Chemistry and Physics of Surfaces and Interfaces

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Lecture - 32
X-Ray Photo-Electron Spectroscopy (XPS): Applications-1

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Lecture 32

- X-ray photo-electron spectroscopy (XPS)
- Applications of XPS

Hello everyone. Welcome back to lecture number 32. So, in the previous lecture what we have been discussing was about the x-ray photoelectron spectroscopy. So, we have actually looked into the details how it works, and then we will basically be just looking in this lecture also about more possible applications of x-ray photoelectron spectroscopy. So, we will take again a few typical examples but of course XPS is not limited to any particular type of material, you can apply to enormous number of adsorbate surfaces interfaces and so on. And this has been a very celebrated technique in surface science as you will see now in the next examples you can basically do enormous lot of understanding about the surfaces interfaces and particularly the chemical structure. So, that is the most important thing that we are going to do with this.

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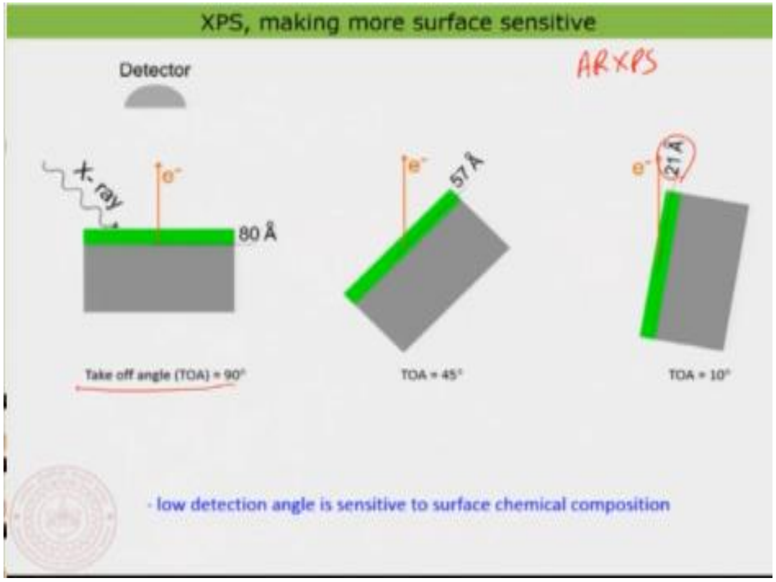

XPS, making more surface sensitive

- low detection angle is sensitive to surface chemical composition

In the last lecture we were talking about basically making XPS more surface sensitive. So, then I have told you that this particular technique which is actually known as the angle resolved x-ray photoelectron spectroscopy is a kind of technique that you can apply in order to do make the XPS more surface sensitive. So, what we have done is we have always the detector and then we have basically just tilted the sample with respect to the detector, and then we call something called a take off angle and I have also demonstrated you an example of silicon dioxide on silicon and then we have seen effectively that this method is very well working in understanding or making the XPS more surface sensitive. So, like you can see here when I have a takeoff angle of about 10 degree, it is a rough estimate. You are basically just getting information from just a 21 angstrom about 2 nanometer. This is normally for a typical material this is about 4 to 5 layers of material. So, that is already good. So, we can basically get information just within the first couple of layers around the surface. So, that is also why this technique is mostly coming under the surface science part because you can basically understand the chemistry itself.

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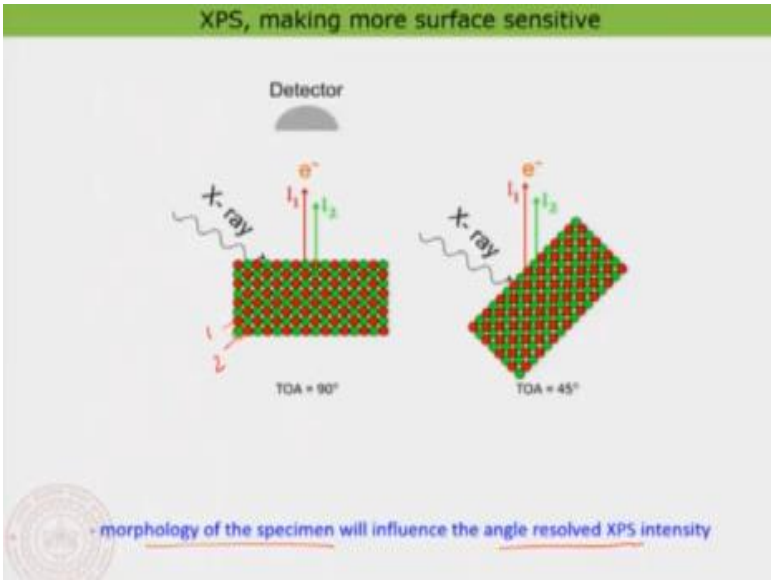

XPS, making more surface sensitive

- morphology of the specimen will influence the angle resolved XPS intensity

But before I go into the application what I wanted to revise here one more important thing is that in case if you are actually working with samples of this type where you can see the green and the red are actually indicating different type of elements namely A and B for example. And if you have like kind of a structure that is more or less like what you are seeing here kind of a mixed structure then the problem is that the intensity of the material like one so like let us call it I1 and I2 so that means this is basically 2 this is 1 that is element 1 and 2. So, if you are basically just looking at the intensity coming out of the atoms in the red colour I1 and the other one basically I2, you are going to get more or less the same intensity in the take of angle 90. But when you tilt the problem is basically that this material is equally distributed in all the layers and therefore your intensity I1 and I2 is actually going to be the same also when you tilt the sample. So, therefore the so-called morphology or the structure itself or the microscopic structure itself of the material is quite decessive in this angle-resolved x-ray photoelectron spectroscopy. So, for what I want to show you is that; for this kind of material it makes no sense to basically do any angle to solve photoelectron spectroscopy because it is not going to give you any special information about the red and the green type of element. But you have seen if the materials are kind of layered with respect to the surface and then it is very much effective and then in that case you can basically see that the angle resolved photoelectron spectroscopy is working very, very efficiently. So, that is the message that I want to pass on. Now we will look into a few examples and will try to understand how we can use the x-ray photoelectron spectroscopy in understanding the chemical structure at interface. So, that is the major thing that we want to do.

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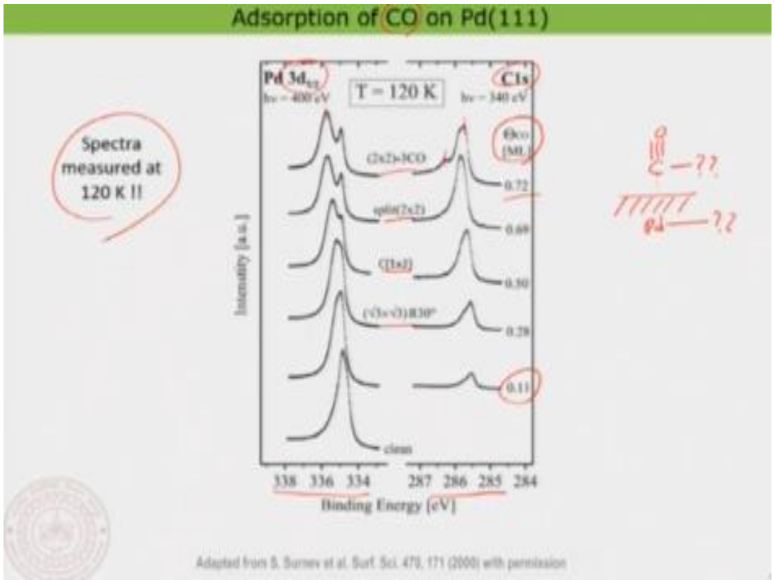

Adsorption of CO on Pd(111)

Spectra measured at 120 K !!

Adapted from S. Surnev et al. Surf. Sci. 470, 171 (2000) with permission

So, here I am taking an example of a carbon monoxide molecule or carbon monoxide molecules adsorbing on different surfaces. So, first I am going to show it on palladium 111 and later you will see that we will also make a comparison on nickel 111 surface. So, these are two reactive surfaces I already told you in the previous class, nickel and palladium are more reactive and this is actually been used widely as a catalytic material. So, for example if you want to crack carbon monoxide or carbon dioxide you can basically absorb them on palladium 111 surface and it actually help in cracking them. So, this is quite the application of that. So, now what you are seeing here is actually set of XPS data of course we are not looking into the survey scan. I told you normally you do first a service can and then you look into the specific energy that you are interested in. But we are not looking at the survey scan in this, we are looking specifically into the carbon 1s region and this is already indicated here and the palladium 3d level. So, these are the three resonances that you are looking at. And now you already see that when it comes to the 3d of palladium you see that the 5/2 is basically representing that you are looking at the 5/2 spin orbit state for example. The 3/2 state is not looked in this particular case because the information that you are going to get from both of them are kind of similar. So, that is why it is not been looked here. But I have a few other examples later in that you will actually see how they are looking. So, I will do that in a few other lectures. Now we have basically the palladium and also the carbon 1s. Why do we look at the palladium and the carbon 1s? Because you know that I have basically the palladium surface here, so this is the palladium surface and then I have the carbon monoxide molecule somehow sitting on top of it. So, like it might absorb like this and therefore what I am interested in looking at what happens to the carbon that is the question and also what happens to the palladium so that is the question. Now in this series of spectra, what is changing is the so-called coverage or the amount of molecule that is sitting on the surface. So, 0.11 monolayer or to about 0.72 mono layer. So, that means it is not a complete coverage but you are trying to put a lot of molecules onto the surface and looking what happens to the carbon 1s resonance and also to the palladium 3d resonance. You clearly see that as a coverage increases, there is a strong change in the resonance energy. So, the resonance energy when I mean you can see somewhat the peak position is basically shifting, and you also see that for the carbon there are also major changes that are occurring as you basically increase the coverage that is quite striking, and you also here there are some names which are given somewhere in between which is probably something you would also recollect. It is something that we have already studied looks like that we are looking at some kind of a wood's notation in fact. So, that is basically showing that as the coverage increases, you are certainly going to make different type of adsorbate structure on the surface. We look into that in greater detail, I just wanted to show you how in general it looks like. So, what we want to now do is we want to clearly understand each of this resonance and basically want to make a summary what is really going on at the interface. Let us do that and please note that this spectrum are actually recorded at 120 kelvin or that means all the process that you are looking at right now is basically on a cool sample. So, just keep this in mind.

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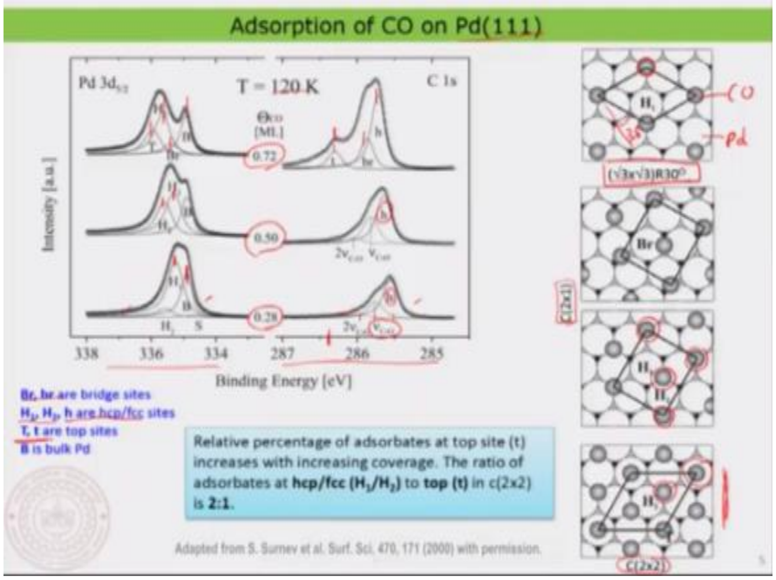

Adsorption of CO on Pd(111)

Br, br are bridge sites
H_1, H_2, h are hcp/fcc sites
T, t are top sites
B is bulk Pd

Relative percentage of adsorbates at top site (t) increases with increasing coverage. The ratio of adsorbates at **hcp/fcc (H_1/H_2)** to **top (t)** in c(2x2) is **2:1**.

Adapted from S. Surnev et al. Surf. Sci. 470, 171 (2000) with permission.

And now what I am going to do is I am going to basically just look at the spectrum that you have seen in the previous slide in a greater detail. So, you can see again the carbon 1s level and here I have basically the palladium 3d levels, 3d resonance and please note that everything is done at 120 kelvin. So, this is quite important. Now normally the peak that you are seeing in XPS one need to basically do something called a multiple peak fitting to de convolute the components that are present inside each resonance. It is not necessary that just one peak corresponding to one resonance. You have also seen partly in the previous lecture, that here it is much more explicit that you can see that for the carbon 1s level and also the Pd 3d resonance. You see like there are multiple peaks added to that in order to fit the experimental data. So, finally what you want to do is by adding more and more peaks, so you can see here I have added basically three resonances. And by adding that what I am basically doing is I am trying to fit the experimental data more clearly or more effectively. So, you can now see that the black line that is going around is nothing but the so called the sum of all the components resonance which is fitted for example, and that should match very well or most effectively with the experimental data. So, that is the criteria and you can also see here in both cases that has been done. So, the so-called peak fitting multiple peak fitting and you can basically convolute something. So, now you see the interesting thing is that the experimental data. Let us concentrate first on the carbon 1s state is basically now resolving 3 resonances. But now the resonance here you can see it is marked with h and the h is basically indicating the position on which the carbon is basically attaching on the surface that is the hcp site hcp or fcc site. You recollect this that we have already discussed and just in the paper so particularly in this paper. So, they have basically used capital H for the palladium resonances and the small h for the carbon resonance. Now you see that the major peak they are actually assigning to the carbon adsorbing on the hcp site. That is the most important thing for us right now, the other peaks are unimportant. But I just want to mention, what it is these other two resonances are kind of equi-spaced with respect to each other and their intensity is also going down gradually. This is indicating that those resonances in this case are not due to any new kind of carbon species on the surface. It is just due to some kind of a vibrational excitation. Because what we are looking at is an electronic state. So, there is always so called electronic vibration coupling that means you can basically see a particular vibrational frequency being coupled when you look at the electronic state and that is what is happening. So, therefore why they have actually indicated it with this new CO, the new is basically representing the frequency of CO vibration. That is how you assign it. But those frequencies are not important for us or those resonances are not important in our context. What is important for us is basically the h peak that is indicating that the carbon that is sticking on the hcp or fcc site. That is what also we would expect, I have already told you in the previous class. Whenever you put an adsorbed on the surface it will always try to go on to a high coordination site, and on an 111 surface what is the high coordination side that is nothing but the hcp or the fcc site. So, therefore it is justified that the peak is actually corresponding to the absorption of carbon monoxide on the surface and this is a schematic just showing the carbon monoxide. So, this is basically the carbon monoxide just the top view and then this is basically the palladium atoms in the first layer. And now you see that all the carbon atoms, the carbon monoxide is sticking at the hcp site and then they are forming basically an adlayer structure which is having this particular wood's notation. It is a root 3 by root 3 R30, you can clearly see that this is basically the orientation of the surface lattice and that is basically rotated by 30 degrees so that is basically why it is called. So, you know that and then the unit lattice vector of the adsorbate is basically root 3 times that of the surface lattice that is the point. Now similarly, if you look at the palladium 3d resonance, you also see that there is actually a peak that is corresponding to atom sticking on the hcp or fcc site. It is clear because now when molecules are actually going and touching the palladium atom then, the palladium atoms on the surface are actually changing it with respect to its bulk nature. So, this B is basically representing the palladium resonance if you would have taken it just for a pure palladium without anything sticking on it. That of course they have done as a control experiment and then you clearly see that I have two resonances which is the simple palladium or the palladium resonance that is coming from the bulk, because we are not always able to get the first layer, it is just also including the second layer in the XPS so you are basically seeing the bulk resonance, and the higher energy peak is basically corresponding to the adsorption of the C on the palladium. Now let us look at what happens if I increase the coverage. So, this is basically the coverage so this is a very very low coverage 0.28 monolayer. Now if I increase the coverage what is interesting is it more or less looks same for the carbon. So, the intensity everything looks just almost the same. So, you have again the h type of resonance. But for the palladium you see that it is basically having one more type of h. The reason is simple that now based on this thing they have actually made a possible pattern. So, the pattern is like that, where you have something called adsorption of molecules at the hcp site, that is this one but now I can basically just form another kind of orientation of the carbon monoxide on the surface by adding carbon monoxide on this hcp site and also placing one carbon monoxide inside the unit cell, that is why you get this kind of c 2 by 1 superstructure. That means right now you can see that I have added one more type of hcp site on the surface, and then you also expect basically that since the concentration, so you can see this is at 0.5 ml that means monolayer. You basically increase the concentration of the molecules on the surface and therefore you are actually going to get a more compact structure, so indeed the C 2/1 superstructure or C 2/1 add layer structure is more compact than this root 3 by root 3 R30 for example. So, that is the interesting thing. Now we can do continue the experiment. Now when I do something at higher coverage about 0.72 or so, that something very interesting happens that I get many resonances, one named as H another named as Br which is actually indicating a bridge site and then t indicating atop site. So, I have actually just given a guide here. So, you can basically just look at that. So, I have that means I am now basically just accommodating or trying to accommodate more and more atoms on the surface. And now you can see that I should basically have a structure where I should have basically like atop site occupation and also hcp or fcc site occupation. Now you can see this is an absolutely compact structure. So, more than that this is not really possible because if you in try to put more molecule, they are actually not getting accommodated because there is also something called a molecule-molecule repulsion. There is molecule-molecule attraction but you know that if the molecules are actually placed more than a certain value they will also repel. You remember that in the when we talked about the different energetic contribution, that means we cannot basically put more molecule than this, and that is the reason why the experiment is typically stopped around that value and then you are actually seeing here mostly structures that are having a very very high packing. So, this is actually a C 2/2 superstructure, and that is reason why you see this kind of a new peak that is actually corresponding to the top site occupation. You please notice that the energy of the top site is slightly higher compared to the one occupying at the hcp site. So, that is kind of strange if you would if you have thought about it. Because what I also told you in the class that when atoms are actually getting occupied within the hcp site that is where you are going to get a high coordination. So, that basically means you would have expected that the hcp site would basically have something like a higher binding energy compared to the top site. But that is not the case what you are seeing. So, here it looks like the top site is basically where the molecule is having a higher binding energy or that is meaning that the carbon is basically at a higher oxidation state. So, we will come to that in a minute. So, when we make a summary at the end of this part so we will basically look into that in greater detail maybe in this lecture or in the next lecture. So, the same thing you can also see that the bulk structure is there, and there is an hcp site, there is a top site, there is a bridge site this is also present in the palladium 3d resonance. So, that is very good which meaning that now I can basically clearly understand what is going on at the surface and as a function of coverage. So, what is really going on is that as a function of coverage you are basically trying to accommodate more and more molecules in the surface. But there is a limit up to which you can accommodate a layer of molecule. But that is something what you can see here this is the highest occupation that is also where you start to actually just start making molecules to occupy normally not a possible occupation sites like top sites. That is only possible when you push the molecule further with a concentration.

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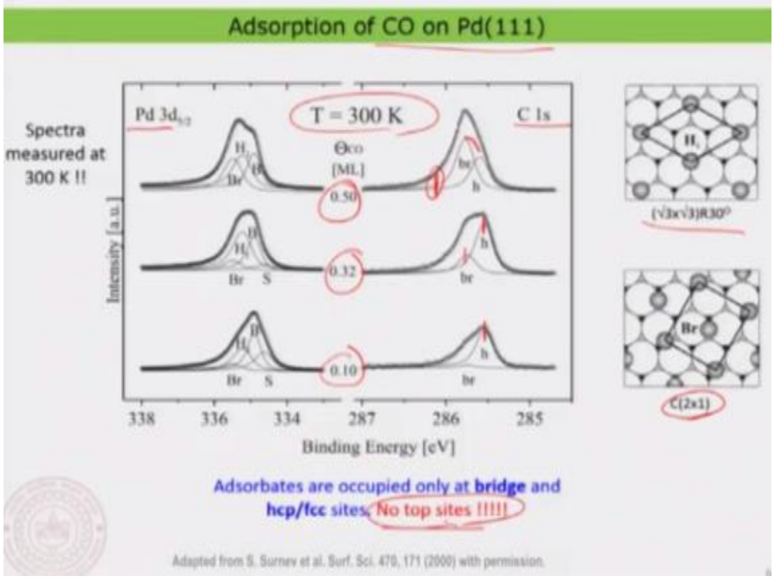

Adsorption of CO on Pd(111)

Spectra measured at 300 K !!

Adsorbates are occupied only at **bridge** and **hcp/fcc** sites, No top sites !!!!!

Adapted from S. Surnev et al. Surf. Sci. 470, 171 (2000) with permission.

So, now let us look at one more example of the same molecule. But now in this case all the experiments are done at 300 kelvin. So, that means now the CO molecules are absorbing on the surface at 300 kelvin. Now again a kind of experiment which is dependent on the coverage and you see something quite striking in this case. What you are seeing striking is that we are unable to occupy the top site. Why do I see that because I do not see any peak that is corresponding to the top site occupation. So, that you do not see in the carbon 1s resonance or also in the Pd 3d resonance. So, you are not seeing that you like in the previous case you mostly see that occupation hcp site then as a concentration increase you can you have basically occupation at the hcp site or fcc site and bridge site, and when you increase the coverage, you have slight variation in their coverage but there is no top site observe. So, the top site should have been observed at this position as per the previous reference. You can also see the same in the palladium resonance. So, what is going on that is quite interesting. So, that actually means the structures that we are seeing are nothing but just the root 3 by root 3 R30 structure. So, that is one structure which we are seeing and then what we are seeing is actually the C 2/1 which is actually a structure where the bridge sites are occupied, and that is actually the structure that you see mostly when the coverage is high because the top sites are not getting occupied. So, this is quite interesting to notice that the top sites are not getting occupied. So, that also indicates that the top site is not a favorable site in fact plus the concentration that you actually just tried to put on to the surface is also quite temperature dependent. If you are basically just doing the experiments at low temperature, you would basically be able to occupy the molecules at even at a slightly frustrated position. But when the temperature is increased you cannot do that because the thermal energy is not allowing them to get into that frustrated structure. So, we will make a summary at the end of this section so then you will understand. So, that is the key observation that you make here that there is no top site occupation. So, let us look at one more example. So, that we can basically understand what is going on.

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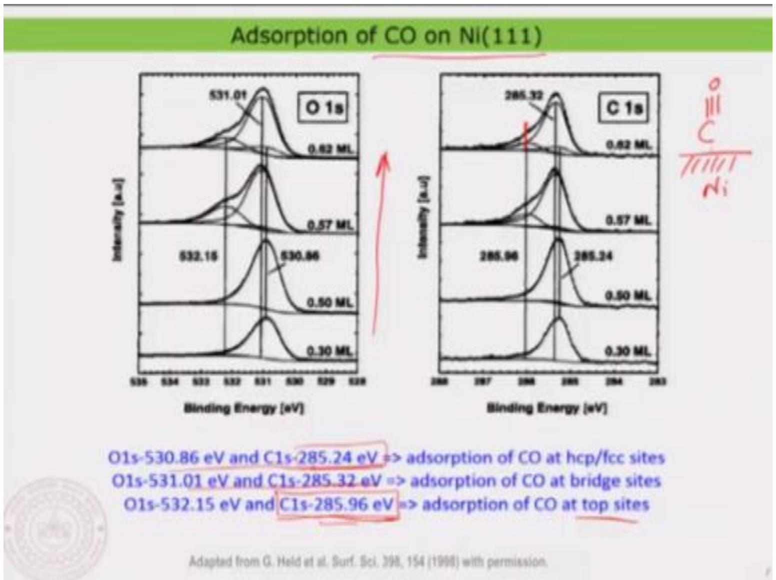

Adsorption of CO on Ni(111)

O1s-530.86 eV and C1s-285.24 eV => adsorption of CO at hcp/fcc sites
O1s-531.01 eV and C1s-285.32 eV => adsorption of CO at bridge sites
O1s-532.15 eV and C1s-285.96 eV => adsorption of CO at top sites

Adapted from G. Held et al. Surf. Sci. 398, 154 (1998) with permission.

So, here is again the same molecule that is getting occupied on the nickel 111 surface. So, the surface is slightly different, but the characteristic is the same in this case as well. I have basically again do an experiment as a function of coverage and in this case I am basically looking at the oxygen or carbon. So, that is also the possibility, I can always look at the oxygen or carbon because whenever the carbon is actually affected. So, this is basically my nickel ya and whenever the carbon is actually affected of course the oxygen is also directly influenced. So, that is the point. So, when carbon is strongly bound then the oxygen resonance should also change. So, that is exactly what you are seeing here as the coverage increases, you see there are new resonances appearing that is actually corresponding to the occupation of the molecules at the top site. So, that is the interesting aspect in this case. So, I have also just made a correlation of the energies here, you can basically see how the correlation of the energy is looking, that whenever there is a top site occupation you can see basically the binding energy is basically just increasing compared to the occupation of the molecule at so called hcp or fcc site. So, you can see here it is 285.25 electron volt, but when it is actually occupying at a top site you can basically see the energy is basically increased by about half an electron volt. So, it is not much but you can see, nonetheless it is quite strongly dependent. So, that is something I also would like to discuss with you in the next class. But now what I want to say again is that here also you see like a strong influence of the coverage and as the coverage increases the molecules are trying to get occupied to top sites, and the bridge site and at lower coverage all the molecules are basically occupying only at the hcp and the fcc site. So, these are actually the sites that are much more favorable for the adsorption in general. But this is also something we have discussed when we were looking at the adsorbate, when we were looking at the energetics of the adsorption, we always talked about that the so-called molecule-molecule interaction and the molecule-surface interaction is quite important. So, you need to have a balance between these two interactions in order to come to the real adsorption structure for example. So, you cannot see all the structures all the time. So, it is strongly dependent on the coverage and it is also strongly dependent on the temperature. So, these two parameters you already see, concentration is kind of a kinetic factor; that normally push things in a non-thermodynamically favorable situation. And that is what you typically see when you increase the coverage and with the temperature you can basically just put things down to a more thermodynamically favorable products of the surface. So, with this I would like to conclude this lecture and we will basically look at the same example and, in a bit, more detail in the next class. Thank you very much.