Chemistry and Physics of Surfaces and Interfaces
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Lecture - 18
Molecular Adsorbates: Factors Controlling Molecular Adlayer Formation- 2

Hello everyone, welcome back to today's lecture, lecture number 18.

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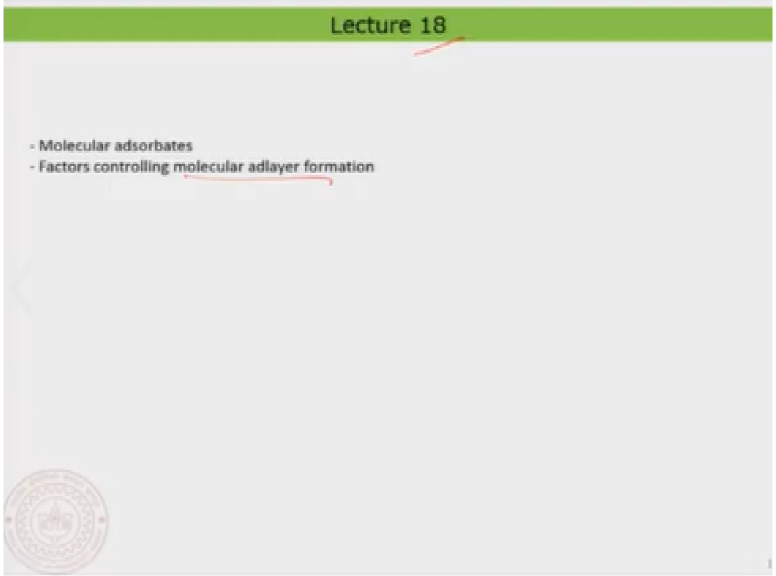

Lecture 18

- Molecular adsorbates
- Factors controlling molecular adlayer formation

In this lecture, we will continue in the molecular adsorbates part which we have been already discussing in the last two classes. Today we want to again look back into the factors that control the molecular adlayer formation because we have seen it is a little more complex than the atomic adsorbate. Then will try to basically understand it completely today and we will try to see how we can really understand the adlayer formation of molecular adsorbates.

Just recollecting what we have done in the last class, if you remember we have been mainly focusing on the molecular-molecular interaction. As we have already seen that is one of the major parts that controls the final adlayer formation or the final assembly of the molecule itself, mainly controlled by the molecule-molecule interaction and the molecule-surface interaction. So, I just want to recollect what we have done in the in the last class.

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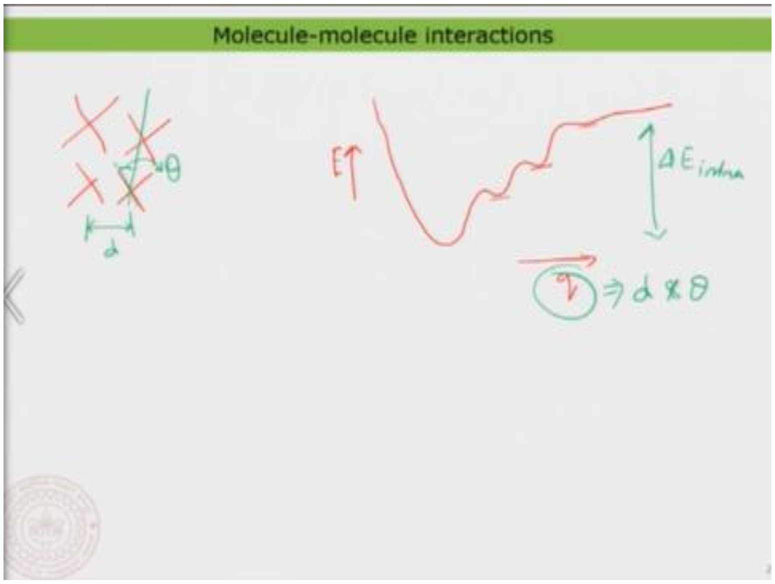

Molecule-molecule interactions

So, you remember that we have been looking at molecules of a shape like this and then we said depending on the way they interact and mainly due to the difference in the possible orientation. It is expected that molecular adlayer can have more possible type of patterns or assembly than you would expect it for like a simple atom like adsorbates. Then we also said that if you would look at the type of potential energy diagram of the molecular adsorbates, it would look more or less like this, where the inter atomic distance and the energy, the potential energy of the so called formation energy of the molecular adsorbates if you put together you would find that there are several minimas. In the previous class, we have already just discussed about that and there may be like 1 global minimum. So, that is something like an absolute most stable thermodynamically favourable project product. But in between you can actually have like additional local minimas which is also a possible type of adlayer assembly that you can expect. So, that is a difference for these molecular adsorbates compared to atom like adsorbates. And the main reason is actually due to the fact that there is molecule-molecule orientation is also playing a role and not just the molecular-molecular distance. Therefore, we want to make a small correction to what we have done in the previous class. We want to basically change now the coordinate of this so called potential energy diagram to something which you can call it a skew which is like a collective coordinate that includes not just one parameter that includes several parameters. What is this? You already see in this particular case the most important thing that controls the assembly of molecule is in fact the distance between the molecules that would be something which we can call it as the d. The distance between the molecule and also the relative orientation of the molecule. If I would just draw a line along the molecular lattice, then you can see that the molecules are oriented with a certain angle, let us call it theta between the molecular lattice and the orientation of the molecule. So, on surface since all other type of orientations for a planar molecule in a simpler case is restricted. We can typically talk about orientations with a respected to the plane of the surface and if that is the case then you already see that the q should contain d and theta. So, q is actually a function of d and theta and then we can somewhat say, that the potential energy diagram of the potential energy surface for the molecule-molecule interaction is not just one dimensional it is basically a multi-dimensional space. But however, we can basically depict them using something like that where we would still call this quantity to be something like delta E intra. So, that is the same or that is actually comparable to what we have done for the atom like adsorbate. So, that is good. Now what I want to do is?

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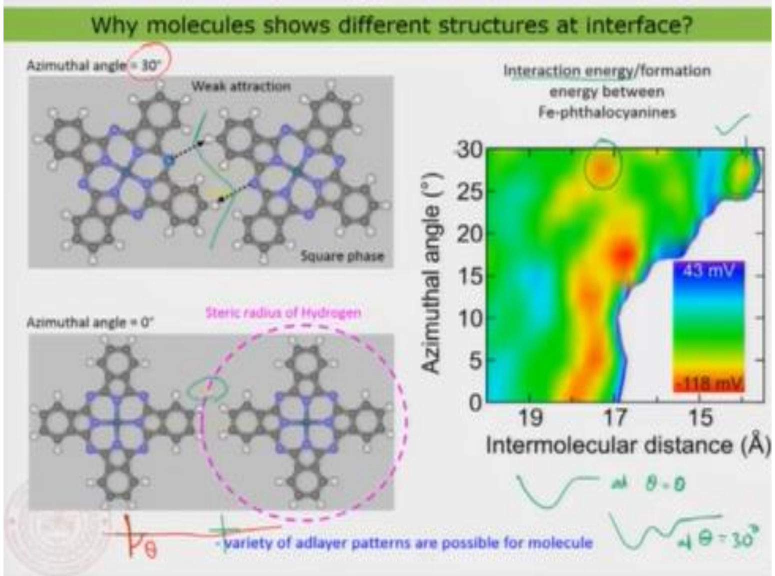

Why molecules shows different structures at interface?

- variety of adlayer patterns are possible for molecule

I want to show you an example of a real system and how the so called molecular orientation and the molecule-molecule distance is basically related and how the so called molecule-molecule interaction is coming into the picture in terms of the interaction energy. So, now you take again this molecule, the phthalocyanine molecule, it is a very nice and model system in fact and phthalocyanine also has been used in many thin films based application because it is a semi conducting molecule. So, that has been widely used in thin film transistors and also inorganic light emitting diodes and these kind of materials or application it is already used. So, it is a kind of very celebrated semiconducting molecule that is now around in the application. So, now when you look at this molecule of course, thanks to the planarity of the molecule. So, we do not need to consider more complex orientations. In this case everything is going to happen on the surface that means a molecular orientation with respect to the surface. So, if this would be the surface plane the molecular orientation with respect to the surface is something that we are going to mainly consider and the other things are not quite important in this case. Now I am defining something called an azimuthal orientation or an azimuthal angle that is actually the orientation of the molecular axis with respect to the lattice. So, imagine that the molecule is forming like this as you see in the image so that means molecules are forming the patterns are coming like that. And then between the molecular lattice and the molecular lattice is somewhat like this and the molecular orientation you see there is actually an angle that is something I am calling it as azimuthal angle. So, that angle is something that we are now going to use in understanding the molecule-molecule interaction. So, now for this particular case, this particular orientation the azimuthal angle is 0, where the two molecules are basically facing with respect to each other. So, of course, the choice of numbers or choice where you start is be quite arbitrary but at the end of the day you would basically just define an angle and you can basically play with that to understand, so that is a point. So, here we define that this azimuthal orientation in this particular case to be 0. Now what I can do is I can take 1 molecule and rotate 1 molecule with respect to the other and if I do that, I will get enormous possible orientations between the molecules. So, that means I can span the azimuthal angle from theta till 360 degree it is possible. But the point is since the molecule is a C4 symmetric or it is a four-fold symmetric molecule of course the symmetry group of the molecule is D_{4h} that is something unimportant in this case but it is of course a C4 symmetric molecule. So, everything between 0 and 90 degree is what is interesting and everything between 0 and 90 degree is basically symmetrical with respect to the orientation. And one need to only consider therefore like from 0 to 45 degree for understanding the entire picture everything else is symmetric otherwise. So, now what I am doing is I am basically just rotating the molecule with respect to each other. And then I am coming to another orientation which is actually having an azimuthal angle of 30 degree. Now, when it comes to the 30 degree is something interesting in this particular case. Because as I have told you in the 30 degree orientation as you can see here the intermolecular interaction is more effective because the area that the two molecules basically just cover is the maximum in that case. Because these molecules are typically interacting through Wander Waals interaction and therefore it is quite important that they share a large boundary between them. That is the most effective in this orientation around 30 degree where you get the best overlap between the molecule. And in addition, there is also a weak interaction which is not necessarily something that is predicted as a hydrogen bonding or something. But you can see there is still a nitrogen which is interacting with the aromatic hydrogen, CH hydrogen for example. It is a very, very weak interaction; it is not necessarily classified as a hydrogen bonding or something like that but it is observed in this kind of molecule. Finally, the molecule is actually arranging in such a way that the hydrogen is pointing towards the nitrogen. Of course, it is a weak interaction. But at the same time there is also this so called large overlap between the molecules due to the orientation. So, now you see clearly that with respect to the relative orientation of the molecule you can clearly see how the interactions are going to occur. So, that is what I want to now put it in some plot which is known as the intermolecular distance that is the distance between the two centres of the two atoms. And this is actually a theoretical calculation what you are seeing here is a theoretical calculation, which is performed by taking two molecules and rotating them with respect to each other then calculating the so called potential energy. Then you actually just subtract the potential energy that you gain from this so called orientation with respect to a single molecule. Then you get something known as an interaction energy. That will tell you roughly how stable these orientations are when they form a dimer, so that is the idea. Now you can see for sure in the azimuthal orientation 0 degree the distance between the molecules is about 16.52 angstroms, the distance between the molecule, that is the most favourable distance. So, that means that along every orientation you can basically draw a potential energy curve of this form. So, it will basically look like that, along every single orientation. So, at theta is equal to 0 theta is equal to 0 and also you can basically just do the same thing for a theta is equal to 1 degree 2 degree like that. Then you basically put those plots together and then you get this so called interaction energy as a function of azimuthal angle and intermolecular distance. Now when you look at this azimuthal angle 30 degree so that is basically this part here then you can see that the potential energy diagram. So, like please also note that yellow colour or red colour is corresponding to low energy and light blue colour or more like dark blue colour is basically representing a high energy. So, whenever energy is negative that is basically meaning that is a kind of stable dimer because the zero is actually corresponding to the energy of a single molecule. So, whenever there is a dimer formed then you would basically compare the energy with respect to a monomer and say how much the energy is stabilized. So, therefore negative is actually meaning that it is more stable. Now what you see is basically along the 30 degree you find that there are several minimas. That would mean; that at around 30 degree you would find that there are several minimas available. So, this is basically a theta is equal to 30 degree. That is the interesting part. So, that means depending on the orientation of the molecule you can actually have not just one minima. So, at 0 degree you clearly see that there is only one minima but at 30 degree you clearly see that there is one minima here and another minima here. So, that means there are two possible orientations which are actually stable that is quite interesting about the molecule. Now you can understand clearly what would happen for the molecular energy or the molecular circle interaction energy as a function of azimuthal orientation and intermolecular distance. Now, you see clearly that this is the picture that you have to consider in finally understanding the complete molecular molecule interaction because there are two independent parameters the orientation and the distance. Because, you also see that when the molecule comes to this 30 degree orientation you see the intermolecular distance is basically decreased to something like 13.49. So, that actually corresponds to this point here and which is actually meaning that when you change the orientation, they are not only just changing the orientation they are also coming closer or going away and so on. So, therefore this picture clearly tells me or clearly tells us what is the dependence of the molecular orientation and the intermolecular interaction? Of course, if I would like to look at it and then basically you can say that this corresponds to this particular point and this one is actually corresponding to this particular point. So, these are two possible ways. So, that actually means when you have molecules on the surface you can in fact form several possible type of assembly on the surface. Therefore, it is also quite important that you understand them in this kind of detailed analysis to clearly understand. Well, depending on the shape and the geometry of the molecule you can always end up in a much more complex diagram. It is may not be necessary that you can just define everything in two co-ordinates you may also require more than two coordinates to define basically inter-molecular interaction. But in this case, it is good enough that we can basically understand. You will also see in the later slides that the molecular pattern itself on the surface is basically the one at 30 degrees and you can actually see like when you cover the surface with one mono layer. You clearly see the pattern that is corresponding to an azimuthal angle of 30 degree. So, that is because it is actually an energy minimum. But you need to have a lot of molecule in order to push the molecule into that; so called global minima or to one of the minima because there are many minima as available on the potential energy surface. Good, now comes to the molecule-surface interaction. When it comes to the molecule-surface interaction; it is again not just the fact that you take an atom and you can actually just go on a given adsorption site. Molecules are much bigger.

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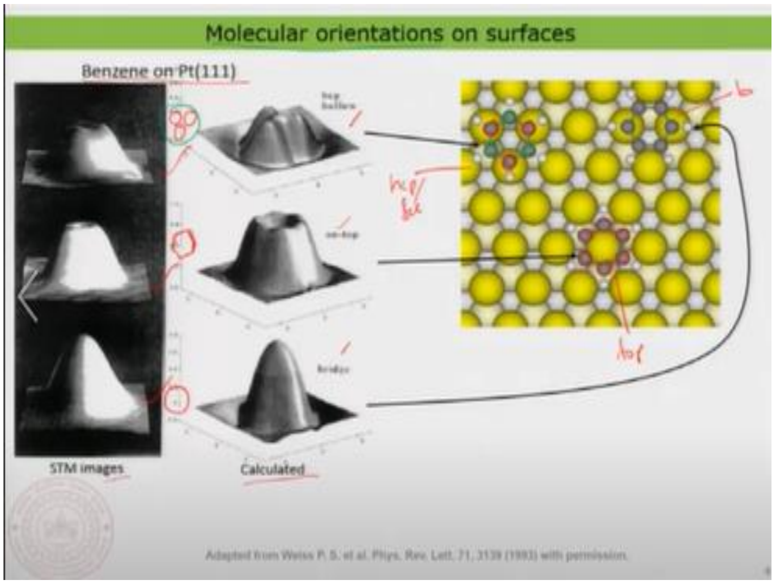

Molecular orientations on surfaces

Benzene on Pt(111)

STM images

Calculated

Adapted from Weiss P. S. et al. Phys. Rev. Lett. 71, 3139 (1993) with permission.

Therefore, you have to also consider something called as a molecular orientation with respect to surface. So, that something we want to now consider because both the molecule surface and the molecule-molecule interaction is finally deciding what happens to the molecular assembly or what controls the molecular assembly itself. Now let us take this very simple example of benzene on platinum 111 surface. Interesting thing what I want to show here is like using the microscopy and also using calculation,what people found when you deposit this molecule benzene on platinum 111 surface, they find three different type of contrast for the molecule itself for the benzene molecule itself. So, one where you just the molecule appear like a bright protrusion and in the other case the molecule appear like something with three protrusions, and in the other case it is more or less looking like a benzene ring, like you would expect. And in the other case it is just looking like a big protrusion. So, then people were asking what is actually behind this or why do we see actually more contrast for one type of molecule. You would have expected to see something like a benzene a hexagon but in on the other hand you would basically observe different type of contrast. By the way in the next upcoming lectures, we will be looking in greater details about the scanning tunnelling microscopy itself. There you will understand that in scanning tunnelling microscopy what we measure is nothing but just the electron density that is actually spread over the molecule near the frontier orbitals. So, therefore what you are also seeing to do something with not just the geometry of the molecule. It also has to do something with the electron density that is distributed around the molecule near the frontier orbitals. So, we will look into that in greater detail but just believe me right now what we see experimentally is these three types of contrast. Now then people have actually also done some theoretical calculation and they could reproduce exactly the contrast as you observe in the experiment. Only when they have actually considered that the molecule can adsorb on the surface at different type of sites. One is known as the top site we have already heard about that another one is actually known as the bridge site. This is the top site, bridge site and then you also have something known as the hcp or fcc hollow site. You can now see when you look at the molecule, you cannot accommodate the molecule on a given surface site that is the key element here, unlike in the case of atomic adsorbates. Here, you are going to accommodate them on a larger area. So, therefore they are going to be multiple sites the molecule is going to occupy. So, therefore you can see clearly if you are putting the molecule in the hcp site, somehow alternate carbon atoms as you see here, alternate carbon atoms are coming on the top, near to the top site and the other alternate atoms here I am marking it with green, the other alternate atoms are actually coming to the so-called bridge site. That means the molecular contrast is at the end enhancing and appearing it as more or less like three small lobes. So, that actually also makes sense at the end, then in the case of bridge site the molecule is basically having a much more complex adsorption geometry. That is actually giving rise to a contrast which is just looking like a bright protrusion and in the case of molecule adsorbing at the near the top side where you can see each of the atoms are actually having a similar adsorption site and therefore, they are all somewhat appearing in the STM contrast and then giving rise to something like a nice hexagonal ring kind of a pattern. So, that is the interesting thing. So, now what we want to see here is that when you talk about molecular adsorbate it is quite important that we also have to consider about the molecular absorption site on the surface. It is not just a single site where the molecule gets occupied. It is actually a much more complex side. So, this is about the case of a small molecule.

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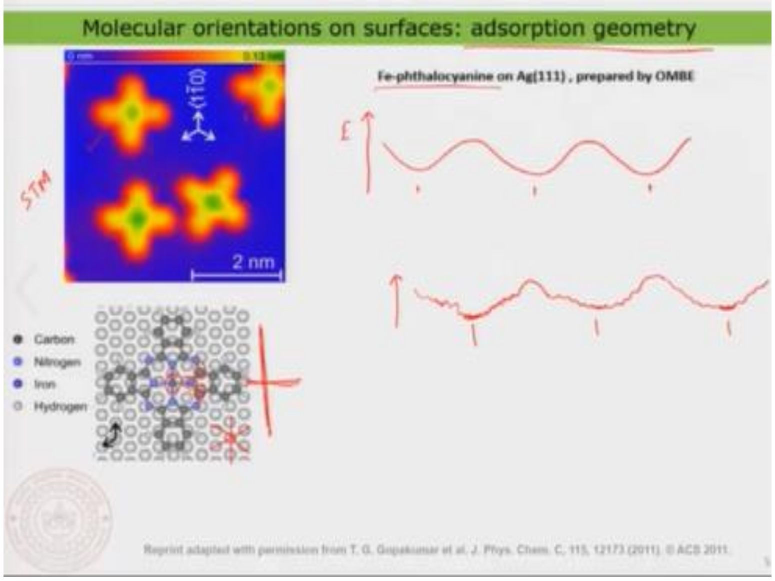
Molecular orientations on surfaces: adsorption geometry

Fe-phthalocyanine on Ag(111) , prepared by OMBE



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But now look at a little bit bigger molecule like the molecule that we have been talking about. It is a phthalocyanine molecule, in this case an iron phthalocyanine molecule on silver 111 surface. Now when you look at the molecule in a very, very low concentration, so what you are seeing here is a single molecule in STM contrast. So, this is again scanning tunnelling micrograph where you can clearly see isolated molecule. It is all controlled by the coverage, so you have a very, very low coverage so you can see the isolated molecule. When you inspect all the isolated molecule what you find clearly is that most of them, all the molecules are oriented just along three different directions. As you can see already here two molecules are actually orienting like this, another molecule is also orienting like that, even this molecule at the corner is orienting like this. When you find another orientation where the molecule is oriented like that. But if you inspect the relative orientation between one of the molecular axis, I am calling this to be the molecular axis. One of the molecular axis and with respect to that of other molecule then you would find they are all rotated by 120 degree each other. Well, it makes sense because the symmetry of the surface is again a three-fold symmetry therefore sorry, six-fold symmetry. Therefore, you would expect that the angle between the orientations of the molecule should also be just 120 degree. Well, that actually makes sense. Now you can see this is actually kind of a theoretical calculation again not experimental determination is not really possible like this way to some extent yes but not really. So, this is a theoretical calculation so, where they have of course checked how the molecule is orienting with respect to the surface and they found that again each atoms on the molecule as you can see here is having a variety of adsorption sites. So, none of the atoms are just looking the same as the other. So, they have a variety of adsorption. So, therefore it is now important to define something like an adsorption geometry rather than an adsorption site. That adsorption geometry includes basically the relative orientation of the molecule with respect to the molecular axis, with respect to the surface lattice. So, here as you can see one of the molecular axis as you see here is oriented along one of the lattice direction. So, this is basically one of the lattice directions so these are the three different lattice directions. Now you can see one of the molecular axes is in fact aligned with respect to that of with respect to the surface lattice. And this makes sense at the end because now, the molecule will be able to somewhat adsorb in a in a better position. So, now the only identity that I can just use is where the centre atom is basically placed. Everything else is much more undefinable. However, if you do calculations, you can clearly see how molecules are adsorbing. So, at the end of the day what I want to say is that the absorption geometry of the molecule is something that we need to now talk about. Now, of course this is kind of an optimum geometry but you would also find if you try to turn the molecule around the surface. You would also find that there are other possible energies or other possible stable energies for the molecule. So, therefore now if you again revisit to the so called molecule-surface interaction, originally we were just telling that it would also look somewhat similar like a periodic pattern. Where this is the energy and this would basically correspond to the position where the molecules are adsorbed. But we clearly know that this is not the picture because this is only possible if an atom is basically adsorbing on the surface. But now since the molecule itself is so large and it has to basically just adsorb on many variety of variety of adsorption sites on the surface. Therefore, it is better to define something like a molecular orientation or adsorption geometry and depending on different adsorption geometry. You may actually have not just one minima, you also will have several minimas basically. So, that means if you would just gently shift the molecule and move the centre atom let us say to the top site. You will also find another minima or if you would move the centre atom to the bridge site you will also find another minima. So, that would basically means for again the molecule surface interaction it will never ever look like just a smooth as this one, it is going to also look much more rough pattern than you would observe it for the atomic adsorbates. Again, but there is a natural periodicity of course observed that actually comes due to the fact that there is a minimum distance up to which the molecule can come closer. So, therefore there is definitely a periodicity because at the end of the day you will find that molecules are arranging with a certain periodicity. However, there are many, many possible minima, so these are all minimas at which the molecule can get adsorbed on the surface. But there will be something like again a global minima global minimum and this is where the molecule is finally going to adsorb. If you push it using additional parameters like temperature, concentration and things like that you can then definitely push to the final structure. But it is not necessary that the molecule will always go there it may also get trapped in some of these little minimas or local minimas that are available on the surface. So, that is clearly the point that I want to mention. So, therefore finally, if you want to take a picture together it is going to be the molecule-molecule orientation and the molecule-surface orientation and is going to define basically the adsorption energy of the molecule on the surface. And that is basically going to define what is the pattern that you are going to finally achieve on the surface. Well, with this I would like to conclude this lecture and in the next lecture we will basically see a bit further aspect of the molecule adsorbates on surface and so on, and a few more examples from molecular adsorbates formed in solid-liquid interface is also something we are going to discuss in the next class. Thank you very much.