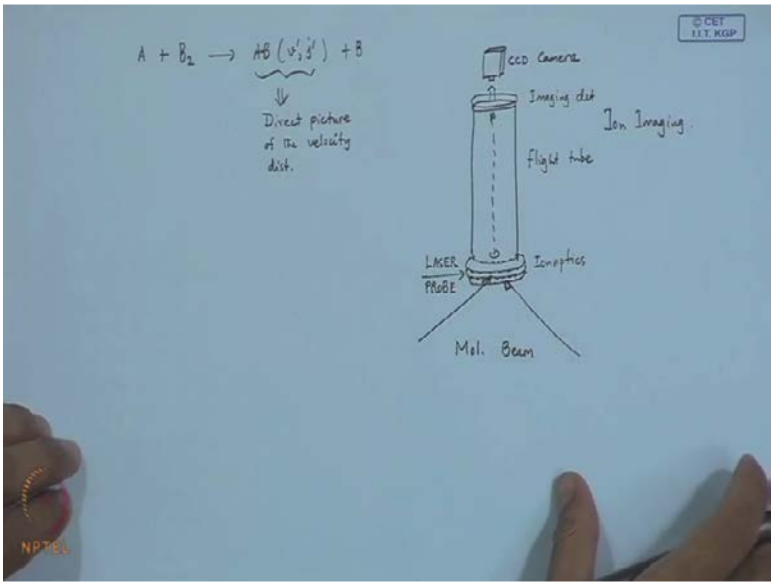

So, you can have a direct picture of the velocity distribution, of the distribution velocity distribution. So, a basic diagram, you have got a flight tube, then you have got a imaging detector somewhere over here, and then you have got your signal over here, which goes into your charge coupled device CCD, CCD camera, CCD camera, CCD camera, and this is your imaging detector, this is flight tube and you have got your ion optics; I mean, ion optics means, you know, focus or defocus your ions, you need to have some electrical arrangement which is called the, you know, which is called ion lens or ion something like that, ion mirror like that. So, this is your ion optics and you have your laser used to probe, laser for probing. And here, you send your, you know, molecular beam. This is your molecular beam. So, in this case, you can have your velocity distribution pattern, because it will, these ions will move this way; ions will move this way, it will enter and then it will move this way; it will fly, it will, it will fly from here to here, and then you can image it. So, that is a typical, you know, the typical description for, I mean, schematic of an ion imaging apparatus.

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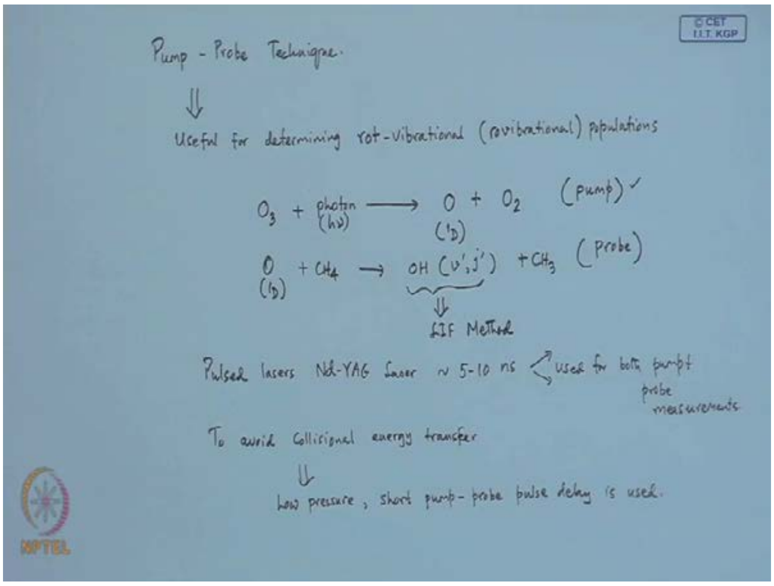

Pump - Probe Technique.

⇓

Useful for determining rot-vibrational (rovibrational) populations

$O_3 + \underset{(h\nu)}{\text{photon}} \longrightarrow \underset{(^1D)}{O} + O_2$ (pump) ✓

$\underset{(^1D)}{O} + CH_4 \longrightarrow \underbrace{OH\,(v', j')}_{} + CH_3$ (probe)

⇓

LIF Method

Pulsed lasers Nd-YAG laser ~ 5-10 ns ⟨ used for both pump+probe measurements

To avoid Collisional energy transfer

⇓

Low pressure, short pump-probe pulse delay is used.

So, ion imaging next is another important method which I might have already talked about in solution phase cases, which is called the called the Pump-Probe technique. And, this is, maybe this may be regarded as alternative to molecular beam approaches. And this is very useful for determining the population; so, useful for, useful for determining, determining rovibrational rotation rot, that is rovibrational vibrational quantum, I mean rovibrational populations. So, that is the population of the, I mean it is very useful and of course, of course for the nascent states. So, useful for determining the rovibrational population, so, that means, various rotational and vibrational quantum states; I mean population of those quantum states.

So, to do that Pump-Probe technique is one of the widely used techniques. So, what you do, like as an example, say you have got ozone, O 3, you shine with light photon; so, photo-dissociation leads to O plus O 2. So, this is your pump and this O, nascent O in maybe in one-day state. So, this state, I mean description of whether it is one-day or 1 p or 3 p whatever. So, this term, atomic terminology, I have not talked about. So, you can consult any standard textbook, like textbook on Quantum Chemistry by one by maybe Levine, maybe by Irene Walter Kimball or maybe any standard quantum chemistry textbook, where this particular thing is termed symbol, that is molecular and atomic term symbols are discussed.

So, actually, this is beyond the scope of this current lecture. So anyway, this is in a 1D state; so, when this 1D, I mean, O in 1D reacts with CH4 giving rise to OH v primed j primed plus CH3. So, this is called your probe, this is called your probe. So, this basically, this is, this photon is your, I mean, h nu is a pump and this CH4 is your probe; and then, what you do, as I already told you that laser induced fluorescence is a is a very sensitive technique, so, using laser induced fluorescence, you can, you can probe this OH v primed j primed. So, then you employ this for the laser induced fluorescence method.

So, from laser induced fluorescence you can also have the information of the various v’s and j states. And, for this one, I mean, to probe this; for this to probe this OH, you have to, I mean, for this particular state, you have to use another laser to probe this one. So, basically to generate the species for probing, you have to use this O plus CH 4 reaction to this, to do to generate this OH. So, pulse laser of the order of... So, pulse laser, maybe typical Nd-YAG laser, which has the pulse width of the order of nanosecond, of the order of say 5 to 10 nanosecond, is used for both pump and probe, used for both for both pump and probe measurements. And also, in this case, to avoid, you know, collisional energy transfer in OH; so, to avoid collisional energy transfer because of, you know, you know, if it is in under high pressure, then there will be there could be problem. So, that is why low pressure is used, low pressure low pressure and short of course, short pump to probe pulse delay, delay is used. That means, you first excite you first do this reaction; so, this is your pump, and then, and then, there is CH4; so, which reacts with this to produce this, the moment it is generated. You should have another pulse to probe into… Because, if you allow more time, there is more possibility of collision so more possibility of collision means, you know, collisional deactivation or maybe collisional energy transfer will lead to, lead to, you know, lead to, you know, scrambling. So, to avoid that, you should you should do the, you know, should have your pump probe delay, less short pump probe delay.

And so, this is important, because, to know the population of these this studies are important to know the population of the, you know, energetically accessible rotation-vibrational levels. So, that is why from Pump-Probe technique, Pump-Probe technique is a, you know, is a very significant technique. As for example, insertion reaction, you know, in initially it forms highly rovibrational excited CH3OH, which lives for a very, you know, short time, few picosecond. So, that is why, you know, that is why what is required that you should, you should you should have your probe pulse, you know; that should come, I mean, that should be present over there, I mean, in the, in the reaction mixture; I mean very, you know, close to your pump. Because the problem is, if you allow more time, then you are in trouble that, like here, I mean, I just gave an example that for certain insertion reaction, you know, like, when you do, when you get like for rovibrationally CH3OH excited, CH3OH excited which has got lifetime, you know, of the order of picosecond, 10 to the power of minus 12 second.

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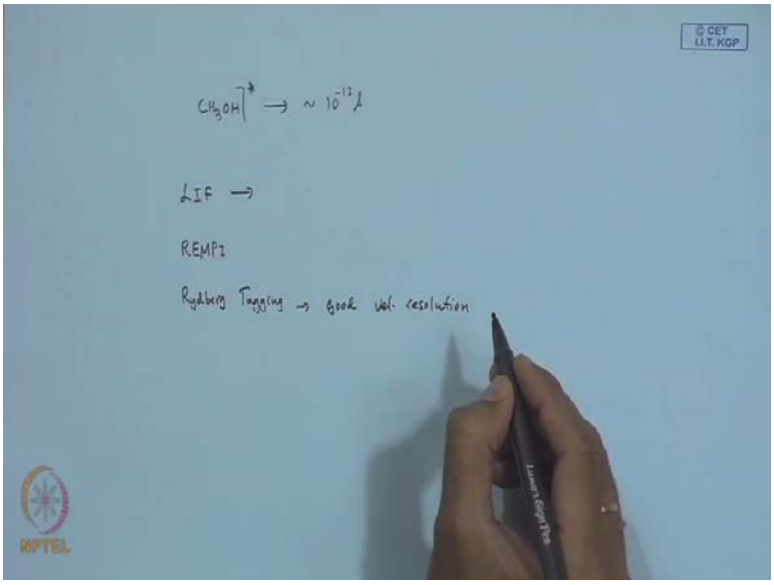

$CH_3OH]^* \rightarrow \sim 10^{-12}s$

LIF →

REMPI

Rydberg Tagging → good vel. resolution

So, then, it is a problem; so that means, in that case the moment, your pump is there, the probe should be should also be present; I mean, very close to that, otherwise you may miss it. So, that is, you know, it is the just, it would be giving you the basic idea of pump probe method in this molecular beam, you know, or may be in gas-phase reaction, Pump-Probe technique.

So, so what we have, you know, learnt in this particular piece of lecture, that we have talked about this laser induced fluorescence, which is a very sensitive technique. Unlike this absorbance technique, it is a very sensitive technique. Only thing is that the, you know, the upper electronic state should have, you know, fluorescence; that is the, that is the important point. So, you should get information on the on the population of the various v levels, vibrational levels. We have we have talked about this ionization methods, like resonantly enhanced multi-photon ionization REMPI. So, that is based on the ionization technique, because ions are easy to detect; and a slight variation of that one is, you know, REMPI's slight variation is the Rydberg tagging, Rydberg tagging. So, you know, that is another, another, you know, a small variation of REMPI, that can also be used; because, in that case, the only thing is that, you use multi-photon ionization and so that you generate a highly excited atom and with the help of a very weak electric field you ionize it.

So, in this case, it has a good, you know, velocity resolution, velocity resolution. Another is your technique is your ion imaging; that is also used to, you know, have a have a picture on the picture of your velocity distribution. Last, we talked about his Pump-Probe technique, which is an alternative to your beam measurements, molecular beam methods, which is a which is also very useful, you know, to look into the population of the various, you know, vibrational and rotational state like rovibrationally excited levels.

So, that is all for today and we will, we will talk, you know in our next lecture, we will talk on this, you will come on; I mean, we will discuss this potential energy surface in the next lecture. So, till then, thank you.