Chemistry and Physics of Surfaces and Interfaces
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Lecture - 19
Molecular Adsorbates: Factors Controlling Molecular Adlayer Formation- 3

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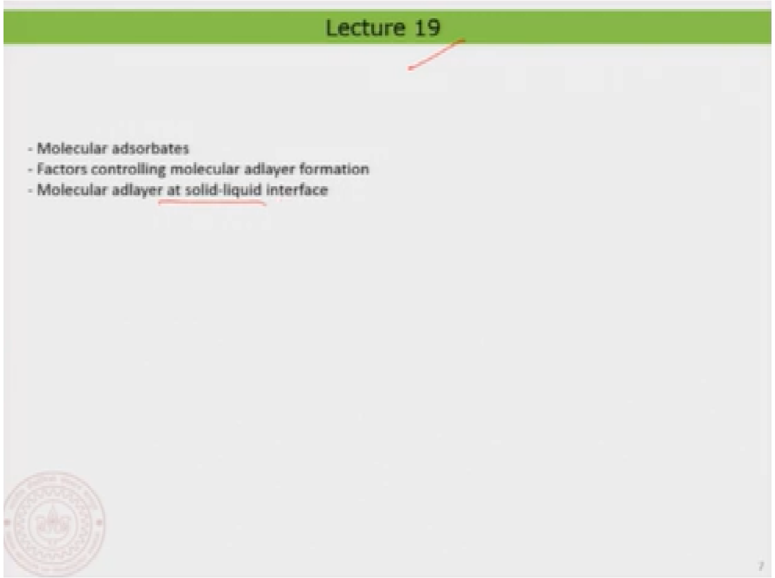

Lecture 19

- Molecular adsorbates
- Factors controlling molecular adlayer formation
- Molecular adlayer at solid-liquid interface

Hello everyone. Welcome back to lecture 19. In continuation we will basically try to summarize the molecular adsorbates and the factor that are controlling the molecular adsorbates and if time permits, I will be also discussing with you the solid-liquid interface, because you can also form molecular adsorbates in solid liquid interface and we will also have a look at that. Because their certain additional interesting factors that are also controlling the final assembly of the molecules on the surface.

Now well, what we have been doing was to understand the molecule-surface and molecule interaction, molecule-molecule interaction separately.

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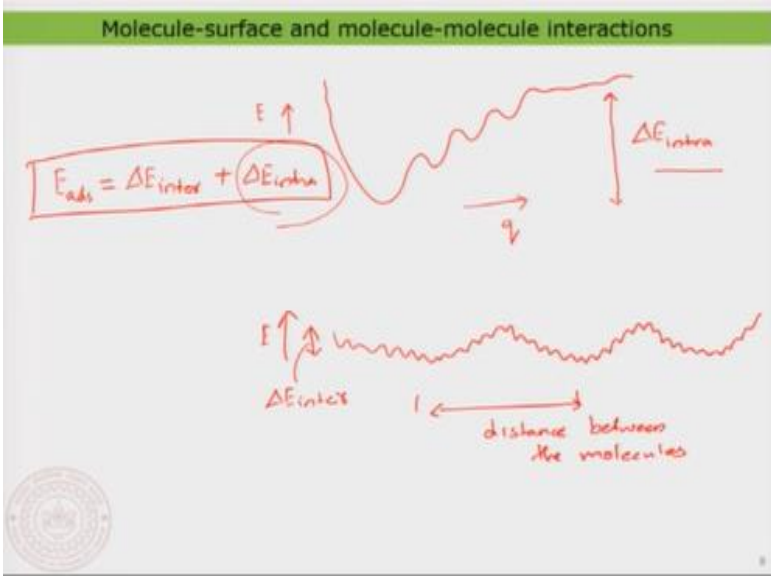

Molecule-surface and molecule-molecule interactions

Now we have come to an agreement that one need to basically consider something like a potential energy surface which is looking more structured. When you want to consider the so called molecule-molecule interaction into account. So, then you would basically have something known as the potential energy and then generally we called this one as the delta E intra. And then we said that there is also something known as the molecule-surface interaction. And of course, the molecule-surface interaction is kind of periodic in nature. But nonetheless due to the fact that the molecule can have many different possible orientation on the surface similar as molecule-molecule possible orientation that potential energy surface is also much more structured than just having a simple periodic function as we have seen in the case of atomic adsorbate on surface. So, then if I would put that into a cone then also you would find that they are much more structured. However, there is a periodicity that something like this one can basically see. So, this would be basically the distance between the molecules. And then you clearly see that this quantity is something which we can call it as delta E inter. So, that is the inter that is basically the molecule surface interaction. And this delta E intra is basically talking about the molecule-molecule interaction. So, now you see how complex the potential energy surface is? The potential energy surface itself containing the molecule-molecule distance, the relative orientation of the molecule with respect to other molecule, the relative orientation of the molecular axis with respect to that of the surface lattice and so on. So, there are much more parameters, much more coordinates that one need to actually just consider.

If you want to finally understand the so called adsorption energy or the interaction energy of the molecule on the surface. So, in general in any case the total adsorption energy would basically be again a sum of the delta E inter plus the delta E intra. So, that is remaining the same. But the point is to understand the delta E inter and the delta E intra it is a bit more complex because one need to consider more possibilities to finally write down the adsorption energy. Because the adsorption energy is something that you would finally say how strongly the molecule is basically binding onto the surface and also within the self assembled pattern or the self assemble adlayer on the surface. And that is basically the case but now you will also see that in the next example that this is clearly the point at the so called molecule surface interface. But when the molecule surface interface is actually getting much more thicker; That means when you are depositing multilayer then the influence of the surface is actually getting much more reduced. And then everything is basically going to be controlled by only the so called delta E intra. But there you have to also see some additional factors may also come into play that the molecule may also just start to orient in dimension as well and not simply like on the surface where we have seen that a planar molecule was just orienting with respect to the surface. So, that is actually the case. But generally, like when you start to make thicker layers everything is basically controlled by the molecule-molecule interaction and the molecule surface interaction is kind of irrelevant in that case. So, that is the kind of summary. Now if you put everything together I have again the same molecule the iron phthalocyanine molecule.

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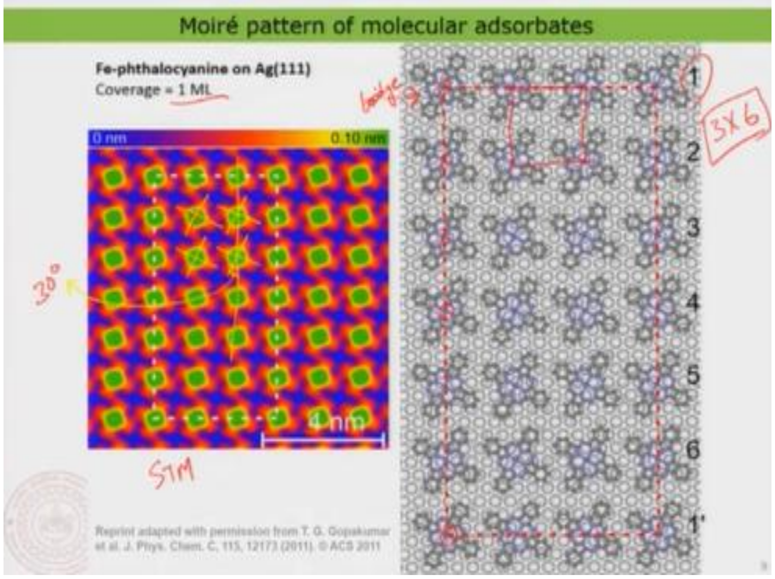

Moiré pattern of molecular adsorbates

Fe-phthalocyanine on Ag(111)

Coverage = 1 ML

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Now you can see the molecule and this is actually the coverage which is much higher so it is about one mono layer coverage. There you can see all the molecules are now coming together and forming this nice very well ordered pattern as you would find here. So, the molecules are nicely arranging like this where you can see the azimuthal orientation of the molecule is about 30 degree. So, that something what you can define here. So, this is basically the lattice and this is somewhat the orientation of the molecule and this is about 30 degree for example. So, approximately 30 degrees the azimuthal orientation of the molecule. So, that orientation comes due to the fact that this orientation actually allows the molecules to interact with the maximum surface area. Because the intermolecular interaction in this particular case is Van Der Waal type of interaction. And therefore, the molecule always try to arrange in a way where there is maximum overlap between the molecule. So, that is the basic key of this. Now but the point is in the STM image so this is again a scanning tunnelling micrograph image so there you cannot see the details. But using some additional experimental parameters you can clearly determine what is the adsorption geometry of the molecule. But then it turns out to be that not every molecule is basically adsorbing at the same type of adsorption geometry or same type of site instead it also has something like a supercell which is basically 1, 2, 3 it is a 3 by six supercell what the molecule is basically forming. Because you would find that this particular molecule is adsorbed at a given site. But when the molecule is actually arranging in the lattice you can see that the centre atom you can pay attention to the atom at the centre is basically just moving away from the bridge site. Because here the central atom was actually at the bridge site and as the molecule moves along the lattice. You would find that the bridge site is basically just changing and then finally at the seventh molecule the molecule retain the original absorption geometry as the one at one position. So, that means there is again a super periodicity along both the crystallographic direction and along the other crystallographic direction the super periodicity is basically about three times of the molecular lattice. And along the other direction it is about basically six times of the molecular lattice. So, it is not just that we can say that this is the unit cell that defines the molecule, it is indeed the other red dashed line represent basically the molecular lattice. So, that means what is going on at the interface is even more complex than what you would imagine in the case of atomic adsorbates. But nonetheless it is kind of an extremely interesting topic to investigate and using microscopy like you see here.

One can understand things at the atomic scale and that will actually just help you in understanding a greater detail or and kind of clearly the molecule surface interface. So, this would be kind of a complete picture of the molecular adsorbate on the surface or directly at the interface.

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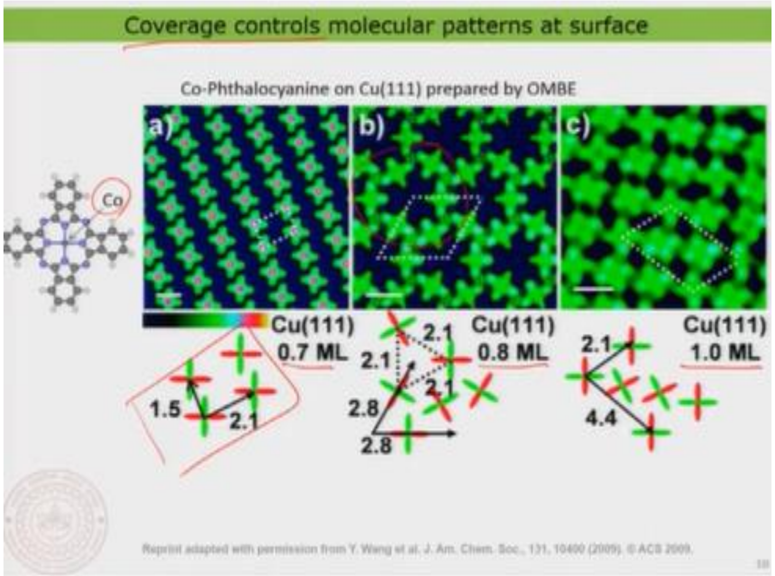

Coverage controls molecular patterns at surface

Co-Phthalocyanine on Cu(111) prepared by OMBE

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Now what I want to also do, before that what I would like to also show you are some additional factors that are going to actually just control the molecular self assembly on surface. So, far what we have seen is that it is basically controlled by the molecule-molecule orientation and also the molecule-surface orientation. But that is not the case, because you would also find that in certain cases or in many cases in the case of molecule.

The depending on the coverage of molecule that you have on the surface. Here for example, I have 0.7 monolayer coverage then I have increased the coverage to 0.8 monolayer then 1 monolayer. So, depending on the coverage you would find different type of pattern. So, you can see here the first pattern it is again a phthalocyanine molecule. But the central metal atom is cobalt in this case that is the only difference. But what you find is that here the molecule again orients somewhat like what we have seen in the previous case. When you increase the coverage, you find extremely interesting pattern. So, you can see here a very interesting pattern is basically emerging and then when you increase the concentration or the coverage very very high then the molecules are actually going down to something like an extremely close packed pattern. So, the point here what I want to mention is again it has to something to do with the so, called possible molecular orientation and the stabilization energy of the so, called interaction energy through the molecule-molecule interaction is the key for it. But that you can clearly control by the concentration. So, depending on how much molecule you drop or how much molecule you deposit on the surface you can actually just decide what type of adlayer pattern that you would like to have. So, that is something quite controllable in the case of molecule. But in some cases, there are only subtle differences between these energies and therefore like control is not as easy as one would imagine. But if there is a clear difference between the different minimas in energy then one can easily control these patterns on surface using concentration for example or in some cases one can also use temperature as a control parameter. You can also just generate different type of molecular pattern on the surface. Now I would also like to discuss with you a little bit away from the surface. So, what happens if I would deposit molecules in a multilayer. Of course, I am not going to consider in my class something like several layers. So, that is something we are not really considering at least in the microscopy part.

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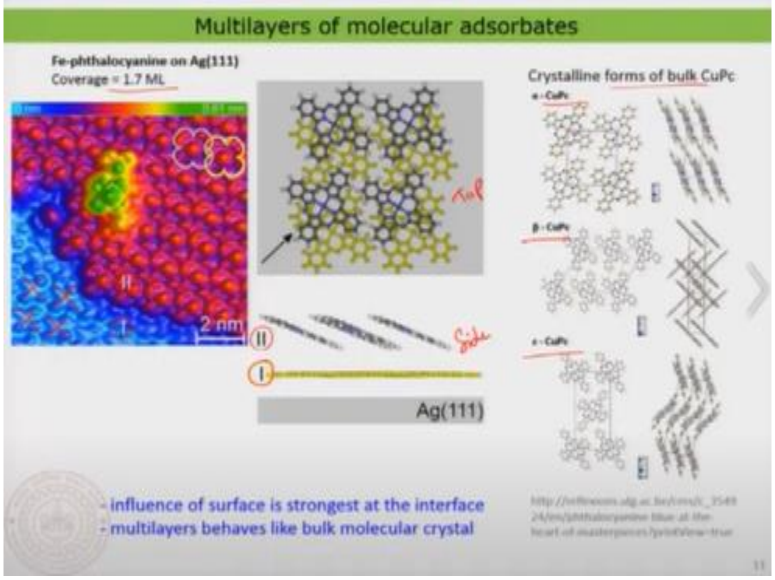

Multilayers of molecular adsorbates

Fe-phthalocyanine on Ag(111)
Coverage = 1.7 ML

Crystalline forms of bulk CuPc

- influence of surface is strongest at the interface
- multilayers behaves like bulk molecular crystal

But what I am going to show you here is actually a coverage which is 1.7 monolayer. So, this is again the iron phthalocyanine on silver 111, a surface so it is the same example as you have seen in the previous slide. Here, I have basically the first layer then the second layer and the third layer and so on. So, this is clearly like apart where I have an overlap between the first layer and the second layer. So, here you can see in the first layer clearly the molecules are arranging like this which we have already seen, it is nice. So, they are basically just doing this nice compact packing of the adlayer in the first layer. And now in the second layer what you find interesting is that microscopically you are unable to image the entire part of the molecule. So, that is what is shown here in this scheme. What you find is that you are only able to just see some part of the molecule. So, that actually gives rise to an impression that they are actually just kind of overlapping. But that is not really possible that two molecules just overlap like that. Unless and until they have some kind of a tilted orientation. So, if you have a tilted orientation and when you look from the top, they are basically appearing like one molecule is overlapping on top of the other. So, then what happens is that in the first layer and in the second layer?

You would find that the molecular orientation with respect to the Bessel plane of the surface is actually changing. So, in the first layer, all the molecules are planar with respect to the surface and in the second layer of course the molecule is planar. But the molecular orientation with respect to surface is not any more planar like this it is basically getting tilted with respect to the Bessel plane of the surface, that is interesting. So, the molecule is getting tilted and this is kind of a side view and this is the top view. I can clearly see in the top view that how the molecular orientation is basically happening. Now the interesting thing that you would ask why is basically suddenly the molecule is changing their orientation, why not just the molecule pack in the same way as you would actually just see it in the first layer. Well, that is an obvious question. But the interesting thing is that when the molecules start to pack in the multilayer, they start to increase the so, called molecule molecule interaction. And for molecule like phthalocyanine which has actually a strong pi electron cloud around the molecule, it is very well known that the molecules are actually some kind of having a strong pi pi interaction. So, if you want to maximize the pi pi interaction what the molecule does is they tilt themselves in order to maximize. The so, called molecule molecule interaction which is again a pi-pi interaction, Van Der Waals interaction, but they try to maximize it. So, how do you clearly say that this is the case. We can understand that if you look at the bulk structure of these kind of phthalocyanine molecules. So, this is basically the packing of copper phthalocyanine in crystal that means the three dimensional crystal of copper phthalocyanine molecules. And there people find different type of packing of copper which is known as alpha copper, beta copper piezo, epsilon copper piezo these are just names. And there they are all basically having some kind of tilted orientation but the slight differences in the relative tilt that is the only difference between the different phases. But in all the cases what you have effectively is the so, called pi pi interaction and to maximize the pi pi interaction.

The molecule actually just get tilted with respect to each other and they pack. And you clearly see when I form the multilayer so that means already in the second layer, the second layer molecule already is tilting with respect to the surface. So, that is something you can already see. And if I would basically grow molecules into the multilayer then their tilt would become larger and then it will basically just remain like in the bulk packing. So, that is the connection between the interface and the bulk packing. So, they are always related. But at the interface there is a strong influence of the surface and therefore the molecule surface interaction prevails at that point at the interface and therefore the molecules are actually just looking more or less flat absorbed on the surface. But as you go thicker and thicker the molecular orientation is changing and they start to basically follow the bulk packing. So, that is the interesting aspect that one can basically see here. Now if you would basically want to finally make a comparison of the solid atom interface and also the molecule solid interface like we see it right now.

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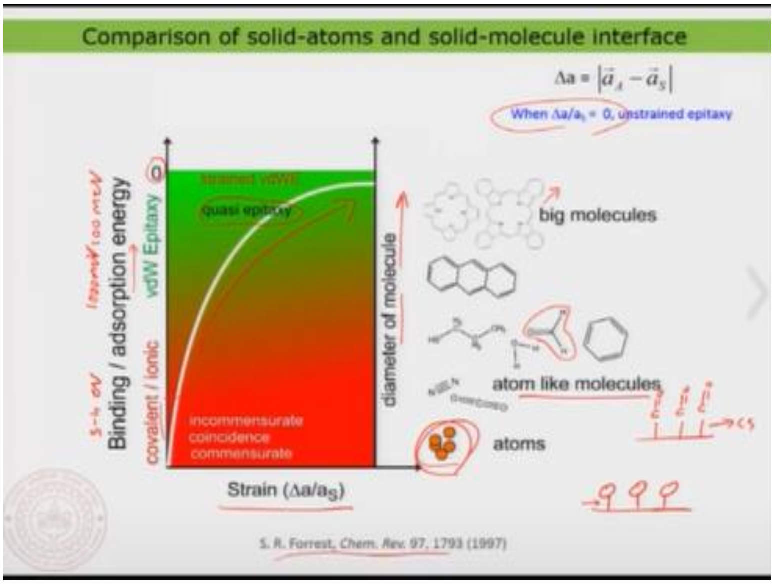

Comparison of solid-atoms and solid-molecule interface

$\Delta a = |\vec{a}_A - \vec{a}_S|$

When $\Delta a/a_s = 0$, unstrained epitaxy

S. R. Forrest, Chem. Rev. 97, 1793 (1997)

This is of course a qualitative picture where one can kind of relate the typical relation between the adsorption energy of an atom like adsorbate on surface or like a molecule like adsorbate on the surface. So, the interesting aspect about the atom like adsorbate on the surface is that they are strongly bonded to the surface. So, like we have already seen. So, they are typically bonded strongly onto the surface. So, in many cases you would even find chemist would happen. And because of that there is a strong chemical interaction between the atom. And the surface your typical binding energy or the so, called adsorption energy is several orders of magnitude higher than that of a typical molecule surface adsorbate. So, that is what we try to show here on a relative energy scale where zero is actually a non interacting adsorbate on surface, that means an adsorbed which is really far away. But as you put this adsorbate on the surface so they start to interact basically in a in a strong way. So, obviously you would find that the atom like adsorbate has the highest binding energy or adsorption energy on surface. That is because of the true chemical interactions between them and that actually as we have already seen in a few cases. It can actually vary from a few electrons’ volt for example. So, you can actually have it in the order of a typical chemical bond like 2 3 4 electron volt is the typical order. But now when you actually just take atom like molecules, so these are actually molecules that would basically just go on to the surface. But you can see a carbon monoxide would adsorb on the surface like this and that is also looking like an atom like adsorbate. Because they are small and then their adsorption energy is also very high. Because they also would form a strong chemical bond or some kind of a chemisorption, I am just calling it a C S chemisorption between the atom and the surface. And in that case also you would find that the energy the so, called adsorption energy is actually in the order of a few electron volt. So, that is the point that you need to consider. But when the molecular size increases so, that is something that what I have here depicted as a diameter of the molecule.

So, of course the diameter of the molecule is quite hard to define, but it is typically something to do with the area of the molecule that is in fact interacting with the surface. So, for a benzene molecule, the hexagonal area itself is the diameter of the molecule and for molecule like this it is typically a bit hard to understand. Depending on whether the molecule goes like this or the molecule stands up and so on. But something like we can roughly say the area of contact of the molecule is something we can call it as a diameter. And now that is something quite important when it comes to the bigger molecule. And the point what I want to show here is that as you go to bigger molecule of course the diameter basically increases and you would also find that the adsorption energy is basically decreasing with respect to a non adsorbed state. So, that means atom like adsorbates or atom like molecular adsorbates are having a very high absorption energy because they do some kind of chemisorption on the surface, it is in the order of a few electron volt. But when it goes to molecule as you have already seen in the case of phthalocyanine, the interaction energy it is of course a rough calculation that I have done. But the interaction energy is typically in the order of a few hundreds of milli electron volt. So, just to give an analogy so it is not very quantitative. So, 100 milli electron volt and typically here you have something like 3, 4 electron volt. So, that is the typical order that we can we can talk about. So, then people generally call it is actually something like a quasi epitaxy, this not really an epitaxy, because epitaxy has to really do something with the surface. Here molecule is not really necessarily following the surface so then you cannot call it really as an epitaxy. Therefore, in some cases people also refer to it as a quasi epitaxy. Now there is also one more interesting factor or parameter that you can plug in that is basically the strain that we talked about. So, in the case of atom like adsorbate, although we talked about a variety of strain. You might notice that the strain that if you would calculate basically in the case of molecular adsorbate is much much much larger than in the case of atom like adsorbate.

The reason is very simple. The lattice mismatch of a molecular adsorbate with that of the surface is enormous, is very large. Because you have to consider the entire molecular dimension and the lattice of the surface is basically very small. So, that is the reason why you would find that the so, called strain is in fact increasing in this fashion, it is a qualitative measure. And then typically this kind of molecular epitaxy is kind of strained Van Der Waals epitaxy. And within this itself Van Der Waals epitaxy or the one where things the molecules are stabilized by Van Der Waals interactions are the one with the lowest adsorption energy. But if you have like strong hydrogen bonding or ionic bonds that would play inside then you could also just get into something like 1000 milli electron volt. So, that is actually possible. So, that is the range what we are talking about. So, like Van Der Waals epitaxy typically a few hundreds of milli electron volt, if it is hydrogen bond you can reach up to an electron volt and if it is basically strong chemical bonds that is forming between the adsorbate and the surface then it is basically three to four electron volt or a few electron volt is possible. So, that is the order of energy that we are talking about. But in generally you can kind of understand the solid atom interface, the solid molecule interface using this kind of a qualitative plot.

You can also just read this article; it is an old review article nonetheless it gives a good summary about molecular adsorbate on surface. You can get a certain important aspects about the preparation and the energetics of molecular adsorbate on surface in this particular review article.

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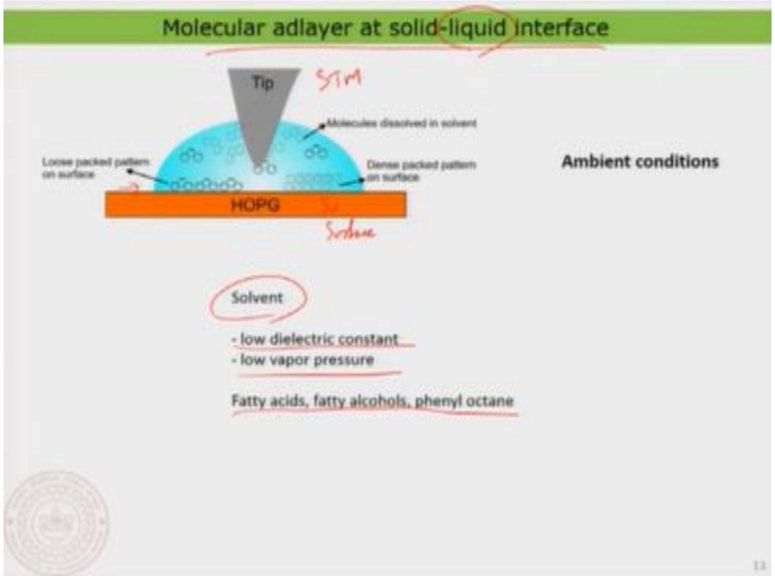

Molecular adlayer at solid-liquid interface

Ambient conditions

Solvent

- low dielectric constant
- low vapor pressure

Fatty acids, fatty alcohols, phenyl octane

Now what I want to actually discuss with you is the molecular adlayers that are formed at solid-liquid interface. So, this is slightly different. Because so far what we have been discussing is actually molecular adsorbate on solid surface and this was actually kind of a solid state film. But now what you can also do so this is basically you are seeing is a scanning tunnelling microscopic itself which is capable of imaging molecules inside a liquid. So, that is the point. So, now what you have additionally is you have the surface. This is the surface and then you have the molecular adsorbates. You can see here they are packing and then you have the atom the sharp, atomically sharp tip of the scanning tunnelling microscope and it basically scans on the surface and try to image the molecule inside the liquid. So, that is the interesting aspect here. So, in this particular case of course molecule do self-assemble on the surface. But interesting fact is that the molecules are actually the solvent that we use is actually going to play. The concentration of the solvent is actually going to play and the nature of the solvent is going to play a strong role in basically just getting the right type of molecular assembly on the surface. Just to keep it in mind that one need to have like this kind of low dielectric constant or low vapour pressure liquids typically to do this study.

This we will revisit when we study the scanning tunnelling microscope, so then you will understand it a bit more in detail. But right now, I just want to tell that the typical solvents that we are going to use. So, the so, called liquid phase medium that we are using is actually fatty acids or fatty alcohol or phenyl octane these kind of alkyl chains we are using typically as a solvent or the liquid medium.

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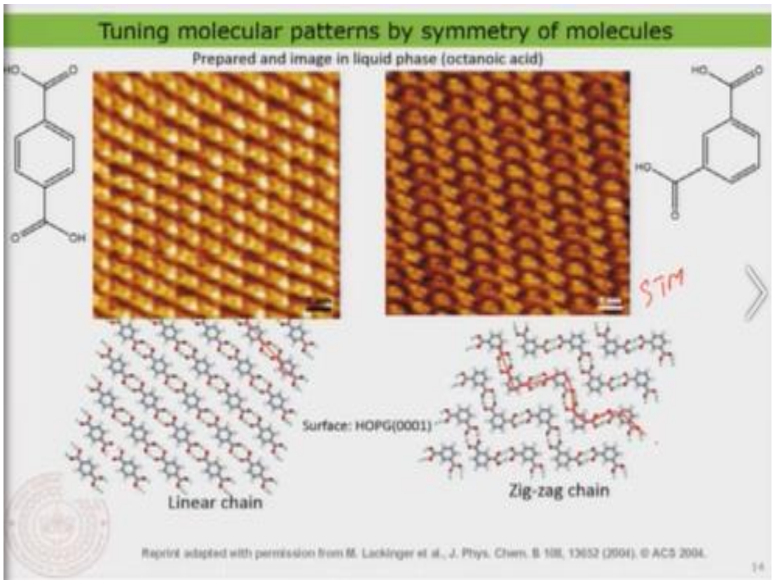

Tuning molecular patterns by symmetry of molecules

Prepared and image in liquid phase (octanoic acid)

Reprint adapted with permission from M. Lackinger et al., J. Phys. Chem. B 108, 13652 (2004). © ACS 2004.

Now let us have a look, this is very simple. So, some STM images of different type of molecules that we can form in the solid-liquid interface. So, you can see depending on the type of functional group and also where you place the functional group. Here, you can see it is a Para dicarboxylic benzene and this is a meta dicarboxylic benzene. So, depending on the position of the carboxylic group you can see they are arranging either in a linear fashion or in the case some kind of a zigzag fashion. That is basically allowed by the symmetry of the molecule. So, you can nicely image molecules at the interface.

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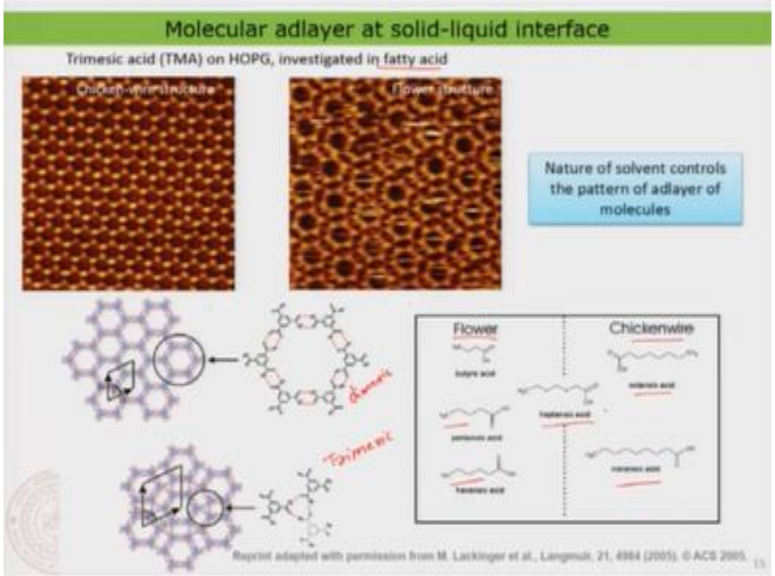

Molecular adlayer at solid-liquid interface

Trimesic acid (TMA) on HOPG, investigated in fatty acid

Nature of solvent controls the pattern of adlayer of molecules

Reprint adapted with permission from M. Lackinger et al., Langmuir, 21, 4984 (2005). © ACS 2005.

Now the interesting thing is again here this is actually the trimesic acid molecule which we have already discussed and we said that this molecule can form either a dimeric hydrogen bonding or a trimeric hydrogen bonding. So, these are the two ways that the trimesic acid can interact with respect to each other and depending on this interaction you can either form a flower structure or a chicken wire structure. But now the interesting aspect what I want to show you is like all this imaging is basically done inside a fatty acid. Now depending on the type of fatty acid that you choose, either you choose actually long chain, really long chain fatty acids like octanoic acid or nonanoic acid. Then you would find that the most favourable pattern is basically chicken wire pattern. And if you would use basically low, smaller alkyl chain length fatty acids like pentanoic acid hexanoic acid and so on. Then you would find that the flower structure is actually the most preferred one. And somewhere in between the so, called border line between these two the heptanoic acid you find mix of both chicken wire and flower pattern. So, you clearly see the nature of solvent is playing a very very crucial role in this case in controlling the type of adlayer pattern that you form on the surface. It is all to do with the length of the chain. Because in the case of chicken wire it is also observed that the molecules, the solvent molecules itself also get trapped inside these kinds of pores and that is being stabilized by the long chain is the origin of this different type of pattern. But you in important aspect what I want to say is like the nature of solvent.

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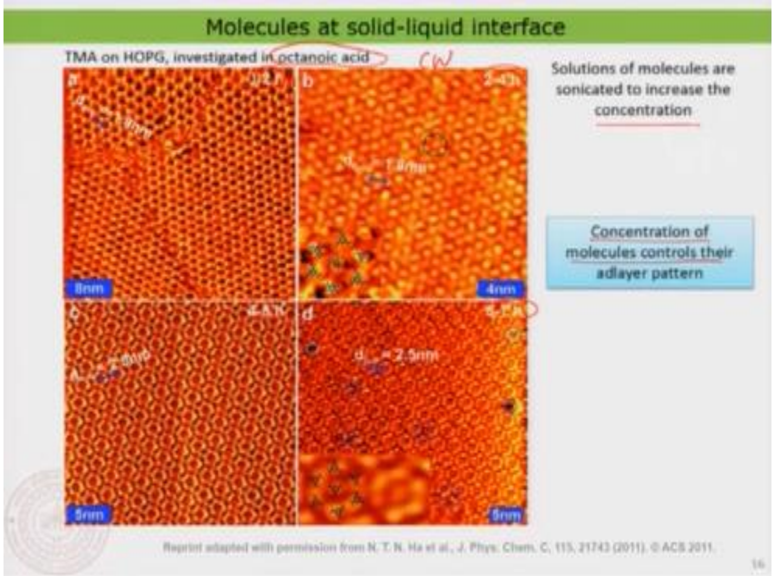

Molecules at solid-liquid interface

TMA on HOPG, investigated in octanoic acid

Solutions of molecules are sonicated to increase the concentration

Concentration of molecules controls their adlayer pattern

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Now what you also can do is you can basically increase the concentration. Now what I am doing is I take again octanoic acid a trimesic acid but what is expected is that this molecule only form this chicken wire pattern what is pattern in octanoic acid as per the previous literature. But now interesting thing by doing sonication so you mix a certain amount of molecule inside the solution make a saturated solution.

Now if you sonicate it for longer time that is what is given here 0 hour 2 to 4 hours sonication, 4 to 5 hour, 5 to 7 hour sonication then what we find is that the concentration of the molecule can be increased if you do increasing the sonication. And then what we find interesting is that when you increase the concentration of the molecule in this liquid phase then we suddenly find that you can find; both the flower and the chicken wire pattern. So that means concentration is also playing an important role in controlling the adlayer pattern.

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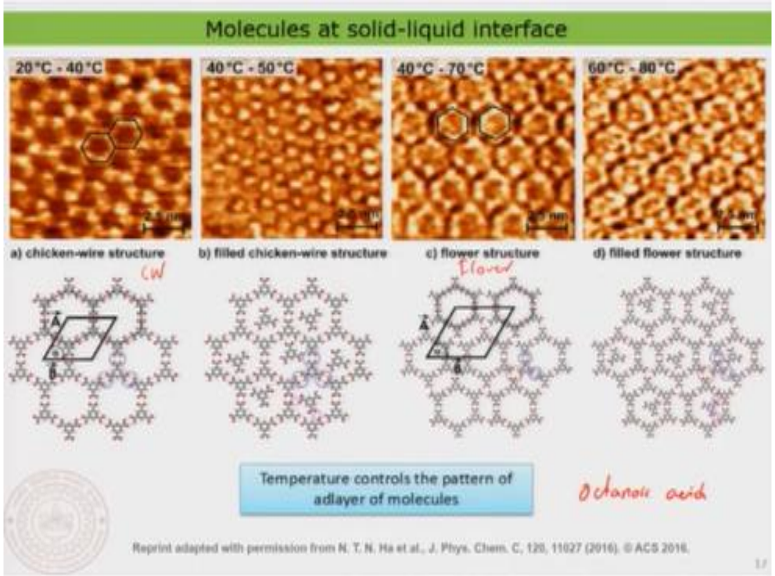

Molecules at solid-liquid interface

a) chicken-wire structure b) filled chicken-wire structure c) flower structure d) filled flower structure

Temperature controls the pattern of adlayer of molecules

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So, finally what I also want to say is that again this is the trimesic acid molecule which is worked out in octanoic acid. And what is interesting here depending on the temperature at which you image the molecule, you also find that you can basically find the chicken wire and the flower structure depending on the temperature. So, finally what I want to say like when you do the solid liquid interface, it is not just the geometry or the shape of the molecule matter. It also matters the concentration the solvent in which you are imaging the molecule or the temperature at which you are imaging the molecule all actually plays a role and therefore you have actually much more important factors that are controlling the self assembly of molecule in the case of molecule solid-liquid interface. So, that is in general about the molecular adsorbates and in the next class we will look at these examples again using different kind of microscopy. And we try to understand additional aspects about these kind of adsorbates. Thank you very much for your attention.