Chemistry and Physics of Surfaces and Interfaces
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Lecture - 17
Molecular Adsorbates: Factors Controlling Molecular Adlayer

So, welcome back everyone. So, we are continuing in lecture number 17, again about molecular adsorbates. So, we have been already looking at a certain factors that would control the molecular adsorbate on surface.

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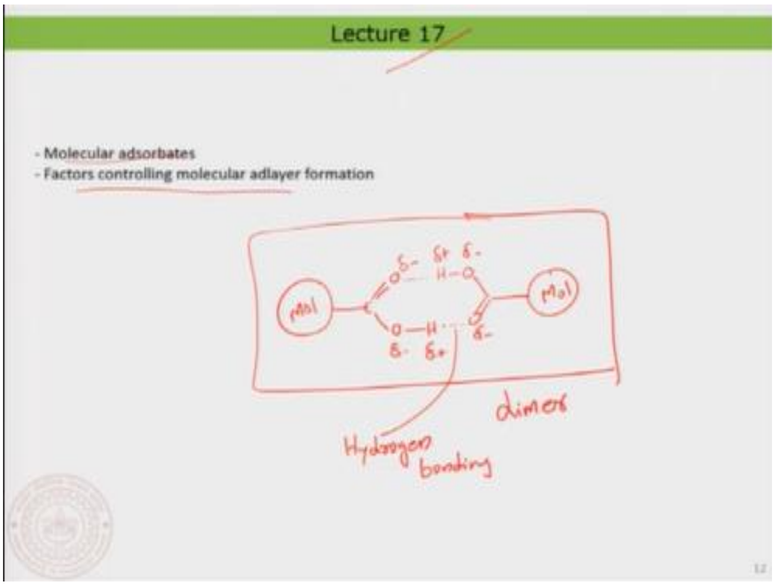

Lecture 17

- Molecular adsorbates
- Factors controlling molecular adlayer formation

And now we try to more or less emphasize a little bit more into the factors that are controlling the molecular adsorbate on surface. So, in the previous lecture you have already seen that, that the hydrogen bonding for example, is majorly playing a role in controlling the self-assembly of a molecule. So, now you see it is important also what type of functional group that you have it on the molecule. If you have of course functional group that triggers hydrogen bonding interactions then obviously the molecule do prefer hydrogen bonding because energetically hydrogen bonding is definitely a much stronger bond much stronger interaction than for example a Van Der Waals interactions or Pi-Pi interactions and so on. Therefore, it is quite important when you design the molecule you have to basically say well whether I need kind of weak interactions to control the molecule or I need actually stronger interactions to control the molecule. But carboxylic group for example is a popular group that people use for making hydrogen bonded based self assembly of molecular adsorbate on surfaces, because it actually goes to something like this dimeric hydrogen bonds. So, what happens is? You have a molecule here. So, I am just marking it as just a circle and you have then the carbon and you have the double bond O and you have the OH here. Now this OH group for example, as I have already told you so this can actually have a Delta positive and the Delta negative charge and this is also a Delta negative charge basically. So, you can now see that this carboxylic group at the same time is some kind of a hydrogen bonding donor and the hydrogen bonding acceptor, it is a donor and an acceptor. That means if you now bring another carboxylic group. So, I am just going to draw the hydrogen atom of the other carboxyl group like this. So, that you have again a delta plus, a Delta negative, a Delta negative and now you have the same molecule. So, let us call this molecule as the as the trimesic acid that we have already seen in the previous example. Now what you see is that the two molecules are actually interacting together using a dimeric hydrogen bonding. And that is what exactly we have seen in the previous lecture we have seen an example. So, this actually forms a nice dimer. So, dimeric hydrogen bonding formation is a very key element of this kind of carboxylic group. So, therefore carboxylic group is routinely used in in molecular self-assembly because that actually helped the molecule to interact via a hydrogen bonding. So, the dotted lines here what I am just putting is the hydrogen bonding, is the hydrogen bonding. Generally known as bonding, but it is more or less a non covalent interaction itself. So, this is what people do generally. So, that is actually what we have seen in the previous example. So, please have a look at the example again so that you can kind of clearly understand what is actually happening in that. So, therefore interactions are very very important, what type of interactions at which the molecules are actually coming together is a very key element in the molecular assembly itself.

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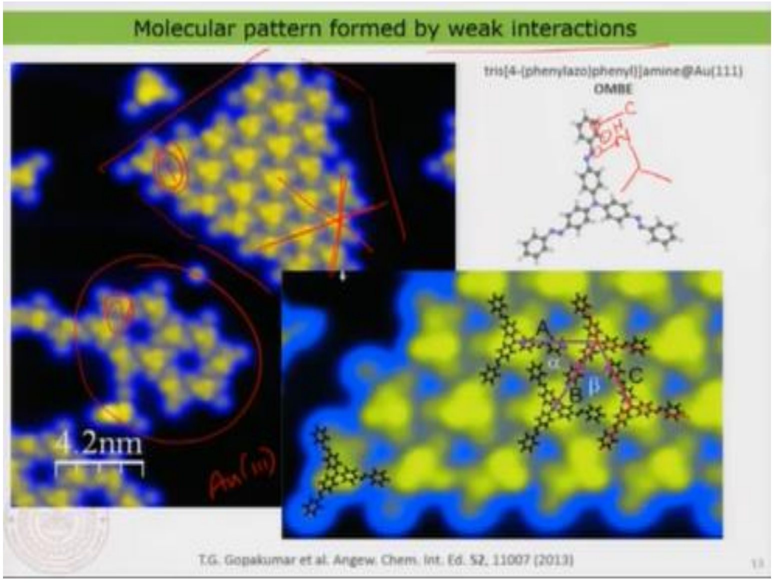

Molecular pattern formed by weak interactions

tris[4-(phenylazo)phenyl]amine@Au(111)
OMBE

T.G. Gopakumar et al. Angew. Chem. Int. Ed. 52, 11007 (2013)

Now let us look at another example. So, in this particular example what is very interesting is that this self assembly the molecule you have already seen that this was actually something I have showed you. So, this is basically a three-fold symmetric molecule. And now you see in this molecule you have your nitrogen, so that this is nitrogen, and then you have here hydrogen, then you have the carbon atoms. But in general, what you see is that this is carbon atom. But in general, you see in this particular molecule there is nothing like a possibility for a hydrogen bonding. But nonetheless, you find that this is actually at a very low coverage. So, this is of course on gold 111 surface, the molecules are self assembling and it is of course an image taken at a lower coverage where you can see that the molecules are actually self-assembling and they are actually just nicely coming together. But now the question that you would ask, well how do they basically self-assemble in this case, because there is nothing that controls there is nothing like a hydrogen bonding possibility between the molecules. What does it control them? Well, that is the interesting aspect here the here the self-assembly is basically controlled by weak interaction. So, the weak interaction when it says it is typically some kind of a Van Der Waals interaction. So, Van Der Waals interactions are ubiquitous in nature and that actually is an interaction which is present in any molecule that that you take. It is of course due to some kind of a dispersive interaction between the electron cloud around the molecules with the other molecular electron clouds. So, this is an interaction that is present which is of course famously known as Van Der Waals interaction or Van Der Waals bonding for example. Now you can see here the molecules are basically just put together like this and of course what is very important if you look at the molecular arrangement, you see they are trying to actually just close back in a most effective way. So, only when the molecule close back in a very effective way, then the molecule can basically just have the highest Van Der Waals interaction possible. So, the highest when I say that the molecules when they come together and they are trying to interact each other, so they need to have a better overlap between each other. The molecular body, the body of the molecule should basically overlap as much as possible and that is what a closed packing in this case means. And then they can come together and they can actually have a larger Van Der Waals interaction between the molecules. So, therefore whenever molecules are actually interacting through Van Der Waals interaction, you will always find they tried to close back in a very effective way, so that the Van Der walls interaction is maximized. Of course, if the Van Der Waals interactions are only between two points of the molecules, then it is not very effective. So, therefore the overlaps between the molecules are very important. So, as to maximize the Van Der Waals interaction, now you can see that in this particular case, due to the fact that it is a three-fold symmetric molecule and also the final symmetry of the assembly is also a kind of three-fold or six-fold symmetry, which actually meaning that the molecule tried to close pack using their symmetry very well. In that case, you can get a very effective packing. So, you can see these are the three crystallographic directions of the molecule are lattice and that is actually giving rise to a six-fold symmetric molecule. This is very very important which shows clearly that the molecular symmetry is also playing a major role. But now you see something also interesting that this is not the only one type of phase that you can form. You also see that there is another type of arrangement of the molecules, which is of course, not as dense as in the first case. So, if I would call this as phase one and this is phase two. The phase two is actually not as dense as the phase one. Nonetheless you can see the symmetry is again a six-fold symmetry, the symmetry is again sixfold symmetric. So, therefore you see that at low coverage you would find these kinds of loose packed faces, nonetheless, the symmetry is maintained. But as you increase the coverage, what we find that the phase one is prevailing. Because you have more molecules on the surface, and then all the molecules try to close pack as much as possible. And then they need to come basically to the phase one, where the molecules are efficiently close packed and that means their Van Der Waals interactions are also maximized. So, that is very, very important.

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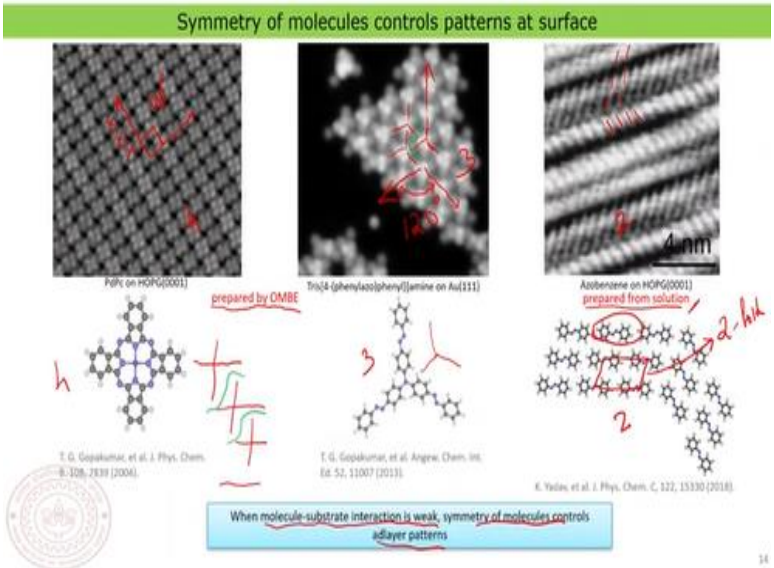

Symmetry of molecules controls patterns at surface

PdPc on HOPG(0001)

prepared by OMBE

Tris[4-(phenylazo)phenyl]amine on Au(111)

Azobenzene on HOPG(0001)

prepared from solution

T. G. Gopakumar, et al. J. Phys. Chem. B. 108, 2839 (2004).

T. G. Gopakumar, et al. Angew. Chem. Int. Ed. 52, 11007 (2013).

K. Yadav, et al. J. Phys. Chem. C, 122, 15330 (2018).

When molecule-substrate interaction is weak, symmetry of molecules controls adlayer patterns

Now let us have a look at the summary of all the cases that we have seen particularly where the molecule-molecule interactions are predominantly Van Der Waal in nature. So, this example we have already seen, so that is a palladium phthalocyanine. And we know that this is actually a four-fold symmetric molecule. So, let me just depict the molecule using a cross. So, now if you look in the STM image, you can see that these crosses are basically depicting the single molecules. Now, if you look at the molecular lattice, so this is actually one of molecular lattices and this is the other molecular lattices and the angle between the molecular lattices are about 90 degree. So, that means the symmetry of the molecular lattice is basically four-fold. So, that means the symmetry of the molecular lattice and that of the molecule is kind of matching. That is interesting. Now if you would look at the packing of the molecule, so the molecules are packed effectively in this fashion. So, the molecules are packed effectively in this fashion and the area between the molecules if you see, so they are very less. So, why do we do that, this is actually done to show that the molecules are effectively packing. Therefore, the Van Der Waals interaction is effectively bringing the molecules together. So, that means, when there is no functional group in the molecule, the molecules come closer, and then they will try to maximize the Van Der Waals interaction and then try to pack into a more condensed phase or to a more close packed face. This is a very generic observation that you would not for a Van Der Waal interacting molecule. But for example, in the case of trimesic acid we have already seen that everything the molecule-molecule interaction is typically controlled by the hydrogen bonding interaction between the molecules. Now, let us take a few more examples and then we will get the understanding. So, let us look at this molecule which we have already seen in the previous slide. So, this is again a molecule having three-fold symmetry. So, let me just represent the molecule using a tripod and now if you look in the STM image, you can basically see that the molecules are actually packed like this, this is the first molecule, I am just picking randomly a few molecules. So, this is the second molecule I am picking and then you can also pick one more molecule just to see how they are arranging. So, these are the molecules. Now, you can see that the molecules are packed very effectively, so that the Van Der Waal area in between the molecules are very high. So, this is the key in general because the molecule would always try to pack as close as possible in order to actually just maximize the area of contact between the molecules. So, that the Van Der Waals interaction is very effective. Now, you also see that how the molecules are arranged here. So, this is the lattice of the molecule, one of the lattice of the molecule and this is the other lattice of the molecule, and then the third lattice, we can basically mark in this direction. So, now you see that the angle between the lattice vectors are about 120 degrees. So, that means this is basically a three-fold symmetric assembly. That is also something you have seen the previous slide. Now, let me also show you one more example. So, before that, you please notice that this both examples are prepared using that organic molecular beam epitaxy. That means they are prepared inside an ultra-high vacuum chamber. Let me also show you an example of self assembly of a molecule namely azobenzene. This is the basically the azobenzene molecule. And this molecule is basically prepared from a solution phase that means the preparation is basically done in ambient condition. And even then, the preparation is not going to affect basically about the symmetry of the assembly but now you can see the symmetry of the assembly is basically dependent on the molecule-molecule interaction. It has nothing to do with the preparation condition. Now you all will see that the molecules if you look at these are basically the molecules. So, these are long azobenzene molecules and they are also packing in the other direction itself. So, this is about three molecules in this direction. And now if you look at the symmetry of the packing, so the molecule is packed like this and this is a long oblique and the symmetry of the oblique is the long oblique is basically two-fold. And that is also matching with the symmetry of the molecule because a molecule is also a two-fold symmetric molecule. Now let us look at in general. So, this we have here a four-fold symmetric molecule, a three-fold symmetric molecule and a two-fold symmetric molecule and now also have a look at this symmetry of the packing. This is again four-fold symmetric packing, this is three-fold symmetric packing and this is two-fold symmetric packing. That means, if the self-assembly of the molecule on surface is purely controlled by molecule-molecule interaction and also Van Der Waal interaction, then in all the cases you would find that the symmetry of the molecule will be implemented in the symmetry of the self assembly. One more thing you need to keep in mind here, that in case if the molecule-substrate interaction becomes predominant even when the molecule-molecule interaction is Van Der Waal, then this is not valid and therefore, this is actually a case where the molecule-substrate interaction is also very very weak. That means, predominantly the molecule-molecule interaction which is Van Der Waal interaction is predominantly present. In those cases, the symmetry of the molecule will control the adlayer pattern or the symmetry of the molecule will be duplicated in the adlayer pattern. Well, there are slight differences in certain cases that we will also see particularly when there are functional groups and functional group mediated interaction. But in all these cases, you can see all the molecules here, there are no functional groups attached to the molecule therefore, the interaction is predominantly weak Van Der Waal interaction plus the molecule-substrate interaction is very weak. And therefore, completely the symmetry of the self assembly is mimicking the symmetry of the molecule itself.

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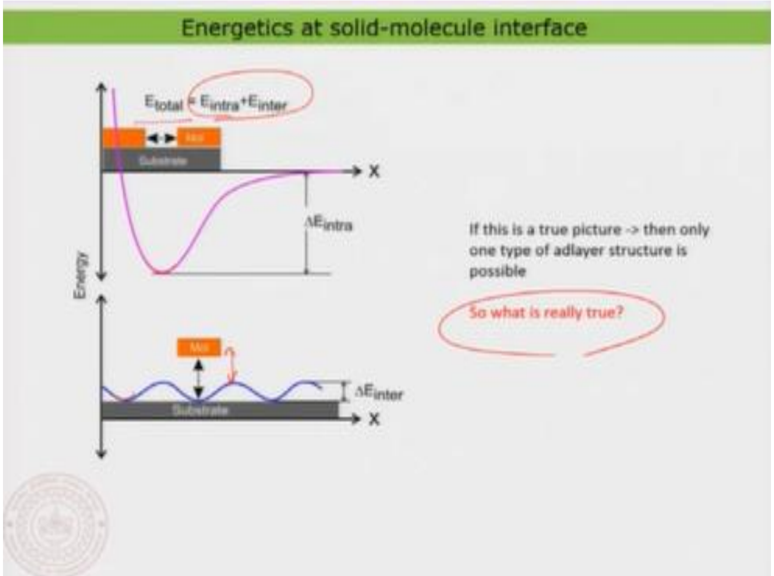

Energetics at solid-molecule interface

If this is a true picture -> then only one type of adlayer structure is possible

So what is really true?

Let us move on. Now we want to basically put together all the information and so far, we have gathered. We want to understand whether we can copy the same understanding of energetics as we have done in the case of atom atomic adsorbates. Well, you remember that we have actually just familiarize that there are two major interactions that plays a key role in the case of atomic adsorbates, which were basically the adsorbate-adsorbate interaction and the adsorbate-surface interaction. Now, well when it also come to a molecule, if you assume that the molecule is a point object, then you would say well, there has to be two type of interaction, which should be basically a molecule-molecule interaction and a molecule-surface interaction, as simple as it is. Well then, we can write down the total energy of adsorption, or something known as the adsorption energy is controlled by these two contributions that is the E intra and E inter. Where E intra is basically the intramolecular interactions and interest basically, the molecule-surface interaction. We can write down everything, as simple as it is. But the point is if you would say well, everything is controlled like this, then one should have only observed one type of self assembly for a given molecule at a given conditions of deposition. But that is not the case. We do see that at a given condition, one molecule can have one more than one type of self-assembly or more than one type of arrangement of the molecules on the surface. Then this cannot be justified because what you find is that there is one minima here, and other minima here, and they will coincide and that would mean that you should only be forming one type of assembly of the molecule. But that is definitely not the case. It looks like there are much more interactions or it looks like there are more possible ways then the molecule can actually arrange on the surface. That itself means this is not the simple energetics that should control the adlayer formation. So, what is really true then? So, that is actually the question and we will try to understand that a little bit more in in detail by looking at the molecular molecule interaction itself.

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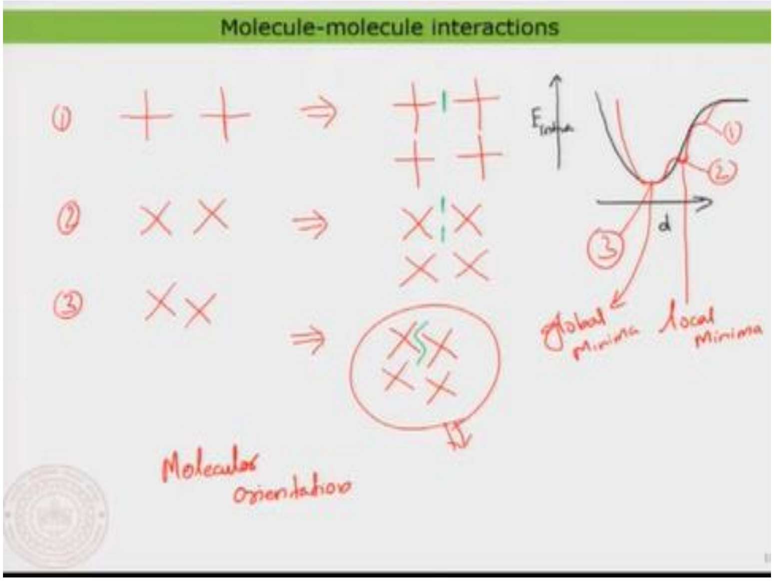

Molecule-molecule interactions

Now how can we understand the molecule-molecule interaction in greater detail. So, we have already discussed that the molecule-molecule interactions are controlled by different type of interactions, non covalent interactions. Now, let us take an example again. So, here a very schematic example that I am taking. So, let us take a molecule that is just looking like a cross shape. Now of course, when you take the two molecules and put them together, I can of course put the molecules in various ways. These are just two molecules representing two molecules in various ways. You see that I can actually take the molecule, so here, the example is basically phthalocyanine and because it has that cross shape. Now when you take these two molecules together, I can basically just put molecule in the first way. So, let us call it one, two and three just for our convenience of a discussion. So, the form one, where the two edges of the molecules are interacting somewhat like this, that is a possibility. So, then that would give rise to something like a self assembly that should look like this, nice not bad, or I can actually just take the second case and then put them together and they would basically form a self assembly which is looking like this, nice. So, I can have another possibility, where I take all these molecules in this particular way, where the interactions are slightly more close pack. In that case, I am just going to end up in preparing an adlayer, which is looking like this. So, the difference between two and three is actually the way they actually close pack or the relative orientation of the molecule. So, that means, when you now come across the self assembly or the adlayer formation of the molecule. It is quite important to notice that the molecular orientation with respect to each other is very very important. So, that means; molecular-molecular orientations, orientations between the molecules are very, very important. So, here you can see that the molecules are orienting like this, in the other case, the molecules are orienting like this, and in the other case, the molecules are orienting like this. So, this is quite important. Now depending on the orientation of the molecule, I do find that the effective overlaps between the molecules are different. And that is also something I have talked about. So, here you can see this is the effective overlap, but here I can see that there are more effective overlap possible and in this case, I can see that the much more effective overlap between the molecule possible. So, therefore, definitely, that would means the stabilization energy due to the molecule-molecule interaction is not just looking like a single potential energy diagram. Like in this case, so let me just use a different colour. So, let us we have already seen this. So, this is basically the molecule molecule distance and this is the energy for example, the so called interaction energy, and this we have called it as E intra and it is not just going to look like a simple potential energy diagram, because when the molecule come together you can definitely see that the distance between the molecule in the case one is much larger and in the case two, the distance is much closer and in case three, the distance is basically much more much closer. So, that means when the molecule come closer and closer, it is not just one possible way that you can basically put the molecule together. You will have like no more possible way. So, you can actually find one minima here, another minima here, and one more minima here which is meaning that the potential energy surface is not necessarily just looking like a single loss potential, it can look like many many different ways. So, I am just for convenience I am calling this as one this is two and this is basically three. So, that is meaning that the way the molecule orient and the distance between the molecule is greatly controlled, and that is going to have to give us more possible ways that we can put the molecule. But now of course, you will find that number three is actually the most energetically favourable or the most energetically stable situation because you are at the bottom of the potential well, so you would assume that okay that is the case. But now, you see two for example, is a case where the molecule can get trapped because it is known as a local minima. So, this is actually known as the local minima, local minima, and this one is actually known as a global minima, a global minima. So, that means if the molecules while they are actually just rearranging and coming together, if they get trapped in the local minima, so then they will basically just feezed inside that particular minima. And then you would only be forming a pattern, which is based on two. So, therefore, it is quite important that additional factors need to be put inside to finally achieve the final self-assembly or finally the most thermodynamically favourable self-assembly for that you need to push the molecular self-assembly with additional factors. So, you see now the more clear picture is that you are not actually just looking at a single potential energy minima. You are actually basing looking at a landscape of many, many, many minima’s and the molecule while they self assemble or while they interacting each other, so they can get trapped in any of these minima and then the self-assembly is completely triggered by that particular arrangement of the molecule. So, now you see that the only case we have considered is the molecule-molecule interaction. And similarly, you would find that the molecule-surface interaction is also much more complex in this case, as compared to the adsorbate surface, as compared to the atomic adsorbates on surface, because that was a point object. So, they could always go on a given adsorption site. But here since the molecules are much more larger, so this is a particular area, for example, you cannot simply put a single molecule on a given site. It has to have a kind of area at which the molecule is basically adsorbing. So, that is meaning that with respect to the surface, a molecule is going to occupy, a molecule is going to occupy several atoms on the surface. So, therefore it is important, how the molecule is actually arranging with respect to the surface. And that is also going to play finally which is the assembly that you are going to look at. So, in the next class, that is what we are going to look at, in greater detail and then we will finally summarize the energetics that controls the molecular adlayer on surface. Thank you very much for your attention, and I see you in the next class. Thank you very much.