Chemistry and Physics of Surfaces and Interfaces
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Lecture - 16
Molecular Adsorbates: Preparation

Hello everyone, welcome back today’s lecture 16.

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Lecture 16

- Molecular adsorbates
- How to form molecular adlayer?

And in today's lecture we are going to discuss what we have started yesterday in the previous class we will look at the molecular adsorbate. So, you had already just have a look at a quick look at the molecular adsorbate, but today we are going to discuss a little bit more in detail and then we will also try to see how to form the molecular adlayer the strategies that you need to involve in forming molecular adlayer and so on, because you will find that the formation of molecular adlayer is clearly different from that of the atomic adsorbate on surfaces. So, therefore one need to plan a bit more in this case and then one need to strategize additional factors that was not present in the case of atomic adsorbate. So, that is what we are going to look in this case. Let me just quickly go through what we have done in the previous class.

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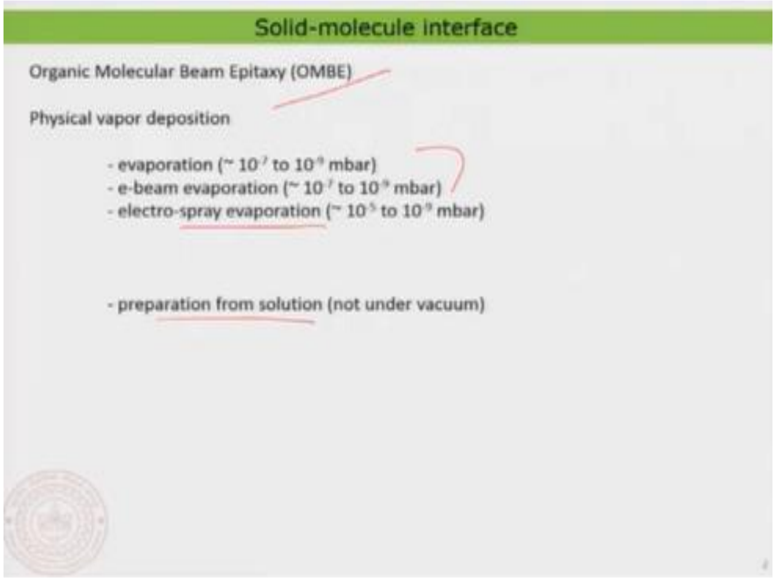

Solid-molecule interface

Organic Molecular Beam Epitaxy (OMBE)

Physical vapor deposition

- evaporation (~ 10^{-7} to 10^{-9} mbar)
- e-beam evaporation (~ 10^{-7} to 10^{-9} mbar)
- electro-spray evaporation (~ 10^{-5} to 10^{-9} mbar)

- preparation from solution (not under vacuum)

So, we just said that it is going to be an organic molecular beam epitaxy that we use and typically it is like evaporation or e beam evaporation both method can be applied or I have also told that we can use something like an electro spray evaporation for the preparation of molecular adlayer. I will also show you an example from the preparation from solution, because that is also like a very economic method in preparing molecular adlayers though not very clean as the one you prepare from the vacuum deposition or from simple evaporation technique.

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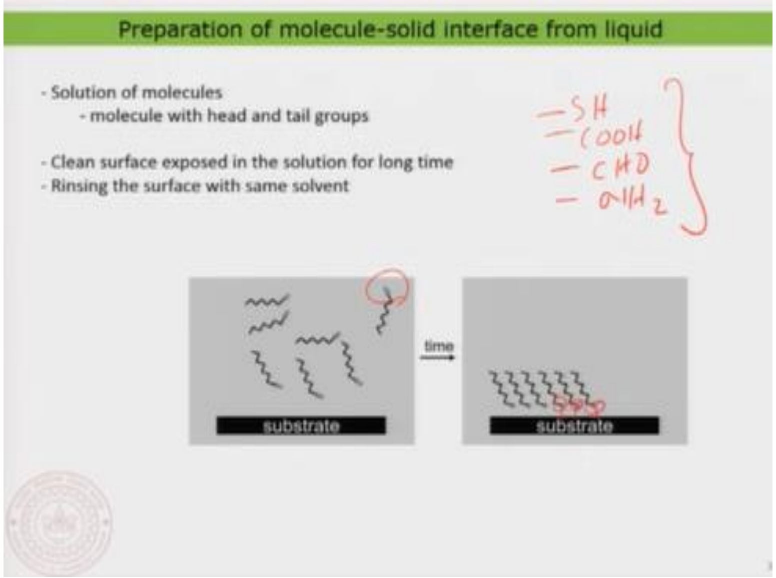

Preparation of molecule-solid interface from liquid

- Solution of molecules
  - molecule with head and tail groups

- Clean surface exposed in the solution for long time
- Rinsing the surface with same solvent

$-SH$
$-COOH$
$-CHO$
$-NH_2$

We also had a look at the preparation in a greater detail. So, we have already seen that one need to think about different type of functional groups for example SH group is a popular functional group or you can use carboxylic group or aldehyde group or you can use NH_2. Different type of functional group need to be on the molecule in order to form these kind of adlayer as you see here, where a kind of strong chemical interaction is induced between the functional group, this kind of functional group and that is what is getting finally interacting with the surface and then the side chain you can choose as you like or as the requirement, for example. One can use this methodology, so this is actually something called a deposition directly from the solution which is a very popular method people use. So, in my lecture I am not going to go into greater detail of this type of preparation but I nonetheless I want to just mention this type of preparation because you would also have an awareness that this is also one of the methodology that you can use in preparing molecular adsorbate on surfaces. So, we will be concentrating on the vacuum evaporated molecular films and also molecular films that are prepared at a from a solution but in a solid state not a greater detail about this particular type of molecular adlayer.

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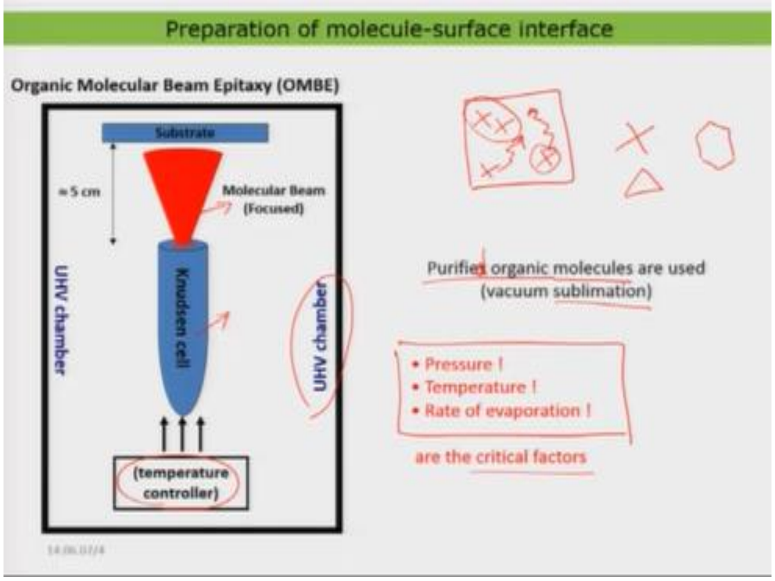

Preparation of molecule-surface interface

Organic Molecular Beam Epitaxy (OMBE)

Purifies organic molecules are used
(vacuum sublimation)

- Pressure !
- Temperature !
- Rate of evaporation !

are the critical factors

Good, now let me just show you how to prepare an organic adlayer or molecular adlayer on surface? So, what we need is an ultra high vacuum chamber so that something I have already told you that we are going to prepare everything using an evaporation technique. So, we really need the vacuum chamber. Now, the point is exactly like we have seen in the case of atomic adsorbates here also you are going to use something like this. That is actually the Knudsen cell which is either a ceramic crucible or you could also use a metallic crucible but the metal should be actually more inert at the moderate temperature range and then you can use like molybdenum is actually a favourite choice because their reactivity is very poor at normal conditions. So, if you have this then what you need is a temperature controller so that would basically kind of adjust the temperature of this Knudsen cell and when the temperature of the Knudsen cell reach actually the temperature of the sublimation of the molecule then what you create is actually a molecular beam. So, this is actually the molecular beam and as I have told you in the previous case you basically just create a beam which is a diverging beam normally because you have a kind of small opening here and through that molecular beam is coming. And the most important thing and that is the reason why you call it molecular beam is that the molecules are coming one by one. So, this is quite important in the molecular beam epitaxy be it atomic adsorbates or be it organic molecules, it is quite important that you generate the molecular beam that the molecules are actually just coming separately and once you deposit the molecules on the surface the molecules so the once you have the surface. And then now the adsorbates are looking slightly different let us call it with the shape so let us say like I have a cross shaped molecule that is getting absorbed on the surface and then they start to move around on the surface randomly and then finally they start to form some kind of a cluster and then that cluster grows further and further and then you form the island and that is actually the general principle or general scheme of any sort of adlayer formation. So, where the impinging first molecular or atomic adsorbates first would land on the surface then they would move around on the surface and then finally they kind of come together and form a stable adlayer. Now the you will actually just see that the things that controls the molecules assembly or molecular adlayers on the surfaces is slightly different from that of the atomic adsorbates the reason is because you see here there is a shape associated with the molecule. So, I have for example here depicted a molecule with a square. You can also have a molecule which is just looking like a triangle or you can actually have a molecule which is looking like a hexagon and so on. So different shapes would appear and that shape is also going to play a major role and also because the molecule itself is much much larger in size than atomic adsorbate things are actually quite different. Nonetheless, let us actually look at the most important parameters to actually just do this evaporation. So, you need to have of course a highly purified material organic molecule to be present in the Knudsen cell so that is actually very important and then the molecule should also be like sublimable, so this is actually another requirement the molecule should be sublimable should not actually degrade with the temperature or should not melt within the ultra high vacuum chamber. So, these are actually two important conditions to be satisfied. And then the pressure in the chamber the temperature at which you evaporate and also the rate of evaporation that is also very important and you can control all these parameters now a days very precisely and if you precisely control these parameters, you can actually form a beautiful adlayer of molecules. Now we look into some of the examples and will try to understand.

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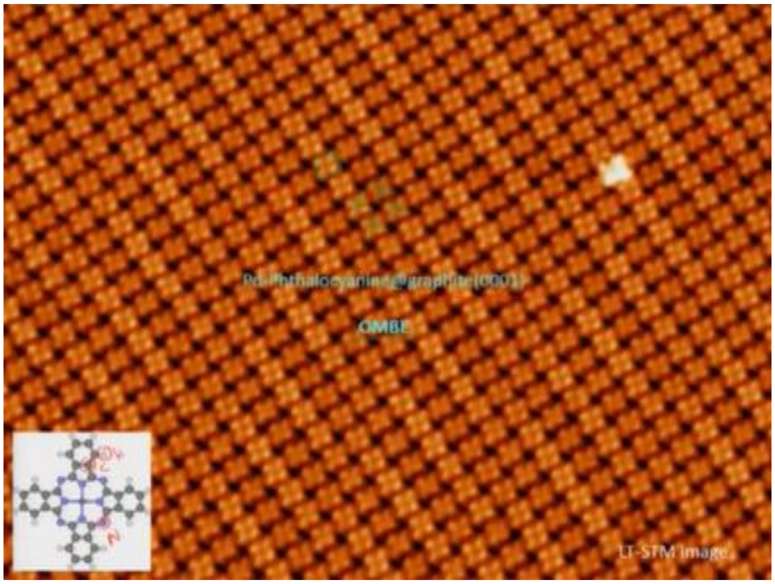

So, let us look at a nice example of a molecular adlayer. So, I have to just remove this molecular adlayer. So, this is actually a molecular adlayer on the surface of graphite 1 0 0 0 1 surface and the molecule is actually nothing but a phthalocyanine molecule. So, phthalocyanine molecule where you have here nitrogen atoms and you have your carbon atoms and then you have here hydrogen atom. So, this is actually a molecule which is having a cross shape and now the molecule when you deposit on the surface what you would find that the molecules comes together and form a nice island. Now let us look into the details here. Each of this point or each of this different piece here what you are seeing is nothing but a molecule, you can see it has actually a cross shape you can also mark it using a cross. You can see these are actually different molecules that is absorbing on the surface. And now what happens is actually the molecules when they are so they actually just go around and then basically just assemble together. So, in the case of molecular adlayer you call it that they self-assemble on surface. So, this is not triggered by anything it is basically just controlled by a certain parameter we look into that in in greater detail. So, using these certain parameters the molecule itself would assemble on the surface and form this kind of beautiful pattern. So, this is of course done using an organic molecular beam epitaxy inside a high vacuum chamber the molecule is actually a metal phthalocyanine molecule palladium phthalocyanine adsorbed on graphite 0 0 0 1 surface. And the image that you are seeing is actually a low temperature scanning tunnelling micrograph image. So, the low temperature is very important and that is also the reason why the images are looking extremely nice and highly resolved. At room temperature you cannot achieve this kind of high resolution, that is the reason why these molecules are imaged at low temperature. That is just the technique itself we will look that in greater detail in in the upcoming lectures. And now what you find is that the molecules are nicely arranging. So, you can see this is actually a lattice of a molecule, this is another lattice of a molecule and you can see that the molecules are arranging in a fourfold symmetric manner on the surface and you also see partly that this symmetry of the molecule is also kind of fourfold symmetry. So, that symmetry is basically implemented also in the final assembly of the molecular adlayer that you have formed on the graphite 0 0 0 1 surface. So, as we have already seen that the graphite 0 0 0 1 surface is actually a sixfold symmetric surface. So, that means the graphite is not really playing a role. If you recollect before if everything is controlled now by the molecule-molecule interaction, will look into that in greater detail. Then the graphite is not really playing a role and you directly see that the outcome or the adlayer itself is basically controlled by the molecule-molecule interaction. That is what the reason why you see this well-ordered pattern. And as I told you if you maintain all those critical parameters, you can cleanly form this film. And this is actually a single monolayer film and now you can deposit more and more molecule on top of it and then you can create a thick, a thin film ideally of many layers of molecules. So, that is what ah one can basically just do.

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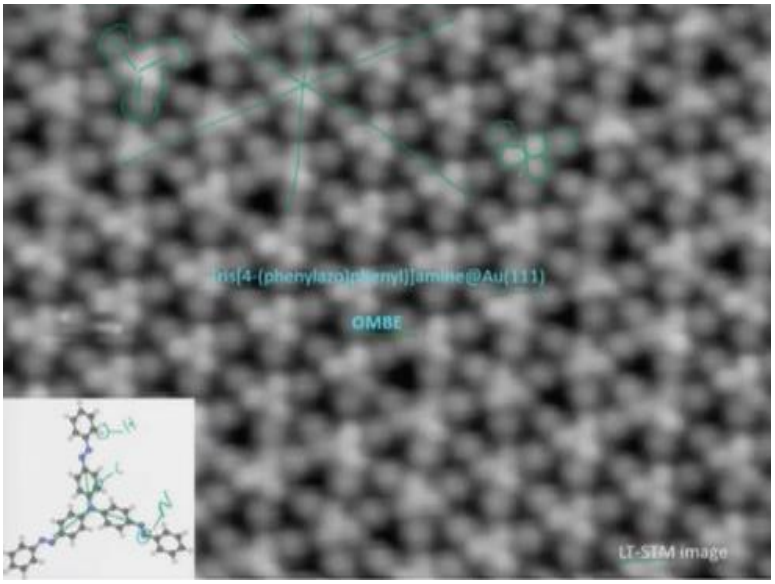

Now just to make you convince that we can do it with other molecules too. So, this is another molecule the name is given here and this is actually a threefold symmetric molecule. Again, here the blue is representing the Nitrogen and this is Carbon and here we have Hydrogen. So, that is a threefold symmetric molecule. It is unimportant what exactly the molecule is but what is important is that when you look at the molecular lattice. So, let me just show you that this is actually a single molecule that you can recognize and you also see that the molecular shape is also somewhat threefold symmetric. And also, the surface itself you can see this is one of the lattice of the molecular adlayer and this is another lattice of the molecular adlayer and this is another lattice of the molecular adlayer and you see that is actually kind of a sixfold symmetric surface a sixfold symmetric adlayer and this is of course done on gold 1 1 1 surface and using OMBD OMBE so that is the organic molecular beam epitaxy and the imaging is done at low temperature scanning tunnelling microscopy. That is also the reason why you can clearly see a lot of interesting details about the molecule itself so you can see here three lobes, here another three lobes and that basically form the molecule itself. So, we will definitely understand why we can image the molecule like that in the upcoming lectures when we look at scanning tunnelling micrography but here at the moment you have to keep it in mind that you can image a molecule at its molecular resolution and to understand the self assembly of the molecule. This is a practically very good technique the scanning tunnelling microscopy. But what you see is again uniform defect free nice adlayer of molecule on the gold 1 1 1 surface. This is again a single monolayer but you can deposit more molecule on top and you can create basically a thin film of such molecules.

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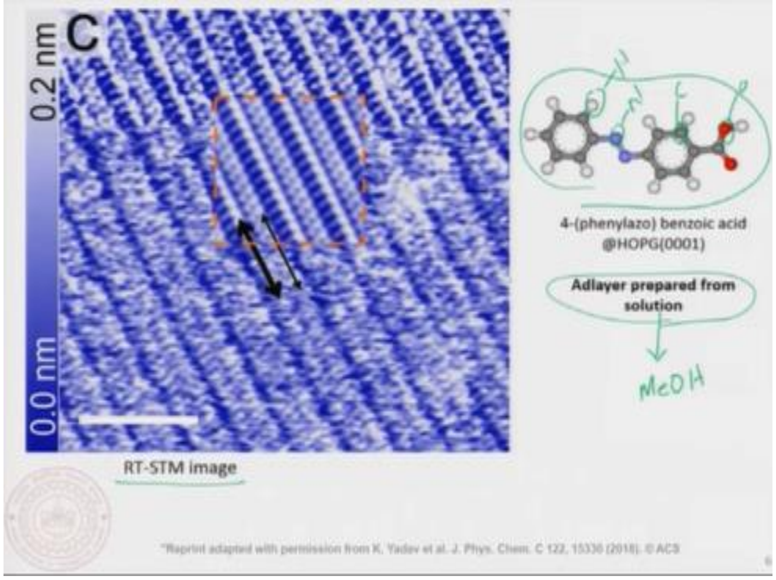

4-(phenylazo) benzoic acid
@HOPG(0001)

Adlayer prepared from solution

RT-STM image

*Reprint adapted with permission from K. Yadav et al. J. Phys. Chem. C 122, 15330 (2018). © ACS

Now I also want to show you the preparation performed in solution. So, the question of course comes actually whether we can only make things in an ultra-high vacuum chamber? No, this is absolutely not the case. We can also prepare beautiful thin films also from in ambient conditions and particularly this film what you are seeing here is actually an Azo-benzene molecule with a carboxylic group. Again, here we have the Nitrogen, we have the carbon, we have here hydrogen and we have here Oxygen. So, this is basically a COOH group, a carboxylic functional group. And the molecules are basically dissolved in a solution so the solution of methanol. So, you dissolve the molecules in methanol and then prepare a very dilute solution of molecule in methanol and then you simply drop cast on graphite 0 0 0 1 surface. Then what happens, you see that nicely they form a well ordered adlayer, but the resolution of the image is not that good quality as in the previous case. Because these images are actually performed using room temperature scanning tunnelling micrograph. There the quality is not as great as in the low temperature STM, because naturally there is this thermal noise existing in this case. Now nonetheless by doing some kind of averaging technique you can clearly see what is a molecule. So, you can see here molecules are looking like linear bright contrast. These are each of this molecule and you can also somewhat see the length of the molecule and with that you can basically understand how the molecules are arranging on the surface and things like that. But what I want to show you here is that you can also hear using the solution base preparation you can also form nicely single monolayer or depending on the concentration of the solution that you use for the solid for the preparation you can also basically just prepare layer by layer on top of each other and then you can basically for multi layer and you can form thin film nicely. Well, there is always a question of solvent getting trapped within this, because we do not really image the solvent molecule itself. So, there is always a negotiation about the quality of the films that are prepared from solutions and that is also the reason why in many a times people do prepare things by evaporation technique or in in high vacuum so that the purity of the film is very high. However, one can actually after preparing the film you can actually anneal the surface and then try to evaporate all the solvent, because you can see the solvent used here is methanol and you can actually evaporate the methanol from the film, if there is some traces present by annealing gently the surface after the deposition. So, certain parameters need to be actually controlled within this particular case and then you can also prepare high quality thin films of molecules using solution based preparation. Now you have already seen nice examples and also examples where we prepare things from inside ultra-high vacuum chamber or using solution preparation. Now the question basically is that what are the things which is controlling basically this kind of molecular adlayer? Can we use the same type of understanding as we have done in the case of atomic adsorbate on surface? Well, the answer is yes and no it is partly yes and no. The important thing here when it comes to molecule as you directly see in this particular molecule there is a shape associated to the molecule. There are not one atom present in the molecule, there are more atom present in the molecule therefore one need to consider all the interactions that are present in the molecule between different atoms of one molecule to the other and also each atom how they interact with the surface. So, these are the two important components so therefore generally we can call it everything is controlled by something known as molecule-molecule interaction and molecule-surface interaction. It is exactly the same as in the atomic adsorbate like atom-atom or adsorbate-adsorbate interaction and the adsorbate-surface interaction. Similarly, here it is basically the molecule molecule interaction and the molecule surface interaction. But there is much more complexity associated in this case which also having a certain shape and symmetry. So, therefore the molecule-molecule interaction is a bit more complex than just simply the adsorbate-adsorbate interaction because they were just two dots.

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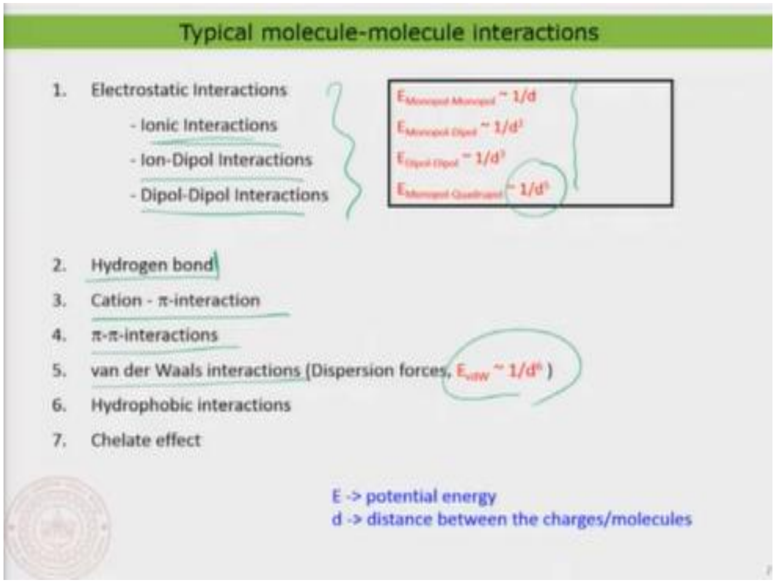

Typical molecule-molecule interactions

1. Electrostatic Interactions
   - Ionic Interactions
   - Ion-Dipol Interactions
   - Dipol-Dipol Interactions

$E_{Monopol-Monopol} \sim 1/d$

$E_{Monopol-Dipol} \sim 1/d^2$

$E_{Dipol-Dipol} \sim 1/d^3$

$E_{Monopol-Quadrupol} \sim 1/d^3$

2. Hydrogen bond
3. Cation - π-interaction
4. π-π-interactions
5. van der Waals interactions (Dispersion forces, $E_{vdW} \sim 1/d^6$)
6. Hydrophobic interactions
7. Chelate effect

E -> potential energy
d -> distance between the charges/molecules

Now let us have a look at the typical molecule-molecule interactions that leads to the formation of this very nice well-ordered patterns of molecules. Well, the major interactions are all non covalent in nature. So, that is the interesting and the first and foremost important aspect here. In the case of atomic adsorbates these interactions where in many cases or in most cases it was basically some kind of covalent or strong ionic interactions. But in this kind of molecular adsorbate the interactions are interactions could be ionic in nature but this is not necessarily like two point charges interacting to each other. So, this is basically some kind of an ion-dipole interaction or dipole-dipole interaction and so on because the molecule itself is actually much more complex from the point of view of its number of atoms present the type of atoms present and also the shape. So, typically you can call the first and foremost interaction is basically the electrostatic interaction. And the electrostatic interactions if you look at the potential energy of the interaction, they are strongly distance dependent and as you make the poles more complex that means dipole or monopole or quadrupole and so on as you make the poles more more complex. Then the distance dependent is becoming more complex. Therefore, everything is going to be controlled by the distance between the two molecules. Then you have another and very important interaction which is known as a hydrogen bonding interaction. And that hydrogen bonding interaction is a type of interaction that you would find in water molecule which is not really a covalent interaction, it is basically a non covalent interaction. However, the interactions are ionic in nature where you have a partially positively charged proton and a partially negative charge oxygen is basically interacting between the adjacent two molecules which is leading to the leading to a strong non covalent interaction namely known as hydrogen bonding interaction. Then you have like many several interactions which are known like cation pi interaction pi pi interactions or Van Der Waals interaction which is a ubiquitous interaction which is present everywhere which is actually having a strong distance dependence of d raised to – 6, and then you also have hydrophobic interaction, chelating effect many many such interesting interactions are actually present. That is typically what is going to control the molecule-molecule interaction. And that itself is the reason why it is not as clear and straightforward as in the atomic adsorbate here. So, one need to consider basically many important interactions that could be possibly happening between the molecule and molecule. Before you start basically depositing them or before you started basically preparing the molecular adlayer itself. So, that is something quite important.

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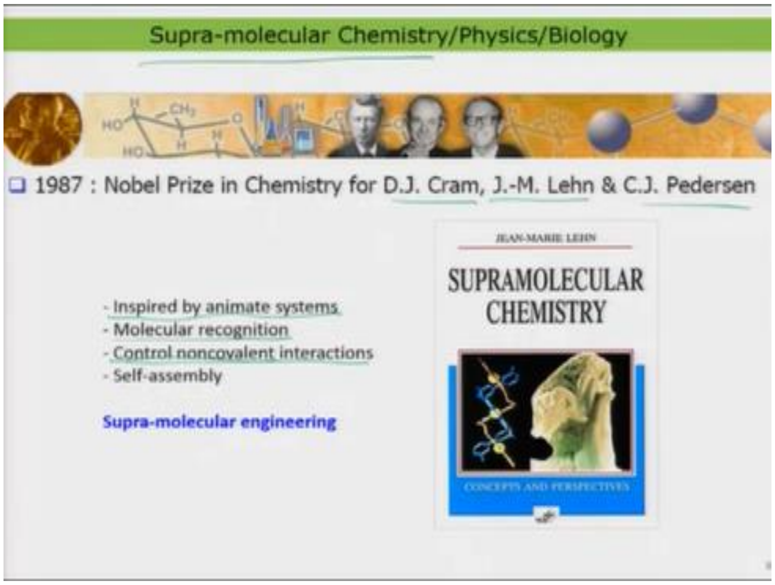

Supra-molecular Chemistry/Physics/Biology

❑ 1987 : Nobel Prize in Chemistry for D.J. Cram, J.-M. Lehn & C.J. Pedersen

- Inspired by animate systems
- Molecular recognition
- Control noncovalent interactions
- Self-assembly

Supra-molecular engineering

But some good message here is actually there was famous people like Cram, Jean Marie Lehn and Pedersen were actually three people who strategized this so called molecular self-assembly. By carefully controlling the interactions between the molecules and they actually just call it as supramolecular chemistry, supra molecular physics or supra molecular biology is already existing in nature and we can basically by looking at animate system. One can actually strategize this sort of interactions between the molecules and one can make use of this strategy to finally control the non-covalent interaction. So, that is the most important part. If you would simply take two molecules and put it on the surface, they would self-assemble you do not have a control so they would self-assemble that is itself the name suggest self-assembled and you do not have a control. So, therefore it is very important by learning it from the animate systems and using something known as molecular recognition and selectivity one can basically control the non-covalent interactions. And once you control the non-covalent interactions then you can call that we can do something known as supramolecular engineering which is like you take two molecules and actually make the molecule in such a way that they can actually assemble in the way we want. That is the most important part which is meaning that you have actually a greater control on the molecule-molecule interaction or you can basically trigger or externally control the molecule-molecule interaction. And that is what these three people have strategized and they won the Nobel prize in chemistry in 1987. One can have a look at this book which is written by one of the author one of the Nobel laureate himself. Jean-Marie Lehn and he has actually just written his book about supramolecular chemistry which is actually something which is beyond chemistry. In a normal chemistry lab what you do is you take two atoms, put them together and form a molecule. But now what we do is we take two molecules and we try to build structures out of molecule. Well nature has already done it for several millions of years and that itself is why we are all leaving because everything in our body is basically controlled by the supramolecular interaction. But now we actually just inspire by this animated system, do strategize different type of molecular interaction and then control this non covalent-interactions and finally we make something called a supramolecular engineering.

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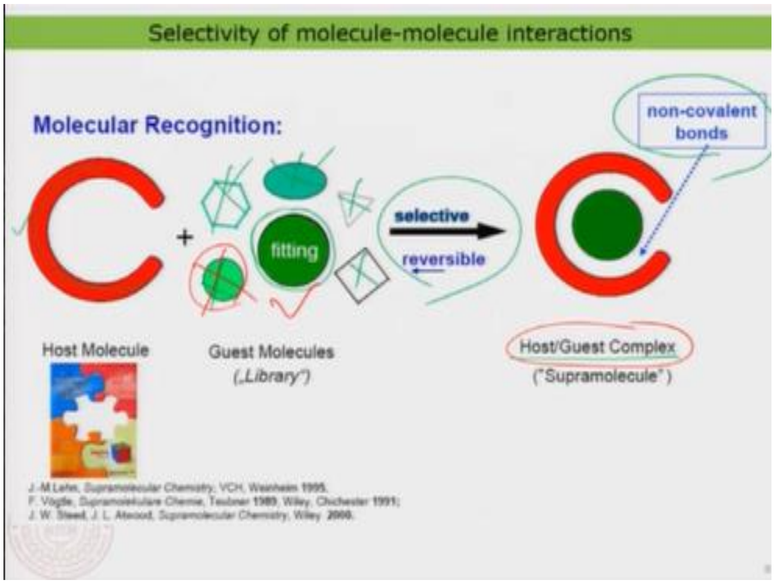

Selectivity of molecule-molecule interactions

Molecular Recognition:

J.-M. Lehn, Supramolecular Chemistry, VCH, Weinheim 1995.
F. Vögtle, Supramolekulare Chemie, Teubner 1989, Wiley, Chichester 1991;
J. W. Steed, J. L. Atwood, Supramolecular Chemistry, Wiley 2000.

Now what is the key of the supramolecular engineering? So, that is quite an important thing to consider here. Of course, everything is going to be non-covalent interactions here. So, the since it is non-covalent in nature, one can basically say that these interactions are dynamic in nature. If you would form basically a carbon carbon bond it is hard to break them you need to basically supply a lot of energy to break it or if you make a hydrogen molecule itself you need a lot of energy to break it, but in the non-covalent interactions based supra molecular structures everything is controlled basically by non-covalent interaction. So, if it is non-covalent interactions the interesting thing is that they are dynamic in nature and also, they are reversible in nature. So, that means if you form something you can simply unform the same thing. Now what you do is, you take a molecular species and you take another molecular species. But the most important thing the shape of each of this molecule must match in a way that you have something called a Host Guest complex or something like a key and lock method. Only a single key would fit inside a lock. Similarly, you can see if I would take a molecule which is having some shape like C then only this is the fitting molecule no other shape like this this shape or this shape or this shape or any of the shape is not going to fit. Although in this case it is actually or circular you can see since the size of the circle is small this is also not going to fit. So, the only thing which is fitting is actually the one which is having the right size and the shape. So, if they are fitting then they would selectively and that is what the selectivity. In fact, selectively come together and they form something known as this host guest complex. That is a simple strategy of supramolecular architecture or a supramolecular engineering and once you do that strategically you can in fact prepare nice self-assembly a controlled self-assembly you can do.

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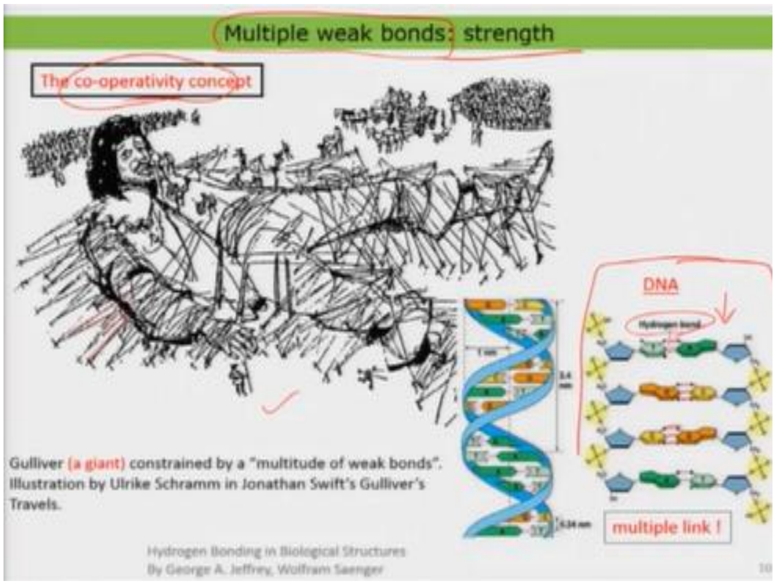

Multiple weak bonds: strength

The co-operativity concept

Gulliver (a giant) constrained by a "multitude of weak bonds". Illustration by Ulrike Schramm in Jonathan Swift's Gulliver's Travels.

Hydrogen Bonding in Biological Structures
By George A. Jeffrey, Wolfram Saenger

Now one more interesting thing is you would ask a question well if the interactions are weak non-covalent interactions. Then what actually makes them strong? Look at the molecule DNA that is a molecule of life. Even DNA the entire molecule is actually constructed by hydrogen bonding weak interaction, but the interesting aspect in this case is that since you have many many many interactions coming together. As you see here in a DNA molecule you have not just one interaction that is stabilizing a DNA molecule. You have millions and millions of weak interactions coming together then you see there will be a strength. So, it is simply an example here I have sited that is the Gulliver who is actually a traveller, this is actually from the book of Jonathan Swift's Gulliver’s travel and you can see basically that Gulliver is a giant who is actually constrained by many many threads. By adding many many threads over the giant, you can basically even constrain a giant. So, of course that is a strategy that nature uses nature basically just built all its important molecules or the molecule of life itself by connecting them through many many many tiny interactions. And now when you put all these interactions together you have something known as a co-operativity concept and then you can basically have a very strong interaction or you can basically build up the strength of the interactions. Now that is the key concept and now if you would basically just consider this that okay let us use many many weak interactions together and you also just have a clear understanding about what type of interactions to use and what type of shape of the molecule and what type of fitting need to be used then one can strategize nicely and then you can basically do the supramolecular engineering and that would give us a chance to basically build up or to form an adlayer of our choice or adlayer of our interest. And that is what is basically happening. Now we are going to do is we will basically look at a few examples and try to understand how people use these kinds of strategies in making the adlayer more conceptually correct or how do you conceptually realize this kind of adlayers on the surface of different type of materials.

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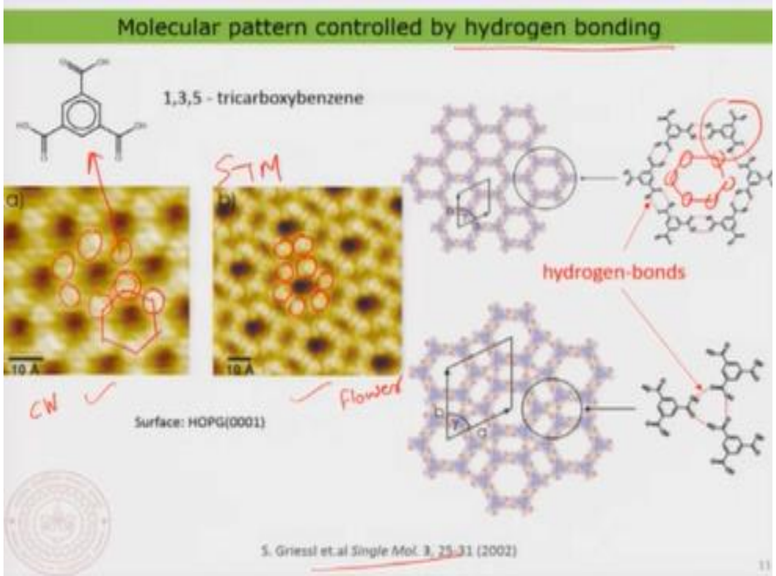

Molecular pattern controlled by hydrogen bonding

1,3,5 - tricarboxybenzene

Surface: HOPG(0001)

S. Griessl et.al *Single Mol.* 3, 25-31 (2002)

Well, let me just show you a few examples. So, this is actually an example where hydrogen bonding is what is used and the molecule is very simple. So, the molecule is 1,3,5-tricarboxylic benzenes so you have the benzene in the middle and then you have 3 COOH group. Now using the 3 COOH group the interesting aspect is that if you deposit this molecule on the surface. Now you can find there are two different type of patterns looking. So, this is quite interesting. In the case of atomic adsorbates whenever you deposit the atom at a given experimental condition you were typically forming one type of adlayer but of course you can control a little bit further using the using the coverage of the atoms that you deposit. But here the coverage is also the same. Nonetheless, they have actually just forming two or the STM image itself. So, the images are basically STM images. The STM images are revealing two different type of molecular contrast. What are they? So, ideally this is basically one molecule. So, these corners are basically just one molecule. So, you can say each of this corner is actually a TMA molecule but in the other case it is slightly different here I have TMA molecules, here I have TMA molecule. Now you would find that immediately the way the molecules in the second structure is actually much more different than the way the first structure looking like.

So, I am just going to call this structure as chicken wire structure and this structure as flower structure. These are the two different names. You can of course get more details in this paper please try to read this paper it is an open access paper so you can basically just get the details. And now you see depending on the way the molecules are arranging I am actually just getting a completely different type of assembly of the molecules. So, what is the key reason behind it? Of course, this is a model and this one is one of the hexagon as you would find here. So, this is basically one of the hexagon and each of this corner is basically a TMA molecule. So, similarly you can see I have a hexagon here and each of this corner is a TMA molecule. So, you would basically say that this TMA molecule correspond to a TMA molecule in the structure. Now what you find is that the TMA molecules are interacting through a hydrogen bonding between the carboxylic group, and the carboxylic group it has actually an OH group therefore you have a partially charged positive, partially charged hydrogen atom and a partially charged oxygen atom and they can basically form a hydrogen bonding. Now, the hydrogen bonding is basically there and what happens is that the molecules are now forming a hexagon by forming some kind of a dimer between the molecules. But in this case what you find is that the molecules are actually connecting together and forming some kind of a trimer. So, now the building block of this pattern the so called flower pattern is a trimer and the building block of the chicken wire pattern is a dimer. So, now the important thing here although both patterns are controlled by hydrogen-bonding depending on the type of interaction of the number of molecules interacting. You would find that they are basically just forming a different type of self-assembly. Well, with this I like to conclude this lecture and then we are going to start continuing understanding further examples in the next lecture. Thank you very much for your attention.