Chemistry and Physics of Surfaces and Interfaces
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Lecture - 25
Scanning Tunneling Spectroscopy: Applications-2

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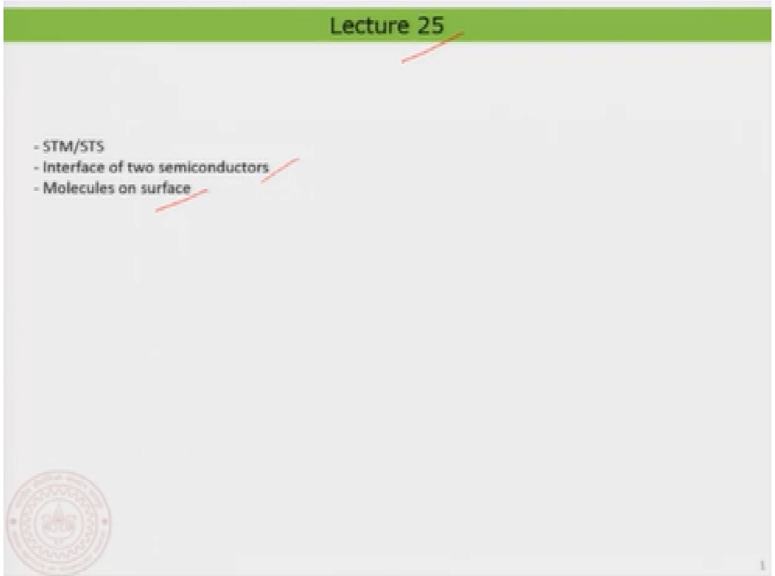

Lecture 25

- STM/STS
- Interface of two semiconductors
- Molecules on surface

Hello, everyone. Welcome back to lecture 25. And in this lecture, we will be continuing the application of scanning tunnelling microscopy. And we have also seen that scanning tunnelling spectroscopy is kind of part of the microscopy itself. And we look at a few more interesting interfaces and surfaces. And we will also basically while we learn the applicability of tunnelling microscopy and spectroscopy, we will also just look into different types of interfaces. So, first we will look into an interface of two semiconductor. Of course, it is a typical example I am showing of course, you can do this to any possible surfaces as I have already told you. And then we will also switch to something called molecules on surfaces. And particularly, I will be focusing in this section; big molecules on surfaces like phthalocyanine and pentacene and things like that if you have already seen in the previous lectures too. So, I will be looking at the spectroscopic aspect of the molecules on surface. So, that is what we will be doing in in this lecture.

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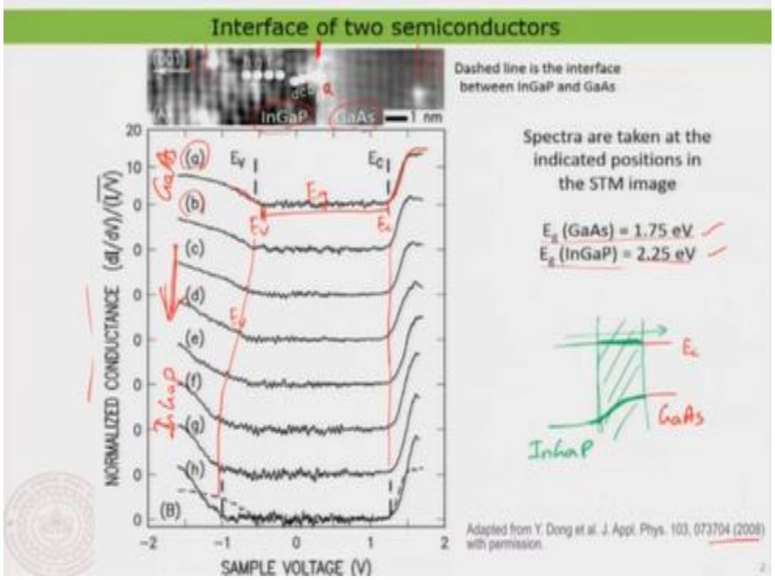

Interface of two semiconductors

Dashed line is the interface between InGaP and GaAs

Spectra are taken at the indicated positions in the STM image

E_g (GaAs) = 1.75 eV

E_g (InGaP) = 2.25 eV

Adapted from Y. Dong et al. J. Appl. Phys. 103, 073704 (2008) with permission

Let me just introduce this interface of two semiconductor. So, what do we have here? It is a typical example I told you. You can do this experiment on any type of interface that you can think of that is not an issue at all. But I have chosen a typical example. So, that we can kind of understand a few aspects of looking at the spectroscopy at interfaces itself. So, what you have here is a gallium arsenide and an indium gallium phosphate interface. Of course, this interface is prepared by an epitaxial method as we have discussed in the previous class. And then after making the interface what in this particular case what they have done is they have actually just taken a cross sectional profile through scanning tunnelling microscopy. So, what you are ideally seeing these bright lines here and nothing but the gallium arsenide lattice, and in this region what you are seeing is actually the indium gallium phosphate lattice. And exactly at this point here, I am just making it a little darker, so that point is actually the interface. How do we know it? Of course, that is also the question definitely because in STM, we know that we do not really distinguish the material but we distinguish definitely the using the spectroscopy we can kind of distinguish, because they are electronic properties slightly different. But let us just familiarize something here. The electronic gap so called gap between the conduction band and valence band for gallium arsenide is 1.75 and for the indium gallium phosphate it is 2.25 electron volts. So, you see there is about 500 milli electron volt difference between their bandgap. Now, the question comes of course, please believe me that these types of interfaces are the one that you are truly using in the modern semiconductor technologies. Semiconductor technologies, where you create many different possible interfaces; in order to come up with the application that you want to do. Well, that is not within our lecture, but I am just telling you that is basically always how you should see the interfaces at all. Now, you see that I have basically kind of a bandgap difference between the two which is about 500 milli electron volts. So, the question that you would ask; when I make an interface between these two materials, how do the electronic structure actually get connected at this interface? This is something quite important to understand because at the end, you want to use these interfaces in your application and you want to create basically a transistor or a diode or whatever you want to name it, you basically need to clearly understand these interfaces. So, that is where these kinds of spectroscopy is playing a major role. Of course, it is not very old literature 2008 now but people do it very routinely, particularly spectroscopy. So, now again, what I am showing you here are dI by dV that means a normalized differential conductance taken along different lattices from the interface. So, you can see here there are letters written as A, B, C, D, E, F, G, H, and this is basically representing the lattice lines at the interface. At the interface it is A then B, C, D, E, F, G, H is actually representing that you are actually just moving away from the interface particularly into the indium gallium phosphate direction. So, this A is exactly the interfacial layer and B, C, D are basically that you are going more into the indium gallium phosphate region. And this would be basically just our gallium arsenide. So, that is it; that is how it is. So, this is how the direction is going. Now, we know that for a semiconductor what do you expect, you would expect basically a band gap. So, that is something you can clearly see here. The onset on the positive side is actually representing the Ec which is basically the conduction band edge and here this is something like the valence band edge that is actually the negative side. So, you know the reason because we have the tunnelling of electrons is quite dependent on the direction of the voltage or the polarity of the voltage and therefore, we can basically measure the conduction band and valence band. Now you clearly see that region here, Eg is basically kind of flat, there is almost no density. So, it is zero that is actually the reason why we call it band gap. And then as soon as you hit this that density basically rises like that, and also on the other side, the density rises like that. So, no surprise, you would get a value which is somewhere around the value of 1.75 which is no surprise because that is what you would expect for the gallium arsenide. But now, when you start measuring the spectrum at each different lattices moving into the indium gallium phosphate what do you find is that the band gap is slowly widening. So, that is what you can basically see you can if I would draw basically a line like this, you can see slowly the band gap widens like that. But what is very very interesting to notice so this is particularly the valence band edge. So, the valence band edge is slowly moving or changing. But the conduction band edge is almost aligned throughout the interface. That is quite interesting. So, now if I would basically just try to depict the energy diagram of the interface of gallium arsenide and indium gallium phosphate then it would look like this that I have basically my first semiconductor that is the gallium arsenide and then I have my second semiconductor which is basically the indium gallium phosphate, and you know that this is actually the conduction band edge of my first semiconductor, and you clearly see in the spectra that the conduction band edge of both the semiconductor are somewhat aligned like this. So, they are not basically shifting with respect to each other. But for the valence band, you see that there is a clear change and that grows almost like this. That means the region which is basically this part is somehow kind of an interfacial region which has a quite a mixed character of both the in gallium arsenide and the indium gallium phosphate. I am thickening the line here. And once you reach here somewhere in here, you have basically the indium gallium phosphate like semiconductor. So, in between you can see the region is basically kind of mix of both. But what is quite interesting in this kind of spectroscopy is that you clearly now know what is aligned and where is the change occurring. This is quite important because when you want to construct an interface you want to basically also think about a device which is more hole conducting or electron conducting or whatsoever then this band alignment is quite an important aspect to consider for example. Now, for example if I want to transport basically like electrons in this, you can see that the bands are basically aligned. So, there is no almost no barrier for the electrons to basically move from one type of semiconductor to the other type of semiconductor. So, that is basically the point. So, here when I am talking about electron, it is basically the so called electrons that are present in the conduction band. So, like that we can think about it. So, it is quite important therefore, for designing a semiconductor device, it is quite important you understand the interfacial structure in an explicit manner and that can only be done using scanning tunnelling spectroscopy. So, this is quite important to notice here. Because with other technique you will also see that in the after couple of lectures, we will also study photoelectron spectroscopy that you will see that that we are going to do something called a bulk measurement or kind of an average measurement. But here, you are basically doing the spectrum, atom by atom or layer by layer in that precision. So, that is the interesting aspect about this spectroscopy that you are seeing. So, therefore you can understand the interfaces in a greater detail at the atomic level. As I told you, we can do the experiments on any sort of interface. You have already seen in the previous class also a couple of examples, but this is particularly a suitable example I found it in the semiconductor class. We are not limited to do the spectroscopy to only these kinds of materials, we can do it on many different materials. So, therefore please read more this literature so you would get a bit more idea and also you can develop your understanding on this topic a little bit further.

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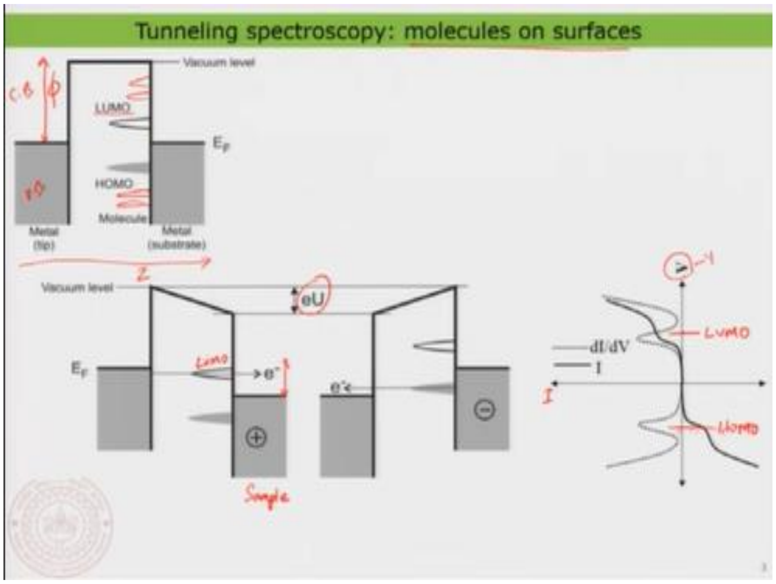

Tunneling spectroscopy: molecules on surfaces

Now I want to switch the tunnelling spectra to molecules on surface. Because we also have talked about molecular adsorbates, and in this context, I am going to talk about really the semi conducting type of molecule because those are the molecule which has been quite celebrated in the field of semiconducting thin film technology. So, therefore we are going to focus on those kinds of molecule particularly. So, we are going to look actually, how the spectroscopy of the molecules on surface looks like. I have here an energy diagram. So, this is again you have the metal so I have my valence band, a conduction band and also you remember that this is actually nothing but the work function of the tip and the same also for your material. Now assume that I have again a metallic substrate and reasonably taking a kind of substance or substrate and metallic tip. Both are having kind of constant density near the Fermi energy is what we are choosing. Now on that particular surface, we are actually just depositing the molecules. So, now the question is when you deposit molecules on the surface, how does the electronic structure of the molecule look like? Well, you know that for molecule they are having discrete electronic levels and not the bands like we have seen in the in metal or in a semiconductor. They have basically discrete energy levels and these are typically known as molecular orbitals. They have an origin from the atoms they are actually forming. So, of course here I am only depicting the two frontier orbitals which is namely the highest occupied molecular orbital and this is basically the lowest unoccupied molecular orbital. And that is also the reason why you see the when you deposit the molecule on a surface; the filled levels, the filled molecular orbitals are actually going to be below the Fermi level of the surface and all the unfilled levels are going to be about the Fermi level. So, that is how it is going to be because also that ensures the charge neutrality of the surface when you put molecules on surface and everything is actually again controlled by the Fermi Dirac statistics. I am only showing here depicting the two frontier molecular orbitals. But of course, you are not limited, you can basically just think about having additional electronic levels like this. We can have many like that. But that depends quite a lot on the molecule. So, normally for a molecule, you would expect that they are just kind of a line that means just a discrete particular energy is that a molecular orbital is. But I have actually just made it a little bit broader and because when the molecule interact with the surface the certain kind of in broadening for this particular state due to the interaction, and then also one can always think about some kind of a thermal broadening due to the fact that we are basically just measuring the spectroscopy. So, in spectroscopy, you can never ever get energy as a delta function because always you have the association of the Heisenberg's Uncertainty Principle. So, therefore always you have something called a lifetime broadening of each stage. So, that is the reason why I have basically made them a little broader. What you would expect is basically these kinds of discrete levels. Now you see that in this is basically the space so this you could call it a Z or something like that. And there you can see like you have the metallic tip and you have the surface and I have the molecule sticking on top of the surface. So, that is basically the thing. Now, I am going to basically, so at normal condition that means when I am applying no bias voltage what happens is that there is no net tunnelling current that we can measure. So, now what you should do? You should do basically just apply a bias. So, I can basically now put the sample or the so called molecule adsorbed on the surface, I am basically just putting. So, this is basically my sample and putting the sample on a positive bias here. So, as we have already discussed we can basically half the alignment in this fashion that means the substrate Fermi level would be lower compared to the metal. Now the interesting aspect is the following. It is somewhat similar like we have seen in the case of those surface states you see that the LUMO of the molecule is now in resonance with the tunnelling electrons. And therefore, whenever the applied voltage so that means the eU is actually matching with that of the energy of this particular distance, that is the energy between the Fermi level of the metal and actually the LUMO of the molecule. If that is actually matching then the; electrons from the tip will tunnel through the molecular orbital through the unfilled molecular orbital to the empty states of the metal. And now when you apply a negative bias on the sample then the opposite happens that electrons would basically tunnel through the HOMO of the molecule to the unfilled level of the tip. So, that basically is again always the case. But now the interesting thing is actually that the tunnelling electron is coming in resonance with the energy levels of the molecule. So, that means by varying the voltage from positive to negative bias, I should be able to detect these kinds of resonances that are coming additionally from the molecule. Of course, you have always the background tunnelling from the metal because the metal also will contribute to the current, but that is constant. So, you will not basically see the change. But you can see the change from the molecular orbitals. So, let us have a look at the current versus voltage. So, for an interesting reason I have plotted here the voltage in the y axis places, recollect it is just for the representation and then I have current basically on the x axis. So, this is basically the current on the x axis here and then here I have the voltage on the y axis basically. Now what do you see is that when I am applying the positive bias and the negative bias at some particular energy, I do see that there is actually a small increase in the current and that current is exactly due to the fact that you have tunnelling through the molecular orbitals. So, you can of course take the first derivative of that and that is what we have also done previously which is known as the tunnelling spectroscopy or tunnelling spectrum. And now you clearly see the peak position are actually representing the LUMO of the molecule and the HOMO of the molecule. That is quite a representation of the interfacial electronic structure of the molecule-surface interface. So, that is quite spectacular. In principle, therefore using tunnelling spectroscopy one can clearly understand or one can experimentally find out the HOMO-LUMO gap. And not just the HOMO-LUMO gap, of course you can also find out the relative position of the LUMO with respect to the Fermi energy and the relative position of HOMO with respect to the Fermi energy and so on.

I will discuss that in a minute, because there is also some interesting aspect to talk about that at the interface. Because what I am showing you here is kind of an ideal situation where the molecule is only weakly interacting. Weak interaction means they are not really true electronic coupling between the molecule and the surface. We will come back to that after a few slides and then we try to understand that. But now, we are going to do is we are going to look a few examples to understand the scenario better.

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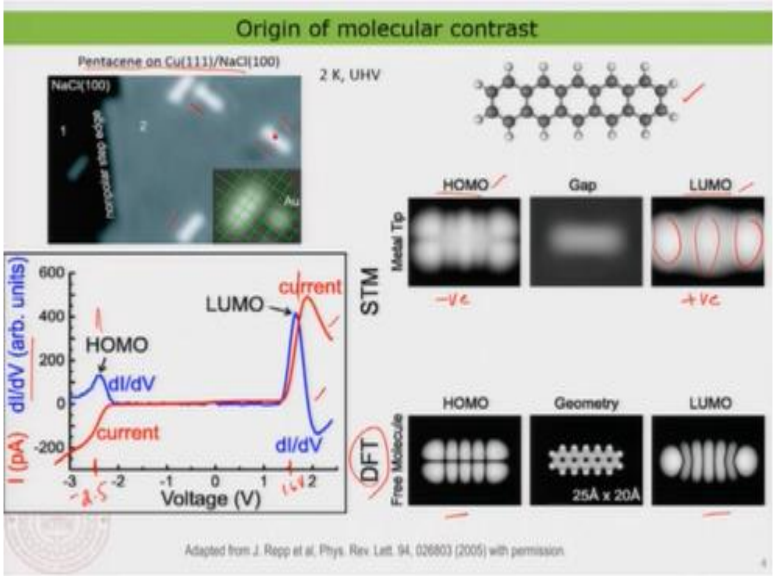

Origin of molecular contrast

Adapted from J. Repp et al. Phys. Rev. Lett. 94, 026803 (2005) with permission.

So, I have here again a pentacene on copper 111 surface. So, I have already shown you this molecule. This is actually a molecule which is quite celebrated within semiconductor industry thin film industry, and what they have done the experiment is basically that you have deposited the pentacene molecule isolated at a very very low dosage. That means the coverage is very less, you can already identify here are some pentacene molecules in the STM contrast but for an interesting reason, they have actually just deposited a made a single layer of sodium chloride on the copper 111 surface and then put the molecule on top of it. I will also discuss why they have done that in like that. But let us just only concentrate right now on the molecule. So, now I can see basically the molecule here. It is nothing spectacular, because you would expect basically it is a long molecule. So, I would expect basically that I would see something kind of a long electron density that actually is coming from the molecule. So, no surprise good. Now, if you now record the spectrum so, the interesting thing you please notice that I can basically just lower the tip just stay on top of the molecule and I can run the voltage. So, remember that we are always doing a single molecule spectroscopy that is very important, that is extremely important. When you do that, you measure the current that is nice like we expected. So, there is an increase in the current and then for a region for quite some time there is no current that is basically due to the fact that there is no electronic state from the molecule at that region. And then you have again an increase in the current and that actually is due to the fact that you have the unfilled orbital. Now, in the blue spectrum, the blue is actually nothing but the dI/dV. So, again kind of an arbitrary unit, at the unit does not matter at this point. When now you see like when you do the first derivative of the current, you can clearly see two peaks here. And those peaks are nothing but the HOMO and the LUMO of the molecule. And that is exactly what we talked about. So, we can basically see it clearly the HOMO and LUMO of the molecule. So, that is beautiful. Now, something interesting you can also do is that I told you, we are basically just applying a bias while we are stabilizing the tip or while we are imaging the tip. Now I can also decide to image the molecule at a negative voltage, let us say likes here somewhere 2.5, minus 2.5 is actually the position of the HOMO and somewhere here about 1.6 volt is basically the position of the LUMO. So, I can also now decide to image the molecule at these voltages is negative 2.5 and positive 1.6 volts. What happens there? That is the interesting question. And something spectacular happens that the contrast of the molecule is looking quite different when I do it at negative voltage and at positive voltage. That is quite interesting. Well, what you would expect is that at negative voltage, I should be basically tunnelling through the HOMO of the molecule and a positive bias and basically tunnelling through the LUMO of the molecule. So, that also means that the electron density that you basically just feel or measure at this particular voltage should also have a control of the molecular orbital that is exactly the HOMO at negative bias and LUMO at positive bias. That is very interesting. This is also some kind of a theoretical calculation; a DFT calculation to check what is the electron density corresponding to HOMO. And you can see clearly that they are actually very well matching. So, this has actually about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 bright protrusions and you can see clearly that that is also something you can reproduce in the STM image, particularly at the negative voltage. But the positive bias of course, it is not that clear. But you still see that there is some kind of a contrast you can visualize here that is somewhat matching with that of the theoretical calculation. So, ideally, what you are measuring if you are selectively measuring at a given voltage is nothing. But the electron density corresponding to that particular electronic state, this is quite important. So, you are ideally imaging the molecular orbital itself. So, that is the interesting aspect about the imaging at different voltage of this kind of molecule. So, you can of course, do that for a few more molecules. I will show you a few interesting example to clearly convince you what is going on.

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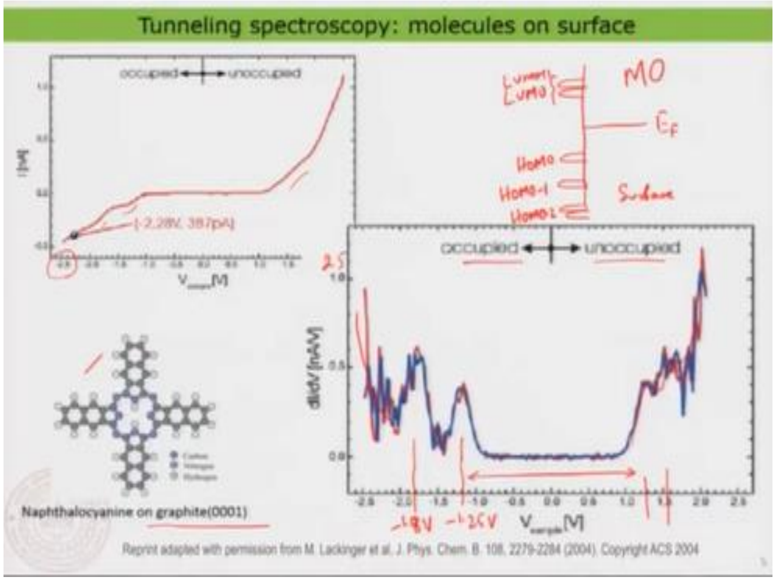

Tunneling spectroscopy: molecules on surface

Naphthalocyanine on graphite(0001)

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So, now this molecule is also something that we have talked about. This is a kind of phthalocyanine molecule it is also a celebrated molecule in semiconducting thin film technology. So, this molecule is in this case, adsorbed on a graphite 0 0 0 1 surface and now you measure the current versus voltage. So, you can see it is measured from 2.5 volt to about 2.5 volt plus or minus and then you basically see that there are nice steps that you can see in the tunnelling spectrum in the current. And if you take the first derivative of this that is what is more important. The first derivative basically of course, the negative side is basically representing the occupied state and the positive side is basically representing the unoccupied state. And now you clearly see that there is a region in inside which is some kind of region were having no density of state. And then suddenly around you can see about minus 1.25 volt, I have a resonance and again when I go here somewhere around 1.7 or 1.8 volt, I have resonance, and then if I go here, there are the densities basically increasing, and on the positive side, it is more interesting because you do not really see discrete levels there but you can see the density is somewhat changing like this. So, that means you might be having electronic state that are very close to each other. So, ideally this represents that if I would like to depict this kind of an interface, imagine that I have the graphite that is kind of a metal. So, I have the surface, this is the Fermi level of the surface and now I can see clearly that the molecular LUMO's are so close to each other and the HOMO is actually quite discrete and then the HOMO - 1 is there, then I have many states that are here. So, this is basically the HOMO, this is the HOMO -1 and then I have here HOMO - 2 and so on. And here I have basically LUMO and LUMO + 1 and so on. So, you can basically now count the electronic state and then you can also see their relative position with respect to Fermi energy and also with respect to each other. So, ideally what you have now constructed is nothing but the MO diagram, the MO diagram of this molecule. So, this is beautiful. So, this is quite spectacular about this kind of spectroscopy. And now believe me that we have done it actually on a single molecule. So, this is my own experiment, you can read more details in this paper and we can basically measure the electronic structure of a single molecule in greater detail. So, this is quite important. And also, I just want to mention one quick important point here, you would notice most of the time that we typically do measure electronic structure around the Fermi level to do something like plus or minus 3 electron volts and not more than that because beyond that there are certain difficulties would also appear in tunnelling spectroscopy due to some other effects like filled emissions and things like that. So, therefore typically we do not do experiments beyond let us say like 4 or 5 volts on both side of the of the Fermi level. But nonetheless this is the most important region, because if you want to understand the electronic structure of the valence band. It is basically this region that you are looking at the valence band and the conduction band.

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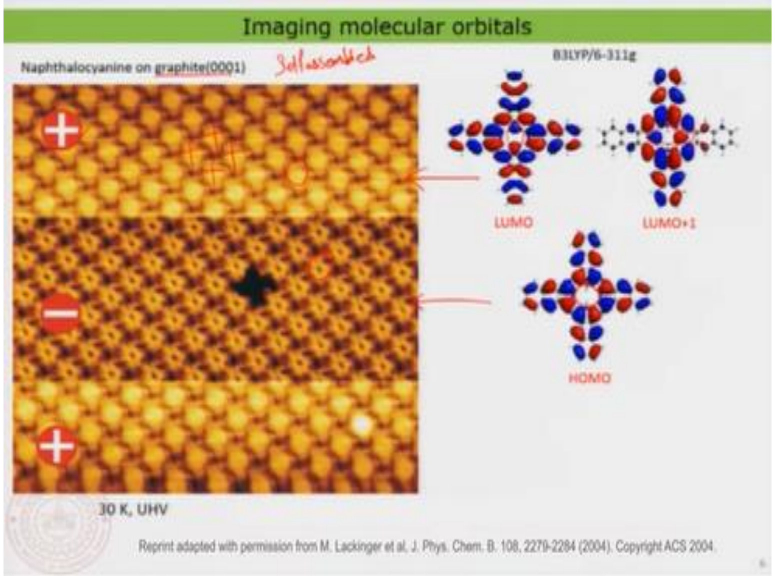

Imaging molecular orbitals

Naphthalocyanine on graphite(0001)

Self assembled

30 K, UHV

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Now let me also just show you the self assembly. So, this what you are seeing is a self assembled layer of the molecule, self assembled layer of the molecule again on graphite. So, this is again that Naphthalocyanine the same molecule as you have seen in the previous slide. And now they assemble and they actually nicely self assemble like this. You can see this is something that we have expected. So, they assembled nicely. But now, if you image them at positive and negative bias you see clearly the contrast of the molecule is different. This is a single molecule and this is a single molecule, you can see clearly the contrast is different and that difference in the contrast is again due to the fact that a positive bias you are basically imaging the unfilled orbitals and in the negative bias, you are basically just imaging the filled orbital. So, this is a clear point. So, because of this nice difference in the electron density. You can clearly see here in the HOMO, there is a hole in the middle and that is exactly what you see also in the image. So, for the other case, you can see there is an electron density that is protruding here, and you also have seen that the LUMO and LUMO + 1 are quite close to each other and therefore they basically just both appear in the image and you can clearly see that in the contrast. So, this is about imaging the molecule orbital and also you can basically just image the electronic structure in greater detail. So, that is about it. And then in the next class, we will look into a few more examples about molecules and then we will actually see additional aspects about the tunnelling microscopy itself. Thank you very much for your attention.