Chemistry and Physics of Surfaces and Interfaces
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Lecture - 27
Single Molecule Manipulation on Surfaces

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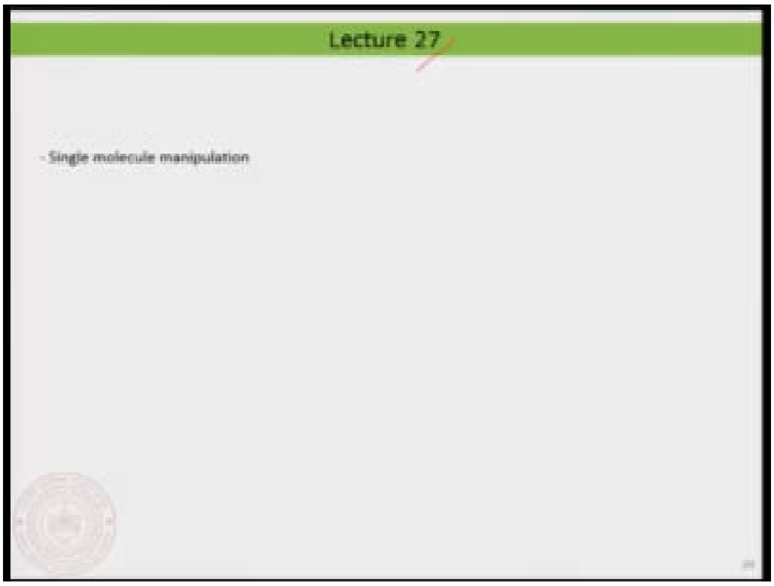

Lecture 27

- Single molecule manipulation

Hello everyone, welcome back to lecture 27. So, in this lecture, we will have a look at something called single molecule manipulation.

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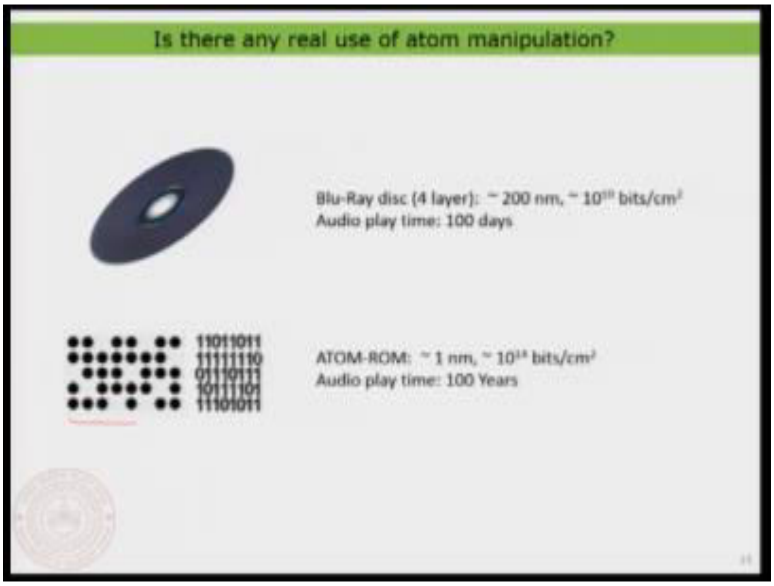

Is there any real use of atom manipulation?

Blu-Ray disc (4 layer): ~ 200 nm, ~ 10^{10} bits/cm^2
Audio play time: 100 days

ATOM-ROM: ~ 1 nm, ~ 10^{14} bits/cm^2
Audio play time: 100 Years

So, you recollect that in the previous lecture, we had look at the atom manipulation on surface. At that time, I have told that we will create these kind of atomic lattice on the surface using manipulation and by basically just creating atom or not adding an atom there. So, you can basically also create something known as an atom row or an information bit based on an atom But the problem although the promises interesting, so, yes, you have already seen the number of bits that you can collect within the centimeters square space is very, very large compared to a typical modern Blue ray disc. The problem is actually to stabilize these atoms on surface. I already told you in all the examples that we have talked about or discussed, mainly, the problem was actually that the imaging was done at very low temperature. The issue is as soon as you increase the temperature, these atoms start to move around. That means, although it is a promising application, maybe in the future, it is going to be interesting or there are people thinking of creating atom in a slightly different way that is going to be another prospective, which I am not planning to go into detail. But in any case, low temperature is somewhat seemingly sufficient that mandatory at the moment. Therefore, people thought we can also use something called molecules as an information bit or if we can try to manipulate molecular electronic structure, we could also basically use them as some kind of an information bit because they can still be operated at room temperature, because you cannot imagine having an atom row operating at 4 Kelvin. So this is practically impossible. Well, in the future, nobody knows what is going to come up. But still, at the moment, it is not seemingly a feasible technology. But this is something in prospect one can think about.

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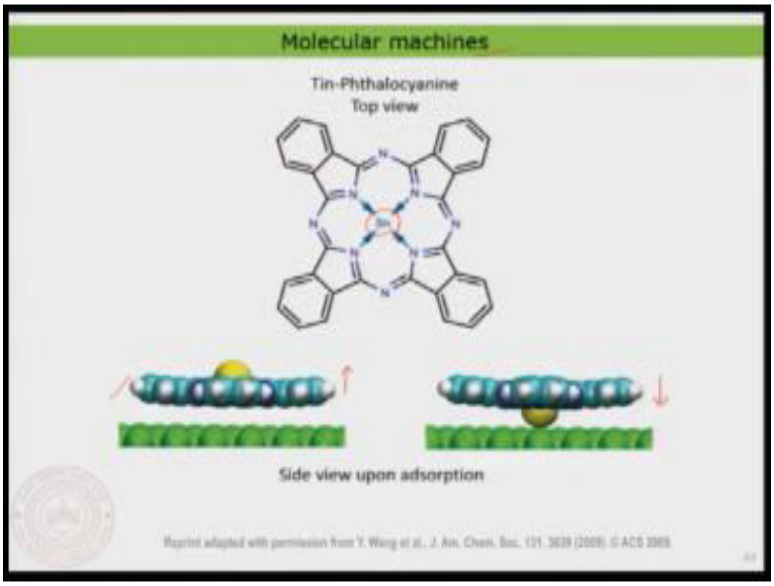

Molecular machines

Tin-Phthalocyanine
Top view

Side view upon adsorption

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Therefore, people thought about molecular machines or molecular information bit. So, the example that I am going to talk about today is actually tiny molecules that actually can change their shape or confirmations. And depending on the conformation, we can basically think about possible applications based on this molecules on the surface. So that is also something like an interesting aspect, a prospect about surface science itself. When you deposit these kind of molecules and surface, there is also molecular machines, also right now, they also can do some kinds of work. And you can also basically just make them operate in a way you want. So that is also was one of the Nobel Prize winning discovery in the last couple of years before, this was actually one major discovery and they actually won the Nobel Prize. For that, but I am just going to put it in a slightly different perspective, which is actually using molecules in kind of; as a molecular memory. So, what do you have here? You have a phthalocyanine molecule, but the difference here is that you have a different type of metal. So, that is also something interesting about phthalocyanine in general that you can actually just put many different type of metal atom in the middle and their electronic structure actually changes.

So, that is also the reason why people consider or people use this phthalocyanine a lot in application. So; here tin is the case. but now when you put the tin in the middle, so, the problem is that the tin, the radius or the ionic radius of tin is much more than cobalt or iron, those examples what we have seen in the previous case, there the molecule still remain like planner, but here in this case, the atom, the tin atom is a bit protruded out of the plane of the molecule. So that means when the molecule adsorb on the surface, you have 2 possibilities. So, you have actually a possibility of having tin up or you have a possibility of having tin down with respect to the surface. What is so exciting about this? So, that is the question. Well, these are 2 independent configurations of the molecule or conformation of the molecule with respect to the surface in gas phase, it does not matter or in solution, it does not matter because they will be identical. But; on surface, you clearly see that the adsorption energy will be different. You also see that the geometry is different, because in one case, it is like this; in the other case, it is like this. So, that is the difference. And at the same time, the metal is also pointing in one case towards the surface and the other is actually upward. So, that means chemical interaction between the molecule to the surface as well as their geometry is different on the surface. So, that is why we have basically 2 different type of adsorption on the surface.

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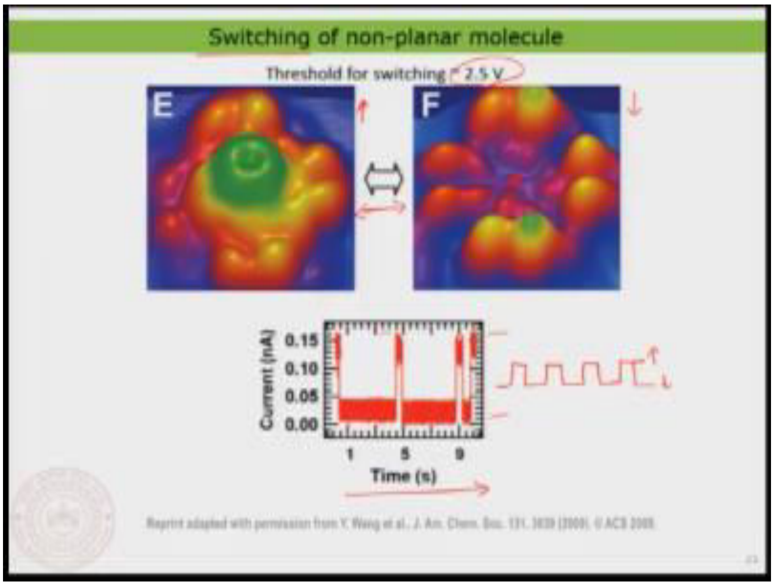

Switching of non-planar molecule

Threshold for switching ~ 2.5 V

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Now, what is so interesting about this? What can we do with this? Well, now something interesting we can do using STM, so, this is actually the molecule with the tin pointing upward and this is actually the molecule with tin pointing down. So, now, the interesting thing is that obviously as you would expect the tin pointing upward where the molecule is having a bright protrusion at the center. So, that is actually due to the fact that the tin is pointing upward. And in the other case, you see that the center is actually appearing rather dark that is due to the fact that the tin is down. Now, what is something very spectacular is that you can actually position your tip on top of this tin atom and apply a voltage like 2.5 volts. So, you apply a voltage and then what happens is; a tin atom moves downward. And then you can again go on to the molecule, which is actually the tin atom pointing down, you again stay with your tip there on top of that molecule and applier buyers, then what happens? The tin basically comes upward that is what is shown by this double headed arrow that means you can basically using the STM tip, push the tin down and take the tin backward. So, that is something like a switch. That is why it is actually called as a switch. And why it is also switch in the context here is that you are basically switching from one confirmation to another confirmation. Well, I told you these confirmations are absolutely identical in solution or in gas phase, but on surface, they are very, very different. Because you can also measure the dI by dV spectrum that means the tunneling spectrum on this molecule. And you will also see that their electronic structure is different. Because in one case, a tin is directly interacting with the surface and the other not that actually causes them to have a strong difference in the electronic structure. Now, what you are seeing here is actually kind of a time lapse; a time dependent current measurement by taking the molecule so, you place your tip on top, and then just apply the 2.5 volt between the tip and the molecule and then keep on measuring the current as a function of time. What you nicely see is that there is some kind of a telegraphic noise down, up, down, up and so on. What is actually happening is that while you are measuring the tin atom is going downward, upward, downward, upward within the molecules. Without changing anything within the framework of the molecule, the tin atom is going down, upward, down, upward and so on. Since, the tin atom is moving down and up, there is a strong change in the current at the tunneling junction. And that is what you are actually just measuring like this. So ideally, you would see some kind of a telegraphic noise that is looking like that. But this state is actually corresponding to something like a tin upstate and this state is actually corresponding to something like a tin downstate. So, you, you can now control that is the interesting thing, you need to have a threshold voltage for that if you have the threshold voltage, you can basically push the tin through the molecule downward. And you can pick that in backward and you can basically switch them up and down. Now, that is something very interesting.

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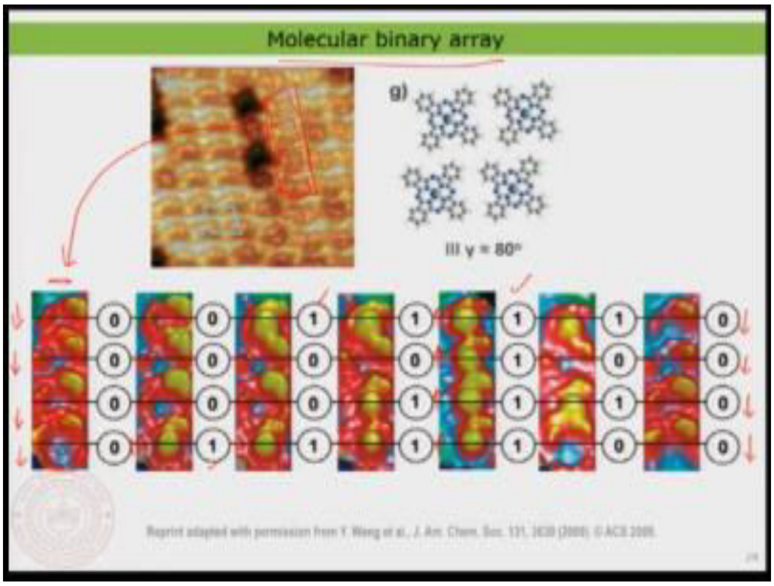

Molecular binary array

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So, can we do something more interesting with that just then then manipulating. Yes, we can, we can do something interesting. So, now what I have here is actually is an array of molecules. So, the molecule you should identify like this. So, this is basically a molecule. So, they are not very clear in this image. But each of this, you can see the clearly a pattern. So, that is corresponding to a molecule.

And now, what I am showing you here is just an array of 4 molecules. So, that means a cross section or just a section from this part is being moved here. And then what I have right now is that all the molecule having the tin down. So, all the molecule, the tin is basically now pointing downward in all the cases. So, this is the first molecule. This is the second molecule. This is the third molecule and this is the fourth molecule and in all molecule that tin is basically pointing down. So, that means it is an array of molecules, where all the tin is down, we call it a 0, because you also have seen in the current signal that down is actually representing something like a lower current. So, that is why I am calling it as actually 0. Now, with the STM tip, I can actually just go to the center of a molecule, so this particular molecule and I can basically just apply the voltage and the tin goes up, the current increases, therefore I am calling it as 1. So, then I can actually start doing it in a systematic way. And you see that I have basically just using this row of atom, a row of molecule, I have created a 0000 or 0001 or 1001 information bit, in a way I want. So here, I have actually just come to something like a completely all upstate here, all the molecules are actually pointing upward that means a tin is basically upward in this case. And then I can put them all back in here, I have come back to something like all downstate. It is clear and beautiful. So, you can clearly do this manipulation of tin upward and backward in a very systematic way. And what you have done is basically you have created an information array with a molecule. So, what is so interesting about creating array of information with the molecule? The molecule is small. It is again, something in the order of a nanometer.

So, that means it is again, you can pack more information in a smaller space compared to the current technology that you are using. That would mean that if you would ever use something called a molecular binary array, you can basically store more information inside. And of course, the suitability is also very, very high. The speed of switching is actually in the order of picoseconds. You do not even measure this here. You can basically just measure them systematically. And you can also nicely create this kind of array. So, this is something spectacular that you can do. So, that is actually a bit in the future, you may also be using something called molecular computers, where each information bit is actually substituted by a molecule itself, then what you are using currently is a transistor.

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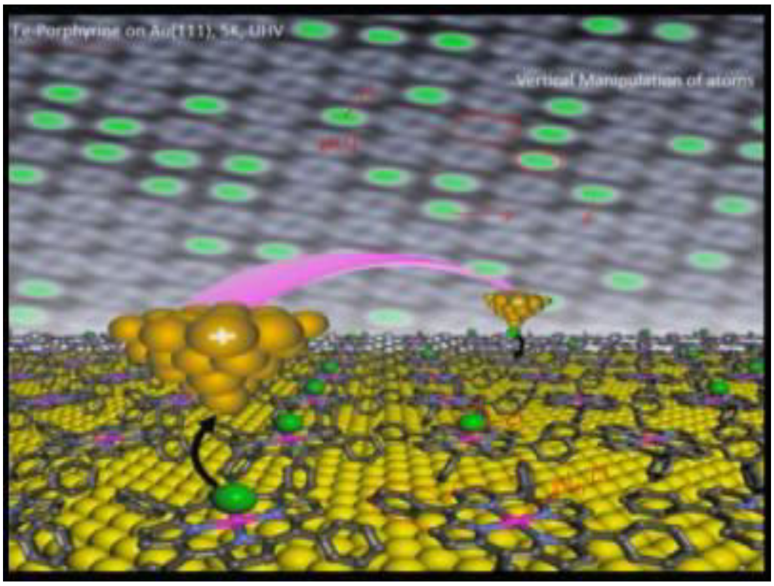

Now, I will show you one more interesting examples. Of course, you can create now. There is a huge amount of research which is going on in this field where people try to create these kinds of information bits and hoping that one can actually use molecule has one day in information storage and things like that. So, I just want to show you a slightly different example. So, this is again a molecule which is actually called as a porphyrine molecule.

So, this is similar to the phthalocyanine molecule, a slight difference in the skeleton in the carbon skeleton. But; now you can also see that the molecule is actually sketched here. So, it is not so important, how exactly the molecule looking like. It is a 4-fold symmetric molecule. And here in the background, what you are seeing is actually the image of a molecule. So, this is nothing but a single porphyrine molecule. And it is an iron porphyrine molecule. So, the iron porphyrine molecule, what you can do is you can dope with chlorine and you can create basically like a chlorinated iron porphyrine molecule. So, this green dots are corresponding to those molecule which are having actually a chlorine atom in the middle of the molecule. Now, I have here an array, a random array of molecules having no chlorine, so this is actually something with no chlorine and this is the one with chlorine. So, that is the interesting thing.

Now, you can also see here in the schematic, so I have basically here some molecule with chlorine. So, this is basically chlorine and some other with no chlorine basically, so there is no chlorine. Now, what I can do is I can take my STM tip, go close to the chlorine atom, switch the bias of the STM tip and then you can pick the chlorine atom from one molecule and you can actually put it to another molecule. So, that basically means I can easily now take these chlorine atoms from one place to another place. What is the advantage of that?

That is exactly the same like we have talked about, I can basically use this again as an information array, where chlorine atom containing state will be kind of one and the non-chlorinated state will be something like a 0. I will also make you convinced that in the in the next slide. So ideally, you can do it many, many times. So, that is something very interesting you can do.

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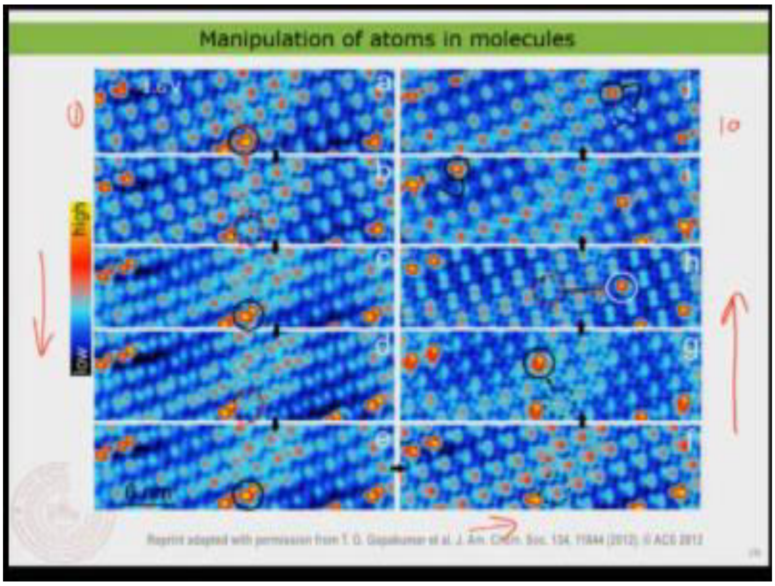
Manipulation of atoms in molecules

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You see here, again a sequence of images starting from 1 till 10, for example, you go like this and then here and then finally, like this. So, you can basically see that I have actually manipulated chlorine atom in a very systematic way. So, you can notice this particular chlorine molecule with a chlorine atom. So, what I do? I go on top of it, I switch the voltage and then I pick the chlorine atom and then you can see now, the contrast of that particular molecule changed because the chlorine atom is now is on the tip. On the same molecule, you can put the chlorine atom back and you can actually get the contrast back again, so it is minor changes in between, but then again, you can remove it, add it, remove it, add it or you can even move from one atom, one molecule to another molecule and so on. So, there is enormous possibility, so, it is up to you what you want to manipulate. And you can clearly go around and do this sequence of manipulation and you can clearly change the atoms from one molecule to another.

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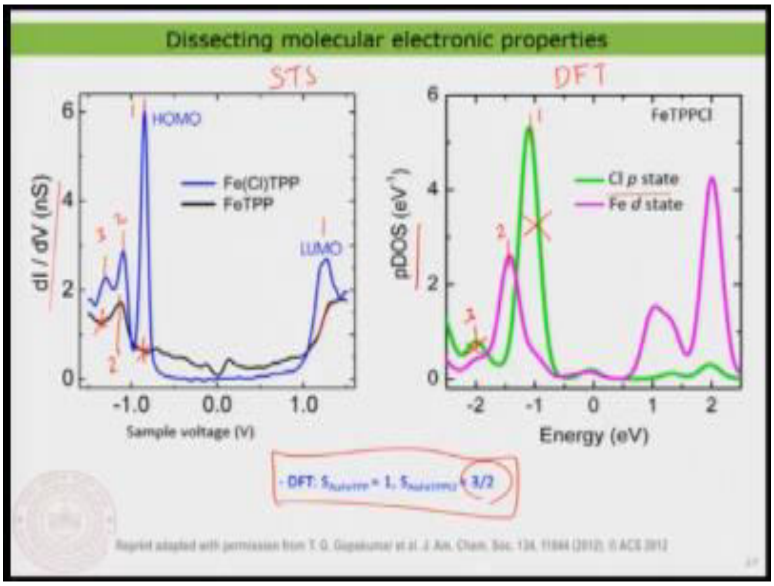
Dissecting molecular electronic properties



- DFT: $S_{FeTPP} = 1$, $S_{FeTPPCl} = 3/2$

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Now, let us look at the electronic structure. So, when you look at the electronic structure, you would understand what is really something we can do. Now, what is done here is actually again, the dI by dV. So, that means it is a tunneling spectrum. So this is really the measurement STS. And this is some kind of theoretical calculation. So; this is a DFT base theoretical calculation, so just for your understanding. So now, when I measure the spectrum on top of the chlorinated molecule, you see, I have clearly this nice peaks here, so I am just calling it as 1, 2 and 3. So, these are the nothing but the homo, homo – 1, homo – 2 and so on. So, that is nice, I have 3 peaks here. And on the right side, I have basically the lumo. And typically that is what I see within the window of my measurement. But now, when you remove a chlorine atom and then you do again the measurement on that molecule, where you remove the chlorine atom, then you suddenly see that the electronic structure changes drastically and particularly, this peak is missing now. So, the peak which was actually we call it the homo of the chlorinated porphyrine molecule is simply missing. And also there is one more peek here is missing.

And the only thing which is remaining here is actually the two, I am just calling it as 2 prime. So, that is actually the one for the iron porphyrine. And on the on the lumo side, you see it is more or less same, but there is tiny differences. So, what is exactly happening? So, we then basically just did some kind of theoretical calculations to understand it. And using theory, you can kind of reproduce the same. So, when you look at the chlorine states, so this is of course, something called a projected density of state that will give you a hint about how the density of state of the molecule is being contributed from the elements separately. So, if you look at the chlorine p state, so you clearly see that there is something here, which I am calling it as 1 and here, which I am calling it as 3.

Now, the D state from iron is actually contributing to a peak here, which let us call it as 3. So, now, you see the correspondence 1, 2, 3 on the experiment and the 1, 2, 3 in the calculation, so they are nicely corresponding. And as soon as you remove the chlorine from the iron, then you would expect that these 2 peaks would vanish. And then the only thing that would remain is basically 2 and that is exactly what you are seeing. So, this is something very spectacular. Now, you can also just see how the electronic structure of a molecule itself is building up, depending on what you are actually just having on the molecule or not. So, it is like, you know, dissecting the molecular electronics structure that is a great possibility that you cannot do with any other technique so far existing. And you can only do with scanning tunneling microscopy, you can really dissect the molecule and you can look at the electronic structure. Now, coming back to the perspective, it is like, you see, the molecule that is having chlorine is having a very strong electronic state corresponding to the chlorine states and the and you also see that the homo-lumo gap is actually much smaller than that actually of the normal iron porphyrine molecule. So, this is also showing you that the electronic structure of the molecule is strongly changing depending on the state of the molecule, whether having a chlorine or not having a chlorine. And that is exactly why I told that again we can use these kind of array of molecule with chlorine and without chlorine as some kind of an molecular information array or the information bit. For example where the chlorinated state will be called as 1, because it is a high conducting state and the non-chlorinated state will be called as 0, because it is actually a low conducting state. So, that is quite spectacular. So, you can basically use this kind of molecular array. In the future, may be something that we would be using in our computer; a good. So, you also see that there is something like a strong difference in the magnetic property also of the molecule. The chlorinated one is some kind of a high spin state and non-chlorinated one is a low spin state. And that also means that we could also use it as a magnetic switch in order to store information. So, this is quite practical.

So, that means in this kind of application, what you would expect is basically that your STM tip is going to be some kind of a head that would write information and read information. And then your surface with the molecules or atom array is going to be actually the component where you are going to store your information basically. So, that is the aspect of it. So, that is the way you have to see the application. But of course, there are a lot of limitations from the point of view of doing this, is actually what is limiting currently using them in any technology, but who knows that maybe in the future, we are going to see applications based on these kinds of systems. Good.

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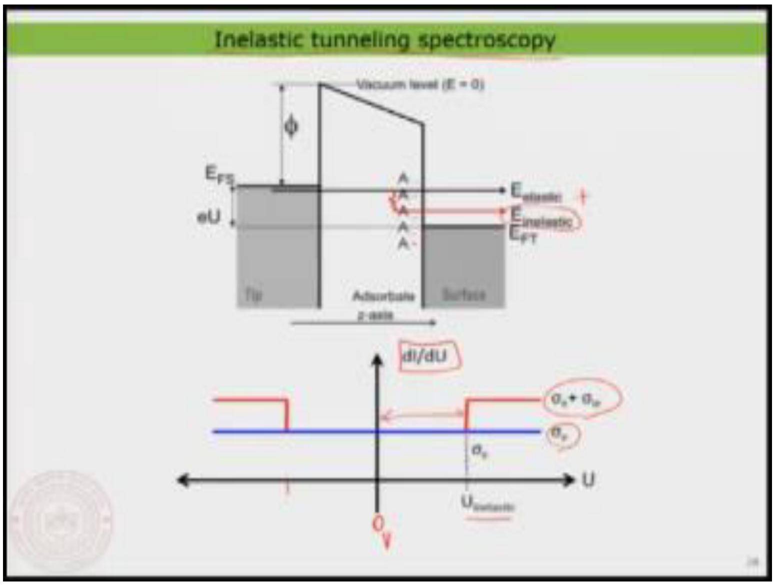

Inelastic tunneling spectroscopy

Now, I want to switch a little bit to one more interesting application of tunneling spectroscopy. This is actually the final thing that we are going to discuss with the tunneling spectroscopy. This is not very celebrated, but it can actually give you very powerful information about the interface and also the surface itself. But of course, technically, it is very, very challenging to do this experiment. And that is why it is not very commonly done, but tunneling spectroscopy is something very commonly done. So, what is this? This is called an elastic tunneling spectroscopy. What is so inelastic in it? So, now, when we talk about the other spectroscopy, where we always say that the electron that is tunneling from the tip to the surface or from surface to the substrate to the tip, in whichever today, you always showed that the electron is basically just staying at the same energy. That means on the route, the electron is not losing its energy. So, that means that wherever it started, it basically ends up in the same level and then it finally just go into the bulk of the material. So, the energy of the electron was never lost while tunneling, but what if the electron that tunnel actually just uses its energy to do some kind of an excitation of the interface and then of course, it will lose some energy. So, that kind of thing could happen, then you can actually have something called an inelastic component inside the tunneling spectroscopy.

The percentage of inelastic component is basically very, very, very less. It is even less than one percentage and that is the reason why this kind of spectroscopy is extremely tough to do and therefore, not very much celebrated in the technicality; technically, it is very challenging, but otherwise, you will see, it is very powerful. So, now, imagine a situation that I have some adsorbates molecules. So, some adsorbate molecules that are sticking on the surface. And now, while the electron is tunneling through if that electron energy is actually matching with some kind of excitation that is present in the molecule like a vibrational excitation or a spin excitation or whatsoever, then what can happen is basically that the tunneling electron can lose their energy and therefore, you can have 2 components called the elastic component and the inelastic component. Well, if that is the case, then what will eventually happen is that when you do the tunneling spectroscopy, you will eventually measure something like both the components, the elastic and the inelastic components. So, generally, you would have expected that there is only elastic component, but that is not true, there is always a very, very small amount of inelastic component. So, that means if the instrument is capable of measuring the change, then in the dI by dV spectrum, you should basically able to see a kind of step like the thing which is indicating that it will be symmetric with respect to a 0 voltage. At both voltage, you should be basically able to see a kind of symmetric step and that symmetric step is basically representing the energy required. That means this particular amount is actually the energy required or u in elastic amount energy required to actually just do some excitation of the interface whatever is at the interface and now, let us look at a particular example.

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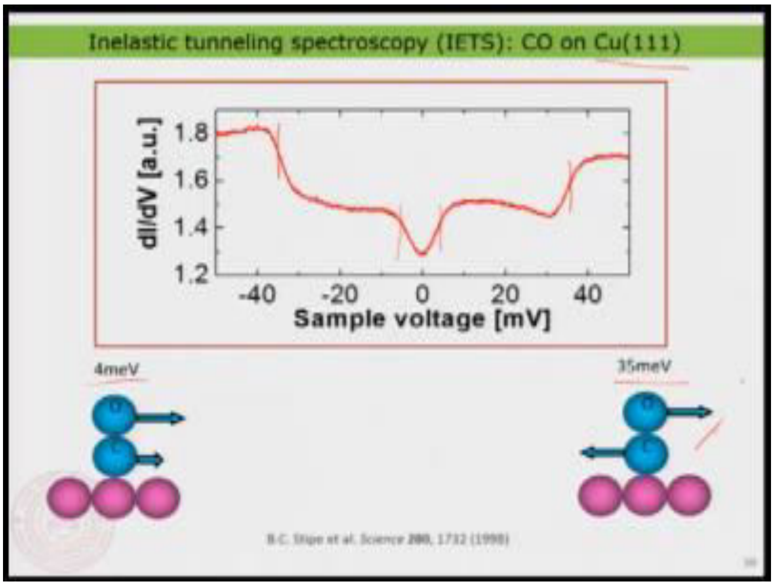

Inelastic tunneling spectroscopy (IETS): CO on Cu(111)

B.C. Stipe et al. Science 280, 1732 (1998)

So, this is a particular example. Here, we have a carbon monoxide sticking on top of a metallic surface. So, it is actually copper 111 surface. We have carbon monoxide sitting on the surface. And now, when you place your tip on top of the carbon monoxide and ramp a tunneling spectrum, then what you see is that there are clearly 2 steps here. So, this is quite symmetric with respect to 0 and there is another one, which is also symmetric with respect to 0. So, that actually happens somewhere at 35 milli-electron volt and 4 milli-electron volt. So, what are they? So, this is exactly how you are going to see that dI by dV, because you will see some kind of a very symmetric step like features. Then this turns out to be; these are actually some kind of vibrational excitation of the molecules that are actually present at the surface. So, that means the tunneling electron; while tunnel, it actually gives a part of its energy to the molecule and then the molecule basically start to do some vibration. So, it actually excites some vibration of the molecule. So, here, in one case, it is some kind of vibration like this. And the other case, where the oxygen goes on other side and the carbon goes on the other side. So, it is some kind of vibration like this. So, this is of course, a high energy vibration. So, that is why it is a 35milli electron volt and this is a low energy vibration 4 milli electron volt and you can basically identify them in the tunneling spectrum.

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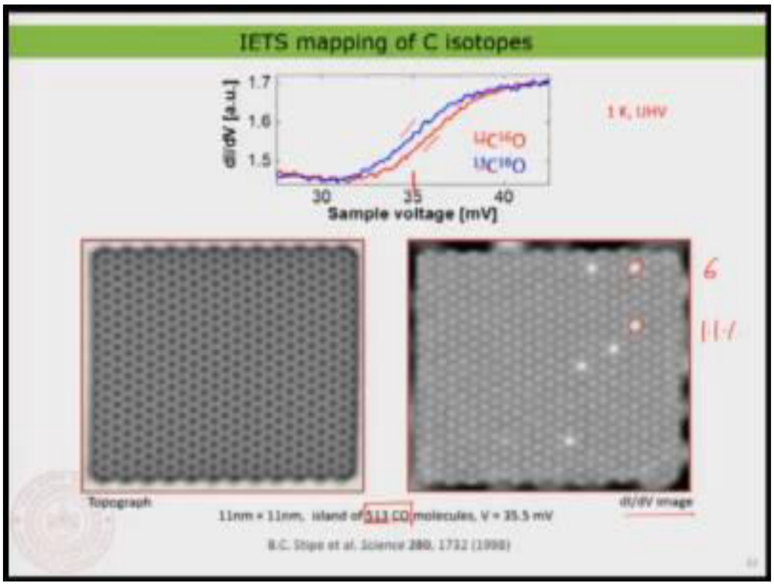

IETS mapping of C isotopes

11nm × 11nm, island of 513 CO molecules, V = 35.5 mV

B.C. Stipe et al. Science 280, 1732 (1998)

So, now, I can also do some kind of a mapping of this. So, when I do the mapping, what I clearly see is that if I would make an array of carbon monoxide on the surface, so, it is about 513 carbon monoxide, I have deposited on the surface. And now, when you basically just measure the tunneling spectrum of independent molecule, what you find is that there are some molecule showing a slight difference between each other.

So, then the question that you ask, what is this difference? Why should there be slight difference between different carbon monoxide molecules? Well, imagine that you have actually just created a carbon monoxide molecule with a 12 mass and another one with 13 mass, then you would have actually just expected that there is a difference in the vibrational excitation energy that you require. Because, it is a different kind of diatomic molecule with different mass m. You recollect that from vibrational spectroscopy, the frequency is strongly dependent on the mass of the atoms that is actually composed in the molecule. So, therefore, what you would expect is actually for C 13, you will require lesser energy to excite and for C 12 oxygen, you would require slightly higher energy to excite a particular vibration that is basically the vibration of the oxygen and carbon moving in this way.

So, if you will map basically the dI by dV image at a given voltage, then you would find that some of the carbon monoxide atoms are looking brighter and some other are looking less brighter. Why is that? It is actually because the natural abundance of the C 13 is about 1.1 percentage of. And if you count, this is about 6 bright dots. And that is basically representing an exactly 1.1 percentage of the C 13 carbon. So that means, when you actually deposit 513 carbon monoxide molecule on the surface, you exactly have about 1.1% is actually just the C 13. And that is why you see this. So, this is something interesting. So, I will also show you in the next lecture, a few more examples, so that you can understand a little bit additional perspective of this, but here, what we clearly see is that you can basically just measure some of the vibrational excitation of a single molecule that is adsorbed at the interface. And you can even detect the isotope effect because you can clearly see that difference in the tunneling spectroscopy. So, with this, I would like to conclude the lecture and I see you in the next lecture with probably one more example from this and then we will try to conclude the scanning tunneling microscopy part. Thank you very much.