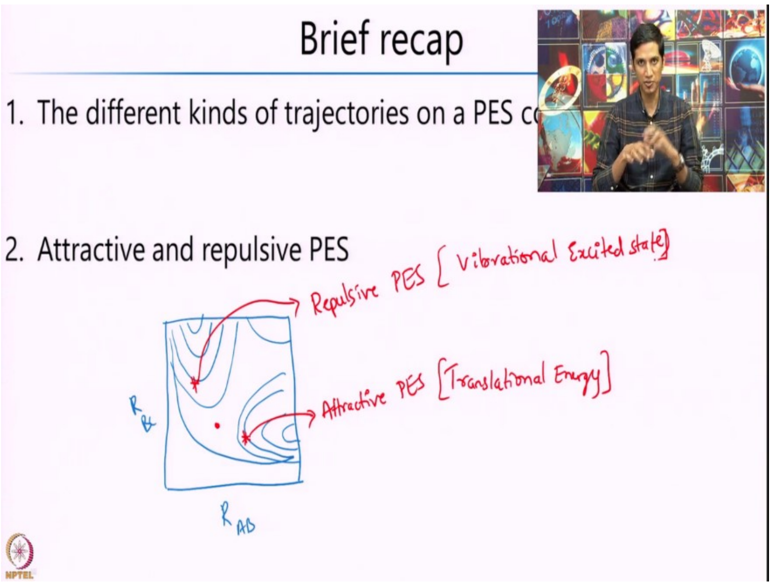
Concepts of Chemistry for Engineering
Professor Chidambar Kulkarni
Indian Institute of Technology, Bombay
Center of Distance Engineering Education Programme
Lecture 68
Potential energy surface of HCN and H_2F system

Hello everyone, welcome to the module on intermolecular forces and potential energy surfaces. We are still discussing potential energy surfaces. And in this lecture, we shall look at a couple of more examples of potential energy surfaces and this would help us to compare and contrast the examples we are going to discuss today with the examples we discussed in the previous lectures that is mostly H3 system. So, before we get into today's lecture, let us just recap what we learnt about the H3 system and then we will go ahead and look at a couple of more different kinds of systems.

(Refer Slide Time: 00:58)



Brief recap

1. The different kinds of trajectories on a PES c

2. Attractive and repulsive PES

So, in the previous lectures, we have been looking at potential energy surfaces of H3 system and also did the different kinds of trajectories on the potential energy contour maps. And we also saw what are called as attractive and repulsive potential energy surfaces. So, just to refresh to your memories, I will try and show that for the AB system A, B, C kind of systems.

So, we had looked at these kinds of maps. And we had said that if the saddle point could be here or the transition state that is 1 and the saddle point could also come closer here that is somewhere here, and it could also be somewhere close to this point. And we had called them by different names. One, this we had called it as attractive, attractive potential energy surface. And this, we had named it as the repulsive.

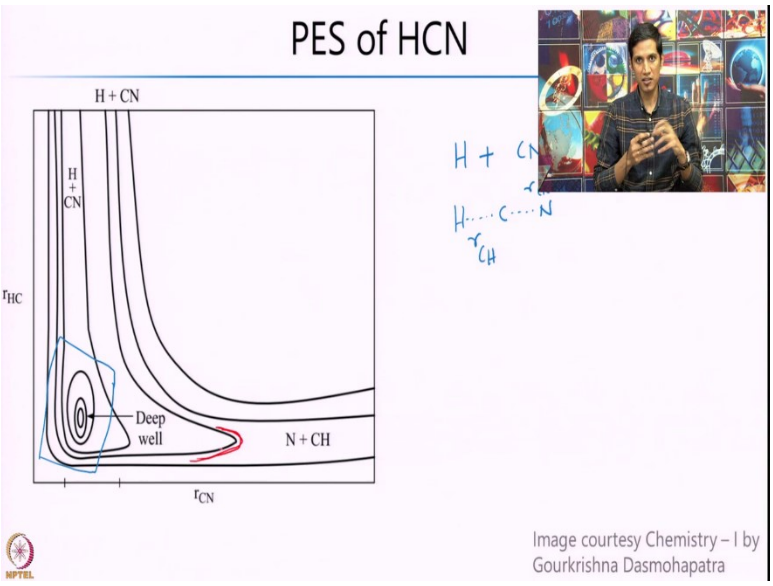
And what we had said is that, in the case of the attractive, the translational energy, if the kinetic energy is completely translational, then you would end up in the formation of the product. So, I would just write it here as translational energy. And, whereas, in the case of the repulsive, we had said that if the molecule is in the vibrationally excited state, then that would lead to formation of product.

This was primarily because if the molecule is in the vibrationally excited state, it could actually sort of go cross this barrier or the go across the corner which it encounters and then go over the saddle point to reach the product. So, then you must be actually thinking, what is the significance of this or why is he even sort of making a big deal out of these attractive and repulsive interactions.

So, the reason why when studies this is that if you actually know, for a given system, whether it is an attractive potential surface or repulsive potential energy surface, then you can actually make sure that the molecules are in the vibrationally excited state by pumping them to higher excited states. That would ensure, that you get the product far more easily.

So, that is the reason why one tries to study these potential energy surfaces and understand whether they are attractive or repulsive in nature. So, having learned this about the H3 kinds of systems now, we will go ahead and take a look at other kinds of systems.

(Refer Slide Time: 04:16)



PES of HCN

Image courtesy Chemistry – I by Gourkrishna Dasmohapatra

So, a classic case is this potential the surface of the HCN or H plus CN system, where what you see here is the potential energy surface on HCN system. So, just to make it clear, I will draw the system which we are interested in. So, we are looking at H plus CN giving HCN.

So, the moment I have this, I will have to now pick the coordinates or the degrees of freedom, which I need to vary.

So, I am sure, you will all be thinking one, would be this obvious one that is the distance between the H and C and the other is the distance between the C and the N, when they are all coming in a colinear fashion. So, this is one that is rCH and then you can call it as rCN as the other degree of freedom.

So, now, if you take these two degrees of freedom as the x and the y axis as shown here and if you now look at how does the energy of the system varies by varying each of these independently and calculating their total energy then you would end up in a 2D contour map similar to what you have, what you see on the screen. So, the moment you say this I am sure you would have noticed it the striking difference is that when the rCN and the H come closer together, you see that there is a very deep hole or there is a very deep well this part of the contour map.

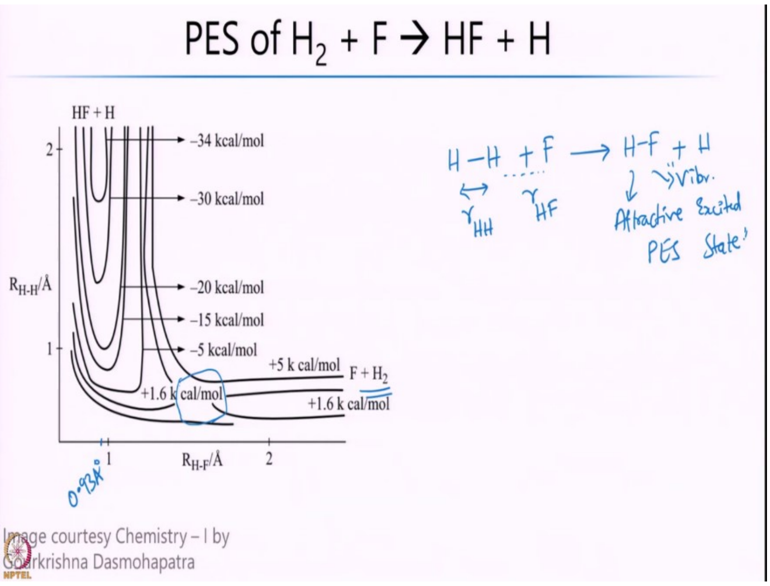
So, what that suggests is that the H plus CN when they come together, they form a very strong bond that is a HCN bond, that is what it indicates, that means, the energy there you have the deepest well. And please, compare and contrast this with the H3 system where what we had was we had actually a, we had a top of a hill at around this point. So, please compare this with the HCN system. In the case of the H3 system we had a higher energy hill state around this position, whereas, when you come to the HCN because of the attractive interaction you have very deep well or a bond formation in this case.

The depth of the well is very large because you are forming covalent bond, and energies is mostly in excess of about 200 kcal per mole and that is a very large number. So, what this also tells you is another feature, that is, if you look at this energy profile a bit more carefully, you will see one more feature here. That feature is if you look at this, you see that the rCN still has this part, there is a contour which is going in that means it is deeper whereas the rCH it is already at very high energy, that means, these are already going to the, there is no lower energy state there.

That is because if you take the rCN and or the C triple bond N that is a very strong bond, that will be considerably lower in energy compared to the CH bond which is going to form. So, typically then the situation would look something like this, you have a CN bond which is here and then the CH bond which would form ultimately would be the energy state would be somewhere here. And the depth of the well is here, it is even significantly lower. So, this is what you see in this contour map, where you do encounter a region where the rCN is showing the lower energy compared to the rCH.

This is just because of the inherent stability of the C triple bond N compared to the CH bond which is going to form. Thus, when these two actually come together you they undergo covalent bond formation and they end up in formation of the product. And this is, so what I want you to sort of notice or take note of this is that this is sort of in complete contrast with the H3 system where you had a top of the hill or a saddle point when you brought the A to the BC system. So, I hope, that gives you a feel of the difference between the HCN and the H3 kind of systems.

(Refer Slide Time: 09:06)



PES of $H_2 + F \rightarrow HF + H$

Image courtesy Chemistry – I by Gourkrishna Dasmohapatra

So, having looked at HCN now let us go ahead and look at another system, which is H2F or H2 plus F giving HF. So, here, what I have shown here is again, both the degrees of freedom what you can think of are shown here, that is, I have a H-H and then F gives a H-F plus F. So, one degree of freedom we can think of wearing is this that is rHH and the other is this the bond which is going to form which is rHF.

So, these are the two degrees of freedom which you can typically think of when the both the systems actually come head on or when the dihedral angle is about 180 degrees between the systems. So, in this case, now if you take these two degrees of freedom and plot a 2D contour map, then you would get a contour map, which is similar to what you see on the screen.

And here, what you see are the different numbers represented where each of the number actually corresponds to the energy or the energy surface of energy corresponding to that slice in the three-dimensional potential energy surface.

So, if you remember in a couple of lectures ago, where we had said that we construct the 2D maps by taking slices in the three-dimensional surface, so those slices or the point where we have sliced are the energies which is shown here, corresponding to different lines. So here, what you see is the following feature that you start with the H2F system on the far right side here, H2 plus F, and as you actually come across then you would hit, then you have a small bump or a saddle point.

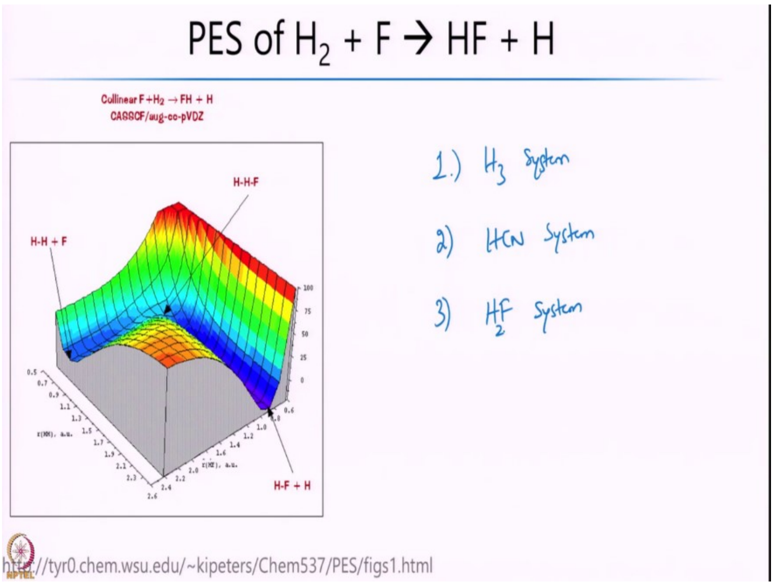
And the moment you actually cross that you would end up going way deeper in energy. That is, you go from about 1.6 kcal per mole to about minus 34 kcal per mole, and that is because you form a very strong HF bond with the equilibrium bond length of about 0.93 angstrom. So, what you are doing is your both H2 and F are coming closer together, and then you are crossing a small barrier of about a 1.5 or about between one and half to 2 kcal per mole. And then once you cross that, then you are going down deep in the energy level or going lower in energy and then you ultimately you form the HF bond which is significantly stable or significantly more stable compared to the starting material.

So, this is what is very apparent from the system. However, there is also a very nice feature which is apparent. If you remember our discussion on attractive and repulsive potential energy surfaces. So, if we now look at this a bit closely, what you see is that the saddle point is somewhere here, which is very similar to what we had seen for the case of the attractive potential energy surfaces, where the saddle point was more towards the right.

And we had said that when you have an attractive potential energy surfaces, then the translational motion or if the kinetic energy is completely translational, that would lead to the product and the product would be in the excited state. Exactly a similar scenario is happening here, that is when the H2 and the F actually come and collide or when the kinetic energy is completely or the activation is just completely in the form of the translational then the collision would take place more efficiently, and that would lead to the product HF which will be in the excited state.

So, I hope, this gives you an idea of a potential energy surface or an attractive potential energy surface. So, let us call this as, and the molecule which is going to come out will be the product will be in the vibrationally excited state. So, this is what a typical potential energy surface would look like for H2 plus F system.

(Refer Slide Time: 13:48)



PES of $H_2 + F \rightarrow HF + H$

Collinear $F + H_2 \rightarrow FH + H$
CASSCF/aug-cc-pVDZ

1.) H_3 System
2) HCN System
3) HF_2 System

http://tyr0.chem.wsu.edu/~kipeters/Chem537/PES/figs1.html

We can actually go ahead and try and look at the same thing in a three-dimensional fashion. That is, if I take the potential energy surface and now look at it in a three-dimensional way, that is before I slice it, so then you would see a potential energy surface like this, where you have the H2 plus F coming from this side on the left-hand side, and you form the, you cross this small barrier here, which is the saddle point. And once you cross that you go deep down in the well, where you end up in forming the products.

And you must noticed it what I have shown here is this something called as I have written some numbers here, CASCF/ aug-cc-pVDZ, that is, the level of competition or the level of competition or their calculation at which this potential energy surface was computed. And typically, I think I told you this in our discussion on potential energy surfaces in the few lectures back that usually the potential energy surfaces are computed by varying the different coordinates that is the H-H, and HF distances in this case, and you would look at what is the energy of the system as you change each of these coordinates separately. That is, exactly what is being done here at the particular level of theory mentioned on the slide and that would lead to the production energy surface you see.

So, you must be wondering now, so, we now looked at three kinds of potential energy surfaces that is, we looked at, first, we looked at the H3 system and we looked at the HCN system and finally, we tried looking at the HF system or the H2F system. So, then you must be thinking why are we even studying this? What is the significance of studying this potential energy surfaces or even computing them or what do they tell us? So, that is a very important question.

And the answer lies in trying to understand the system. So, let us imagine tomorrow you are trying to optimize a new process for any sort of a chemical reaction are any anything which is involved in the chemistry. So, there these kinds of potential energy surfaces actually do give a lot of mechanistic insights. They give an understanding about what is the barrier or what is the amount of energy I need to supply for the process to take place, which is a very, very crucial and an important piece of information to have.

Because if the barrier is too large, then you would think of what are called as catalysts to lower them. If you had no means of understanding or figuring out what the barrier is, then you will actually not even worry about a catalyst. So, one thing which these potential energy surfaces would help you enormously in is to tell you what is the barrier or what is the amount of energy you need to supply to go from one of the reactant to the product or one confirmation to the other confirmation.

And so, the other thing is like we discussed in the attractive and the repulsive potential energy surfaces. So, it would also tell you whether the reactant should be in the vibrationally excited state that is should you take the reactant to vibrationally excited state so that the reaction occurs or you should do it from the ground state. So, these are actually very, very crucial piece of information which would, which can be obtained from potential energy surface. And once you have this information, that helps you to optimize a given process which you are looking at.

As a part of your chemical engineering, you could be looking at many different processes. So, in all of them, one can construct a similar potential energy surface. And in this, in our discussion, we were mostly confined to potential energy surfaces, where a reaction was involved, that is, either like H2 plus F giving an HF or a H plus C N giving HCN.

However, one can also come up with potential energy surfaces for conformational confirmation or conformational degrees of freedom, like in case of proteins, or in case of molecules where molecules can occupy different kinds of confirmations. So, all of this will help you to understand the system better and optimize your process so that you can do it in a more efficient manner. So, with this sort of bird’s eye view perspective, we shall stop our discussion on potential energy surfaces and intermolecular interaction. Thank you.