Chemistry and Physics of Surfaces and Interfaces

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Lecture - 28
Inelastic Tunneling Spectroscopy

Hello everyone, welcome back to lecture number 28. And in this lecture, today, we will be looking at inelastic tunneling spectroscopy a bit more. We have already seen how it works and I will show you a few more example and then to see the additional scope of such an inelastic tunneling spectroscopy.

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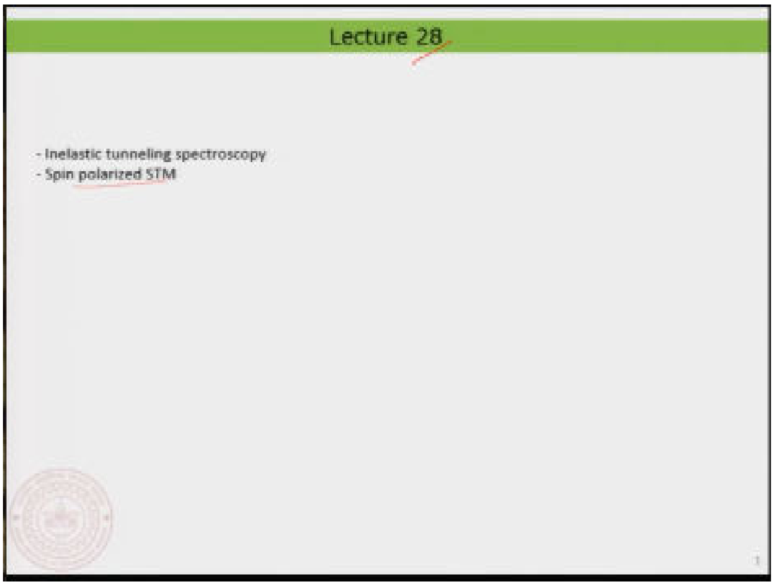

Lecture 28

- Inelastic tunneling spectroscopy
- Spin polarized STM

And then we will move on to something called spin polarized scanning tunneling microscopy. So, with that kind of technology, with that kind of technique, we can actually also resolve magnetic property of surfaces. And particularly, if you are interested in looking at islands that are or materials that are magnetic in nature, you can basically detect the magnetic density of states. So, that is something we will also have a look in that. So, with that, I would try to conclude the tunneling microscopy part.

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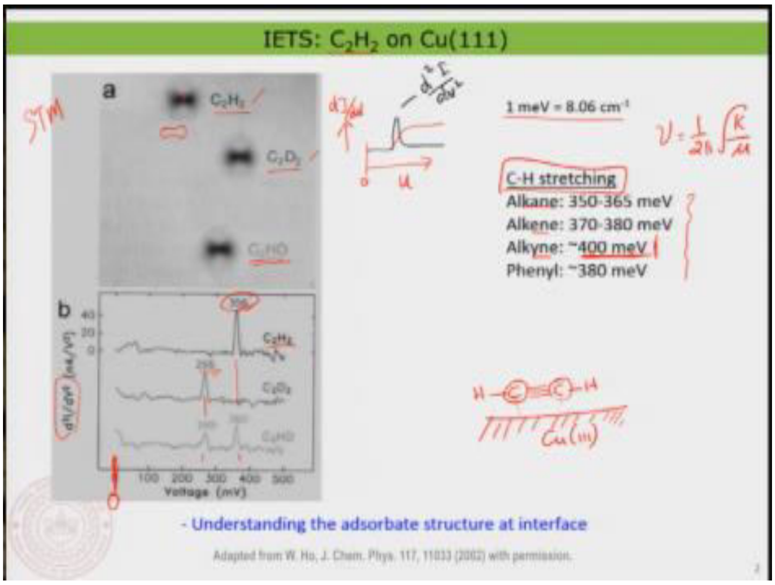

IETS: C_2H_2 on Cu(111)

1 meV = 8.06 cm^{-1}

C-H stretching
Alkane: 350-365 meV
Alkene: 370-380 meV
Alkyne: ~400 meV
Phenyl: ~380 meV

- Understanding the adsorbate structure at interface

Adapted from W. Ho, J. Chem. Phys. 117, 11033 (2002) with permission.

And let me just show you an image of, again, a scanning tunneling micrograph, an image, an STM image of a molecule that is adsorbed on copper 111 surface, so, the molecule is nothing but ethylene. So, the interesting thing is that in this image, you already see that there is some kind of a double or a dumbbell like kind of structure, which you can see on the surface, so, it is somewhat looking like this. So, it gives you a feeling that it may be like something like, you know, 2 carbon attached to each other and something like that. but it is not very obvious, what it is really is that and then also, a few additional images are also shown in the same surface, you see, what is also shown is actually kind of an isotope of the hydrogen with deuterium and then make a C 2 D 2 and a C 2 H D. So, this is something like a mixture of this ethylene and deteriorated ethylene is basically deposited on the copper 111 surface. Of course, you see nicely, the shape is kind of all right, so, this could be like a linear molecule that is fine. But, on the other hand, you are unable to basically detect, what is really the molecule? Is it C 2 H 2? Or is it C 2 D 2? Or is it C 2 H D? That is actually a question.

So, how can we actually just do this to understand and kind of do a chemical fingerprinting of the molecule? So, STM since, we are basically making images and also looking at the electron density of the surface or the adsorbate molecule whatsoever, it is hard to define clearly a fingerprint unlike in spectroscopy. In spectroscopy, for example, every molecule will have a certain fingerprint to say, that is actually that type of a molecule. For example, with a vibrational spectroscopy, you can clearly identify these 3 species nicely. So, that is possible. So, that is where this kind of additional possibility like the inelastic tunneling spectroscopy is going to play an interesting role. That is something, we will basically just see in this. So, now what I am going to do is basically going to measure and IETS, so that is actually the inelastic tunneling spectroscopy on all this molecule separately, because we can do that. That is the interesting thing about tunneling microscope, you can place your tip just on top of the molecule and then you can basically measure the tunneling spectrum but of course, here what we are measuring is the inelastic tunneling spectroscopy. So, of course, you do not need to do anything additional. It is that in the normal tunneling spectroscopy, you would directly find the signature for the inelastic tunneling itself. So, now, what is the tunneling spectrum looks like? We will just notice that here on the y- axis, I have something like the second derivative of current with respect to voltage. because you remember in the previous class, when I was discussing; I told you like if you have an inelastic process that is happening and if there is some kind of an excitation or if the energy is given for some kind of an inelastic process at the interface. Then in the tunneling current, you should be basically seeing some kind of a step like function. This is the current and this is the voltage. This is the voltage. So, you should be normally seeing something like a symmetric step like feature with respect to 0. So, this is actually the zero. I am sorry for that, this is basically wrong. So, I have here the voltage and here the current. So, at with respect to 0 voltage, you would say basically a step kind of feature. But of course, it is a little bit hard to distinguish from the step. Therefore, one can also do something like the first derivative of this itself. So, let me just write. This is basically dI by dV, so, that is what you see. Now, I can take now, the first derivative of that and the first derivative of this would give me something like a peak function. So, that is just the derivative of the step.

So, now, in the black one is nothing but the d square I by dV square, so, that is actually the second derivative of the current with respect to the voltage. So, that is also something very commonly, you would find in the IETS, the inelastic tunneling spectroscopy, because that is easy to distinguish the step rather than just looking at the first derivative. So, now, let us look at the data itself. So, something interesting, you can see that of course, you are actually now plotting only one side of it, so, that is where you have the zero voltage and you are only plotting one half of the voltage. So, because the other half will also be symmetry. So, therefore, it is not necessary. So, now, what is done in this particular paper is that they have performed a tunneling spectroscopy by placing the tip on all the 3 species and then have looked at the spectrum for example. And now, you see something quite spectacular, something quite interesting that there is a peak and the peak position is basically changing for 2 species. And then for one species, there are 2 peaks and the 2 peaks are actually corresponding. So, this is actually corresponding and this is also corresponding. So, now, with this kind of correspondence, people could actually just kind of think about what is actually going on at the interface of. What is this inelastic process that you are actually just looking at? It is nothing but the C-H stretching of the molecule. So, we are exactly looking at the C-H stretching of the molecule. Now, it makes sense C 2 H 2, I would expect one type of stretching frequencies. So, that is basically what you are seeing at 358 milli-electron volt, you can also convert the milli electron volt to centimeter inverse, because also for vibrational spectroscopy, centimeter inverse is more common. So, you see like 1 milli-electron volt is corresponding to 8.96. So, that also you can notice, it is basically something around 358 milli electron volt for one molecule. And for another molecule, you can see clearly that there is another peak, there is only one single peak, but that peak is actually shifted a much lower value of energy so, to about 266 milli electron volt. And for another species, you see that there are 2 peaks that are actually at 360 and at 369. So, this is quite interesting.

So, now, if I would call that this molecule to be C 2 H 2, I would expect 1 C-H frequency and for this molecule also, I would expect basically 1 C-H frequency and for this molecule, I would expect 2 vibrational excitations, because you have the C-H vibration and also the C-D vibration. Now, the question is: why are they different? This is quite simple to understand. Because, you already know that when you have the C-D bond, where you have deuterium being heavier and you can basically just plug that into the frequency equation. So, that is like 1 by 2 pi root of K by mu, where K is actually the force constant. And mu is basically the relative mass and that mu contains basically the mass and now, when 2 heavier atoms are actually vibrating, their vibrational frequency is naturally lower. That is exactly the reason why you would see that the peak is shifted to a lower energy. So, that actually clarifies that what you are seeing is that these 2 are the 2 different species like C 2 H 2 and C 2 D 2. But now, of course, for the C 2 HD, you would definitely expect 2 resonances. Those resonances are actually at 2 different frequencies. And that is also matching very well with the other molecules. So, now, you see, I have a chemical fingerprinting technique. Using the spectroscopy, I can clearly chemical fingerprint, what is the molecular species that is adsorbed on the surface. Of course, it is a tedious process. Of course, the spectroscopy itself is not as simple as you would imagine, you need to have actually a very good signal to noise ratio. So, that also means that this spectroscopy is much more applicable or technically working at the lower temperature that means you need to have like an ultra-high vacuum system and a low temperature system to basically just get this experiment that.

In the room temperature, it is not that easy to find out this signal because I told you always that the amount of the tunneling, inelastic tunneling process is actually just very, very low. It is actually lower than 1%, for example and because of this, you would clearly find that this is technically very difficult to do, but nonetheless, if you can do, you see clearly that there is this nice fingerprinting of the molecule. Now, there is also something interesting you can find, I have here a typical chart of the alkane C-H stretching. So, for different kinds of hydrocarbon, I have given for alkane, alkene and alkyne. And what we should have been expecting is basically an energy something in the order of 400 milli electron volt, because you have the C 2 H 2.

So, your ethylene is actually also expected to give a resonance at about 400 milli electron volt, but what is very striking; your ethylene is actually having a C-H stretching at a much lower energy. So, the question is why is this? Is there something interesting? We can learn from this. That is quite something interesting. We can learn from this, that the downshifting of the energy is clearly indicating that something is wrong with the molecule itself. something is actually just different with the C-C-C and also the C-H bond itself. What should be different? It is a copper 111 surface. As we have also discussed in the previous classes, when molecule adsorb on surface, they also kind of interact with the surface. It can actually be even a chemisorption which would even form a truly a bond.

So, let us just assume that you have your copper 111 surface and your alkene is basically just sitting on top of this surface. So, I have basically a C triple bond C-C-H. So, this is basically what I would expect the molecule to be, but now, the interesting thing is that the copper surface and the alkyne molecule is basically just interacting strongly with respect to each other. So, then what would happen is that there is actually a strong interaction between the carbon and the surface. Now, what would happen is now; is something quite interesting. Now, we can see that the carbon atoms are actually just becoming a little heavier than the previous case, because the carbon atoms are now connected to larger surface atoms. So, that actually makes them a little bit heavier to oscillate. So, that also makes actually the C-H bond stretching frequency to be lowered by a certain magnitude. So, in fact, the magnitude of the shift with respect to an expectation value; so this is about 400 milli electron volts, you can see about 40 milli electron volt downshift is there, which is actually something like corresponding to at least in the order of 50 to 60 milli electron volts. So, that is quite a lot, sorry, centimeter inverse. So, that is actually quite a lot. So, this actually indicating that that there is a strong interaction between the molecule and the surface. So, that is something what I wanted to predict here basically, by looking at this so called shift in the vibrational frequency of the C-H bond. You can basically kind of predict what is going on at the interface or how strongly molecules are binding to the surface and so on. So, therefore, this kind of technique is quite unique and quite strong in understanding and chemical bending, not just the molecule; it is also the molecule surface interface. So, that is the power of this technique.

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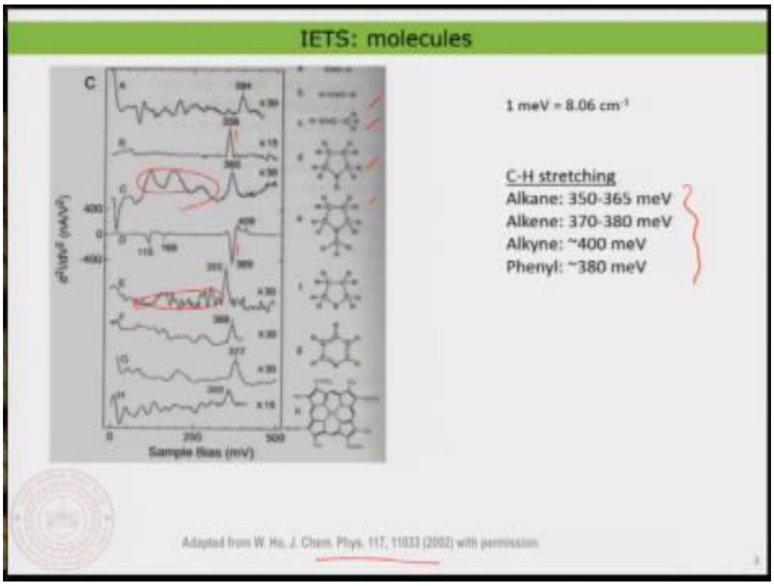

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Adapted from W. Ho, J. Chem. Phys. 117, 11033 (2002) with permission.

Well, we can do it actually on many different type of molecule. It is not just that we can do it only on small molecule, you see a variety of molecule has been tried. And this is the same literature, you can have a look at it for more detail and you can basically just always can the C-H hydrogen stretching frequency and you clearly see that the C-H hydrogen stretching frequency is different. And by comparing it with a standard expectation value, you can basically see how strongly these molecules are kind of interacting with the surface and so on. So, this is therefore quite striking. But you also see that the background here is not so good. So, you see here, the background is not very good. So, this is also something what I was telling you basically that there is a very high, very high chance of getting a lot of noise in this kind of spectroscopy, because you are actually just looking at a very, very weak signal. So, you are taking the second derivative of the current with respect to the voltage that also makes actually even small changes in the current could actually just get enhanced for example. So, therefore, there is typically some problems that is also associated with this kind of technique, but nonetheless if your instrument is actually working at low temperature and also in ultra-high vacuum, you can basically do this kind of measurement. So, this is quite efficient in that way. Well, that is the inelastic tunneling spectroscopy that I want to discuss, but of course, you are one free to choose actually any type of molecule that you think about and one can basically just understand what is going on at the interface. Good.

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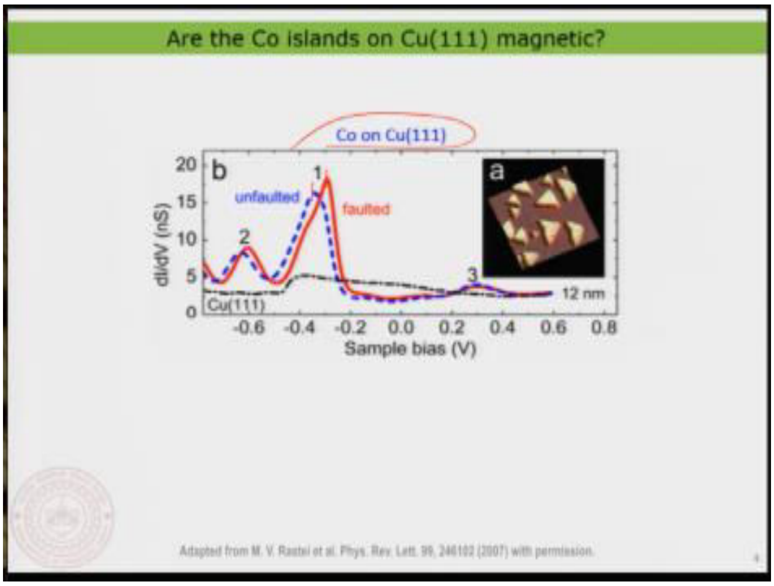

Are the Co islands on Cu(111) magnetic?

Adapted from M. V. Rastei et al. Phys. Rev. Lett. 99, 246102 (2007) with permission.

Now, I want to switch slightly the topic. So, like we will come to something like last part of the scanning tunneling microscopy. So, what I want to ask you a question here is actually that this kind of island that we have already looked at, so, you remember, like we discussed this particular type of material in greater detail at the microscopic level and also, at the electronic structure level. So, the cobalt islands on copper 111 surface, I have just taken this as a simple example or a typical example, but you can definitely do this experiment on anything, any kind of combination of interface, but now, the question is like, can we basically check whether these cobalt islands on the copper 111 surface is magnetic,? Is it possible? Yes, the answer is yes, we can do that. And that is what we want to basically do it.

So, you remember, you just recollect that there is this strong resonance that is actually coming from the D band of the cobalt and they also are slightly shifted with respect to each other based on whether you have a folded or an unfolded type of island on the copper 111 surface. So, that is something, you please keep it in mind.

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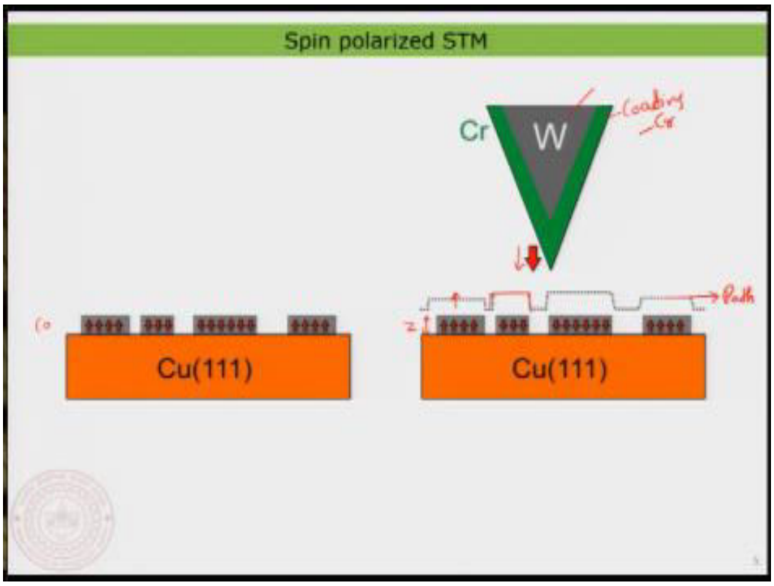

Spin polarized STM

Now, the question is, if you would basically have an island like this, so, this is our cobalt island and if the cobalt islands are having different magnetization so, let us say like some of the islands are having a magnetization in the upward direction and the other having in the downward direction, these directions are quite relative. But if you have like with respect to all the cobalt islands, if they have different magnetization, we should basically be able to detect that magnetization if we use a magnetic tip, so, that is the only difference. So, this is the tip, the tungsten tip that we were using previously. Now, what I have done is; I have made a coating of chromium on top of the tungsten tip. So, this is of course, something you can again do using electron beam epitaxy so that the molecular beam epitaxy using electron beam that you remember, we have actually discussed and using that technique, we can basically deposit chromium on tungsten and you can make a magnetic tip. Now, you see, the tip itself is magnetic, it has a certain magnetic orientation. So, you can see this and now if you take this tip move across the island and now depending on the alignment of the magnetization of the tip and the surface, you can basically get a slightly different topography. For example, here you see that the topography is slightly higher when the magnetization of the tip and the surface is actually pointing in the same direction or when they are matching.

When the magnetization is in the opposite direction so, for example, here you see this is in the opposite direction, then you see that the topography is basically low, because this is actually the path along which the tip is moving. So, this is the path along with the tip is moving. And now, you see depending on the magnetization although the same height for the island, so that is also something you can basically notice here. All the islands are having the same height; z is the same, but depending on the magnetization, the tip is basically retracting or coming closer and so on.So, therefore, you have a difference in the typography itself is something that you can notice. So, that is quite striking. So, we can basically now measure the magnetization of the cobalt of the island. Very nice.

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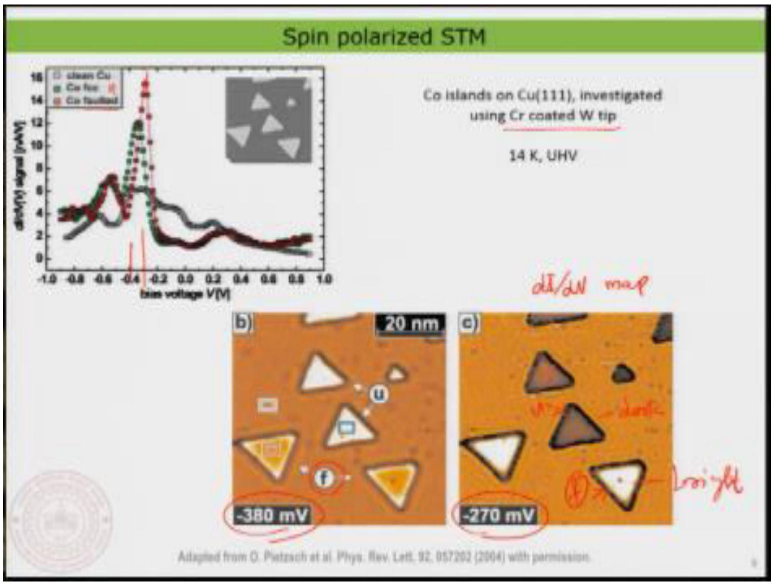

Spin polarized STM

Co islands on Cu(111), investigated using Cr coated W tip

14 K, UHV

Adapted from O. Pietzsch et al. Phys. Rev. Lett. 92, 057202 (2004) with permission.

So, now, let us have a look at some of the experimental results. So, this is actually now again, a tunneling spectrum recorded using a chromium coated tungsten tip. So, that is the difference. Now, you see something striking. So, this is exactly the same type of D band as you have seen in the previous slide. But now, you see, depending on whether I take on the unfolded Island or the folded Island, I see a strong difference in the intensity of the peak. So, that is quite striking. So, that actually is indicating that depending on the type of island, so, I have a strong difference in the D state. And now, the tip magnetization is actually playing a crucial role in deciding how the spin based transport is actually happening. So, now the spin of the electron is also playing a role that means only when the tunneling electron spin of the tip and that of the surface is matching, then you have a high intensity. And that is exactly what you are seeing here, that folded islands are showing actually a much higher intensity compared to that of the unfolded island. That of course, also depending on the magnetization of the tip, because if the magnetization of the tip is reverse, then you would actually see that these 2 green and the red would basically just shift again with respect to each other.

Now, you can also now make an image a dI by dV map so, that is something I have also told you so, we can basically make a dI by dV map. So, you can measure the dI by dV map at this particular energy. So, these are the energies which are indicated 207 and 380. So, now, you see the due to the fact that the intensity of this particular D state is very low for one of the type, you see that one of the type is looking dark and the other is actually looking bright. So, this means that clearly indicating that the density of; the spin density of this kind of an island which is basically the folded island is much higher compared to that of an unfolded island. So, this is actually the folded island and this is the unfolded island. And you can see now clearly that the spin density of this folded island is higher at 270 and 380, you clearly see that it is the reverse that the spin density of the folded island is lower and that of the unfolded island is basically higher. So, this is quite, quite interesting. With that, we can basically now detect what is the magnetization or whether these islands are magnetic or not, because if the islands are not magnetic, if you would have made a copper island for example, you would not have distinguished any difference even when you use a magnetic tip that indicate that they are not magnetic in nature. So, but here you clearly see that they are actually magnetic in nature.

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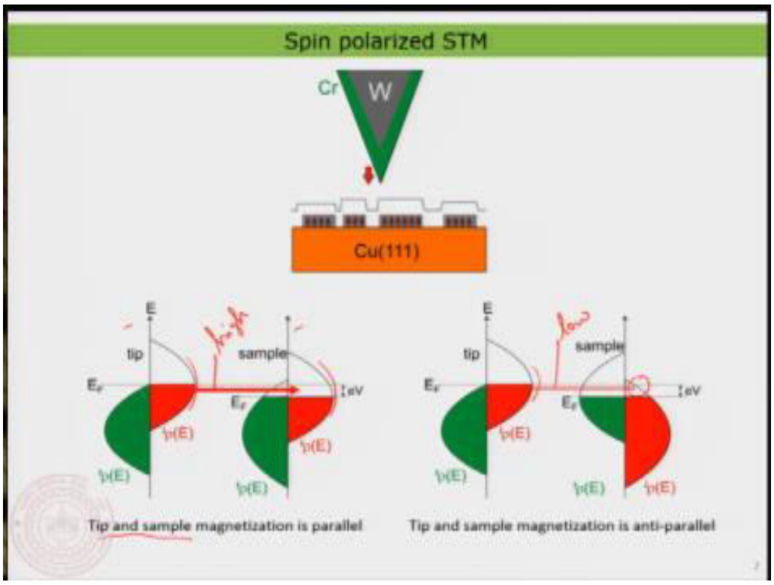

Spin polarized STM

Tip and sample magnetization is parallel

Tip and sample magnetization is anti-parallel

To do something with the spin density as I have told you. So, now, this is basically the tip and this is basically the sample and I am now having a magnetic tip and a magnetic sample. So, that would mean that now, the spin density, the upper spin density and the lower spin density or the majority spin or the minority spin and the spin density of the tip and that of the material that you are looking at should basically match.

So, in this case here, when the tip and the sample magnetization are parallel, so, what is actually happening is that there is a strong overlap, as you can see, here, there is a strong overlap of the spin density. So, like here, I am just indicating this as the down or the minority charge carriers. So, they are basically just having a very strong overlap and also their densities are actually overlapping strongly. So, therefore, I am expecting a very strong current in this case, but when the spin the tip and the sample magnetization are anti-parallel, you can basically see that the overlap between the minority spin of the tip and the sample is basically very, very small. And therefore, what we are expecting is actually a low current and here, a high current. So, that is the difference. So, that is exactly what is happening.

So, this is of course just a typical representation. it is not very scaled or it is not absolutely representative for a material reason exactly simplified scheme to just show that whenever there is an overlap between the similar charge carrier density, so that means basically the minority spin or the majority spin when they are overlap is the maximum, then you will have a high current.

And then when there is limited overlap, then the current is basically lower and that is exactly the origin of the contrast in STM, in this pin polarized STM.

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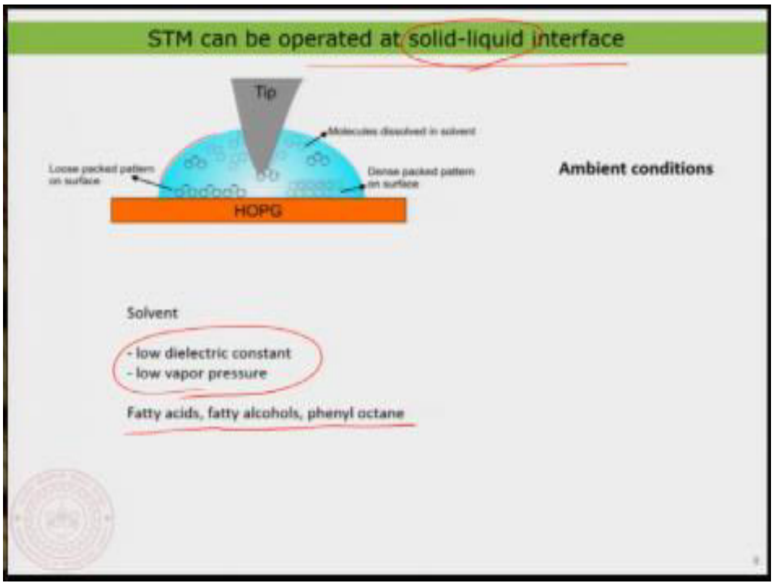

STM can be operated at solid-liquid interface

Ambient conditions

Solvent

- low dielectric constant
- low vapor pressure

Fatty acids, fatty alcohols, phenyl octane

So, now, I also just would like to quickly finalize this by showing; this is something that we have also looked at in the previous classes. What I also want to show you here is that STM is also a technique; not only just capable of working in ultra-high vacuum or an ambient condition, it also can work actually in the solid liquid interface or in the liquid itself. So, what you do ideally is; you take the surface of your interest and take a droplet of the liquid in which you want to scan and then you basically emerge the tip inside and then scan.

So, the interesting thing is that you have a controlled environment, but there are 2 important conditions that you need to take into account that the dielectric constant of the liquid that you are using should be very, very low. So, that there is no ionic transport while you are basically applying the bias and also, the vapor pressure of the solvent should be very low. So, that you can basically just work with a solvent for a longer period of time.

So, for example, like fatty acid, so, fatty alcohol, phenol octane. These kind of molecules are very well celebrated molecule in doing this and what you have to all do is you have to bring the solvent, this is actually the solvent droplet with the molecule of interest and the molecule will self-assemble on the surface and you can simply scan them.

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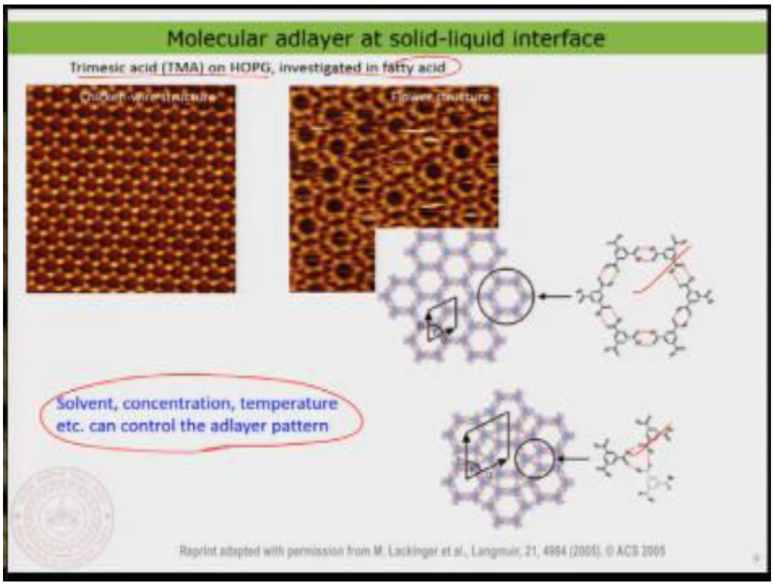

Molecular adlayer at solid-liquid interface

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

Solvent, concentration, temperature etc. can control the adlayer pattern

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

So, this image, I have already showed you. So, this is basically a trimesic acid on HOPG surface, but investigated in a fatty acid. So, this is particularly in octanoic acid or nonanoic acid. So, they can form these kind of different patterns. And we also understand now that you can basically see different kinds of patterns, you can clearly image them and now, you have one more interesting thing to consider when you basically just work in this solid liquid interface.

You can also basically just work with the nature of the solvent, the concentration of the solvent, the temperature of the substrate at which the molecules are assembling can also be added as additional parameters to control basically the self-assembly on surface. So, with this, I would like to conclude the lecture and in the next class, we will be looking at other experimental technique to understand the electronic structure of adsorbates on surface. Thank you very much.