# Chemistry and Physics of Surfaces and Interfaces
**Prof. Thiruvancheril G Gopakumar**
**Department of Chemistry**
**Indian Institute of Technology, Kanpur**

## Lecture - 33
## X-Ray Photo-Electron Spectroscopy (XPS): Applications -2

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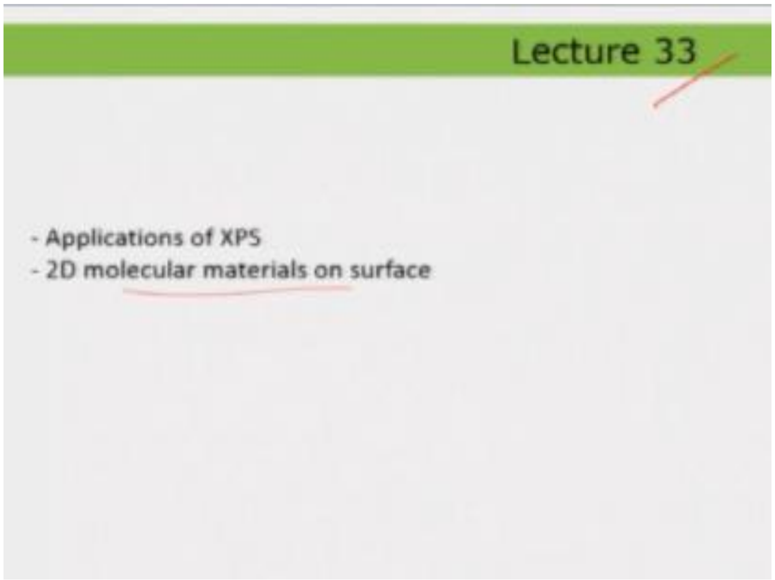

Lecture 33

- Applications of XPS
- 2D molecular materials on surface

Hello everyone, welcome back to lecture 33. So, in this lecture we will continue where we have been what we have been discussing in the previous class. It was about adsorption of carbon monoxide on two surfaces. So, we will basically try to summarize that and make our understanding clear. And, then we will switch to a new topic this is basically about 2 dimensional molecular materials prepared on surface. So, that is also something interesting it is actually a kind of new emerging material which is purely prepared on surface. So, that is a pure 2-dimensional material. So, we look into that as well. And in that example what I am also just planning is basically to bring together the scanning tunnelling microscopy, atomic force microscopy, x-ray photoelectron spectroscopy, scanning tunnelling spectroscopy and so on together in order to basically make some kind of a consolidated understanding of a given material. So, you will also understand how these methods can be together used in understanding a particular type of material. And also, we can learn about this 2-dimensional material as well.

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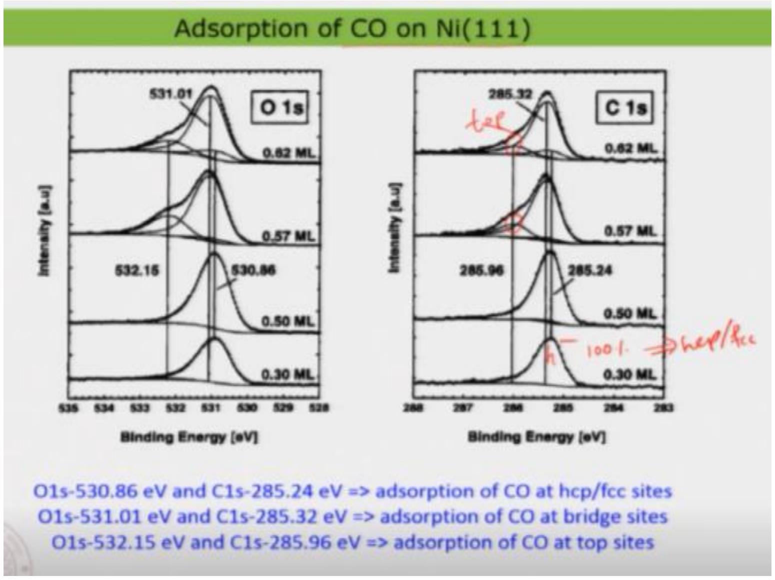

Adsorption of CO on Ni(111)

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

So, let us look at the example that we have been discussing about it was about carbon monoxide or nickel and then we have basically seen the X-ray photoelectron spectroscopy as a function of coverage. And then you have seen that as a coverage increases, we do see signature of carbon monoxide getting adsorbed onto top sites, bridge sites and hcp sites, and particularly at high coverages we do see that molecules are getting occupied onto top sites which is normally not a favourable site. So, that is what we have discussed and now we can basically try to understand it a bit more carefully. So, now you see that something else you can also do with the spectrum because, we know that this resonance is at a lower coverage is corresponding or the intensity of the resonance is basically corresponding to the amount of molecules that is occupied at the hcp site. So, at this coverage I can basically say that 100% of the molecules are occupied at hcp site. This is something hcp or fcc site. So, I am here not distinguishing them so it is with XPS it is hard to distinguish them, so you can basically just say that. But now you know that as the coverage increases what is happening is that you are basically getting new resonances. So, that is basically these ones which are corresponding to the top site and then you would also see that the amount of coverage of the molecule occupying the hcp site would basically go down. So, in fact by analysing the intensity of this peak you can in fact make a summary of what is exactly going on as a function of the coverage and that is what I am doing here.

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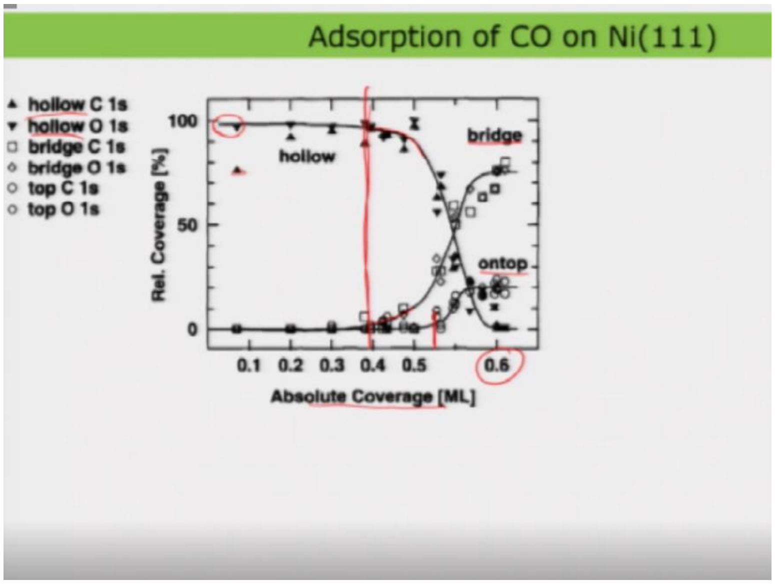

Adsorption of CO on Ni(111)

You can basically see now I have the absolute coverage, here that is in monolayer of the carbon monoxide occupying on the nickel 111 surface. And, you clearly see that at the very low coverage 100% occupation or these are the experimental data and the line is basically just to guide you through and you can see 100% of occupation is basically at the hcp site, so this is quite nice. Now you keep on increasing the coverage and then you measure the XPS spectra. And, then you can basically plot that intensity of the peak as a function of coverage. And then you can basically understand this and as you see here around 0.4 mono layer somewhere around this 0.4 mono layer you see that I am starting to get basically the occupation of the bridge site. So, that is the first thing so you see basically it is branching out and then clearly you see that the hcp site is going down. So, now this is a systematic analysis. Now, as the coverage increases and then when you reach around let us say like 0.65, 0.55 to 0.6 monolayer; you see basically the coverage of on top, the top site is basically increasing. And definitely the hcp sites would go down and as you see when I reached a coverage of about 0.6 monolayer, you see in this particular case there is no occupation of the hcp site and most of the molecules are actually occupying either at the bridge site or the on top site. This is quite spectacular. So, this is quite nice so you can basically understand you can systematically understand, what is going on at the interface as a function of coverage. As, I told you always at the lower coverage hcp site is the most favourable site and that is also an indication what is really the molecule liking with respect to surface? So, that question is very obvious which is basically the hcp or fcc site. So, that is something you can keep it in mind. So, here when they call it hollow site that is basically the hcp or fcc that is always the case.

But question is, when you increase the coverage, so there comes the so called molecule-molecule interaction and the molecule surface interaction and they start to now compete each other to basically get into the most stable structure. So, that is where you would finally find that the bridge and the on top site is occupied and the hcp site is completely gone. So, let me just also show you the different type of structures that is basically assigned a different coverage for this molecule.

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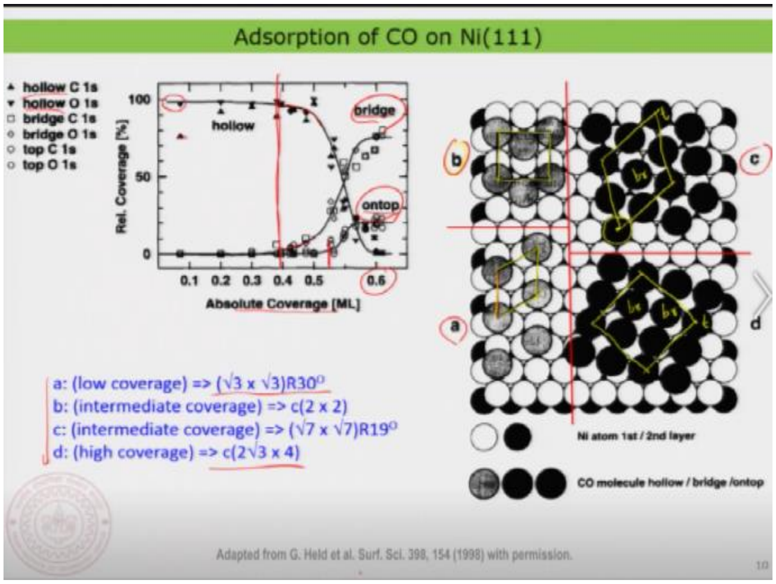

Adsorption of CO on Ni(111)

a: (low coverage) => (√3 x √3)R30°
b: (intermediate coverage) => c(2 x 2)
c: (intermediate coverage) => (√7 x √7)R19°
d: (high coverage) => c(2√3 x 4)

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On nickel 111 surface so this is again indicated by a here, a b c d is basically the same as this one, and you see at low coverage you again have this root 3 by root 3 R30 degree structure that is exactly the same as that you have seen also in the palladium 111 case. That is good, so you can see it clearly, so this is the unit cell, so I am just taking a slightly different marker here, so this is the unit cell so you clearly see the unit cell. So, that is nice. So, this is actually a root 3 by root 3 R30 structure. But now when you increase the coverage, so you basically starting to occupy the hcp and also the bridge site, so that is these structures. So, b and c are structures that are present in the intermediate coverage. So, there you can again see the unit cell is marked again here so this is an old paper 1998 that is why the figures are not that good but it is a very beautiful paper explaining how things happens. So, this is the 2 by 2 superstructure and then you can see here, at moderate coverage I also have this occupation of the top site, so this is basically you can see this occupation is at the top site and this is the unit cell of the molecule and you can see I started to get already the top site and also you can see this is nothing but the bridge site and this is the top site. So, this is good and then when the coverage is basically increasing to higher coverage so then you are getting a completely new structure. So, this is slightly different to what you have seen in the in the previous case there you are basically seeing again occupation of the top site. So, that I am basically marking this unit cell with respect to the top site, so this is the top site. And, then in between you can see here I have basically bridge site. So, that means as a coverage clearly increases to a very very high coverage, you only only have the occupation of the bridge site and the top site. And, that is exactly what you are seeing, and now you can see basically the density of the structure. In the d, the case d, you see the density of the structure. So, this is basically much much more than what you would basically expect compared to a low packing. So, that means that the lower coverage you basically have a very loose pack structure and as the coverage increases you basically have a very high-density structure. So, that is the interesting thing. Now with this you basically can make a nice analysis of the interface structure formation of molecular and so bit on surface. Now, what I want to do is also to kind of summarize these two example and then to recap the energetics that we have talked about. So, that is something which we want to do so in both cases it is quite interesting so both palladium and nickel 111 surface but structurally they are same so chemically there is a difference.

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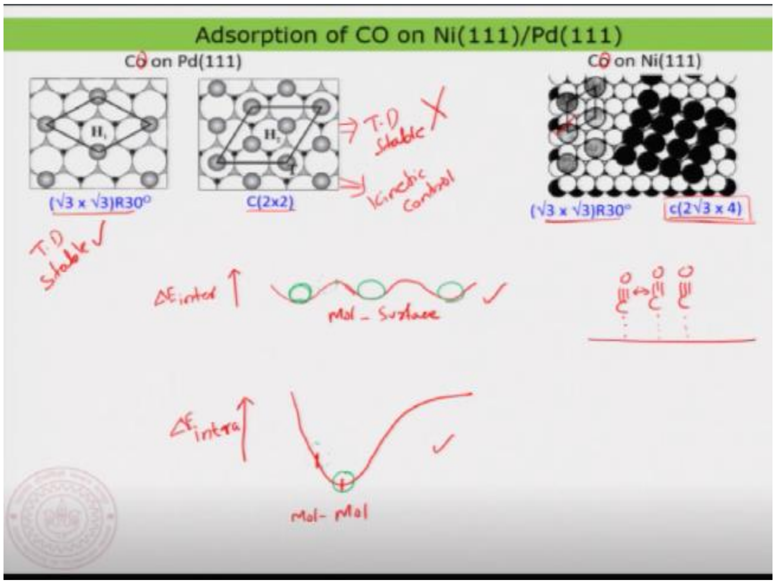

Adsorption of CO on Ni(111)/Pd(111)

But that adsorbate is basically carbon monoxide. So, please excuse me for this, this is both carbon monoxide and not Co, a cobalt. So, both carbon monoxide is basically adsorbing on these two different surfaces. So, now definitely we know that at low coverage both surfaces molecule is forming basically the same type of structure. That is the root 3 by root 3 R30 structure. But, when the coverage increases, you see it actually makes too high-density structure. So, that is the interesting aspect. So, it you make clearly a high-density structure and also you started to see the occupation of the top site. So, now comes the question, so like let us look a little bit back into the energetics that we have talked about. Whenever we talk about the adsorption of a molecule on surface, we know that there are two major energy contributions that come into picture. At lower coverages that is for sure, you have this particular periodic type of energetic that comes due to the delta E inter. And, this is basically from the molecule-surface interaction and then you also have the other contribution that was looking like more or less like kind of a potential, a mass potential and here again the energy is basically indicating something like delta E inter, delta E intra that is about the molecule-molecule. So, let us call it like that molecule-molecule interaction and here it is molecule-surface interaction. So, these are the two major energy contributions that is actually just playing a role and these are the two which is basically calling to the so-called adsorption energy. So, that is something we have already talked about. Now you see that whenever the coverage is very low so we know that from the delta E inter that all the molecule should basically be occupying this particular site that corresponding to the lowest energy structure, that is true. And we know that somehow the top site is not the most favourable, because the adsorption energy at that particular site is not the most stable one because, it is actually having a lower coordination. And, that actually comply with what we experimentally see. But then the question is, why is that the top site is getting occupied when you basically increase the coverage? So, that is of course something that we have also talked about that whenever you have basically a surface. And if you have the carbon monoxide molecule coming together let us call a few molecules this is indicating a case of a very high coverage, and now you see that they also start to basically repel each other. So, that would mean when the coverage is high you are not trying to basically just keep the molecule at molecule-molecule interaction at this so called minima instead, you are probably pushing the molecule to a position which is actually much closer than what they are allowed. So, in that case what would happen is that the molecule-molecule would start to basically also repel. So, but whenever the coverage is very low so then, most of the time you are basically just you do not need to even consider the so called delta E intra, because the molecules are too far away. So, there you only have to consider this particular contribution. But, when the concentration of the molecule increases you need to also consider basically the contribution from the delta E intra, because the molecule-molecule equilibrium distance is also very very important in that case. So, now you see that, when you want to actually just occupy more molecule on the surface now, I need to make a compromise. So, in that case it is not necessarily that you are finally making this to be a thermodynamically stable structure. This is not thermodynamically stable structure because, you are definitely not letting the atoms to occupy in the most favourable position. The most favourable positions are indeed these two positions. So, these are the most favourable position but you are probably trying to occupy the molecule at this particular position or this particular position. So, then of course you see that energetically they are not very stable. But there is something interesting that you also might have noticed that in the XPS data that the energy corresponding to the top site was actually just looking at a higher binding energy. But just keep it in mind that is actually the binding energy corresponding to the oxidation state of the molecule and that has nothing to do with the energetics that we are talking here. So, this is quite important, but there it indicates that when the molecules go on to the top site the carbon is basically much more oxidized. So, most likely the carbon is kind of giving away a lot of electrons to the surface and therefore the carbon is mostly kind of oxidized in that case. So, that is probably is what is happening at the top site so that is probably the reason why you have a higher binding energy in the XPS top resonance for corresponding to the top site. But that is not corresponding to the energy that we are talking about here. So, now let us just come back again to this particular case of molecule being on the nickel 111 surface, you also see that we have basically kind of a high-density structure. Again, there also you can see you are kind of trying to occupy the molecule inside into kind of not energetically very stable positions that is actually indicating that the coverage is pushing it. So, at the end of the day, what I want to summarize here is that whenever you actually just play with the adsorbate on the surface you can always form a thermodynamically very stable so this is a TD stable structure. So, this is a thermodynamically stable pattern, and that is only occupied when you are actually able to provide so called minima of both the energy contribution but when the coverage is basically increasing you cannot provide that because the molecules need to be put together and that is also why we are actually just calling normally these kinds of structures to be something like a kinetically controlled. Because, you can clearly see here the control parameter is the concentration. So, these are actually kind of kinetically controlled structure, so this is actually possible. So, now with what I showed you in this example is that using XPS we can basically determine a lot of chemical information about the adsorption of the molecules on the surface and you can also look into the interesting details about the molecular adsorbate their adsorption position and things like that.

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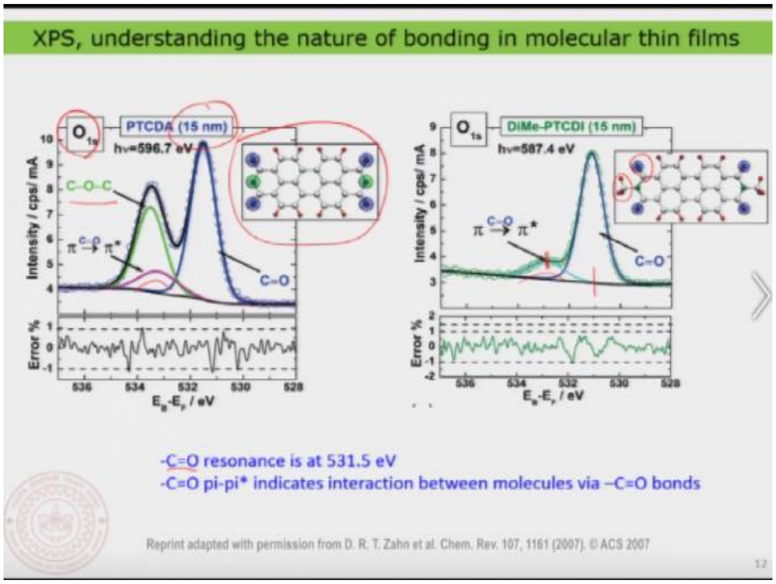

XPS, understanding the nature of bonding in molecular thin films

-C=O resonance is at 531.5 eV

-C=O pi-pi* indicates interaction between molecules via –C=O bonds

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Now, I want to take you to a little bit bigger example. So, the bigger examples are this, that we want to look at the big molecules adsorbed on the surface and in this case the same example as we have actually looked at in the UPS this is that PTCDA molecule that is something I have already told you, it is a molecule that is been used in the organic molecule semiconducting industry and here what you are looking at is actually the XPS data of the same molecule, and it is also basically done from the same film, you remember that time we were also just looking at the valence band structure, valence band electronic structure of the same molecule of a 15 nanometre thick film. And here what I am looking is basically of the same film, but I am doing the XPS, that is actually to look how the molecules are interacting. But that is the interesting thing, so UPS would basically tell me what is the electronic structure of the valence band, because that is quite important when you want to talk about the transport property of the film. But when you want to look at the chemical structure or how molecules are interacting and so on then you will have to actually just understand the XPS. So, what I am looking at is actually the oxygen 1s resonance of the two molecules, one is slightly modified having a methyl group additional and that these two molecules. And, you clearly see that I am expecting 2 types of oxygen in this which is actually a C double bond O oxygen. And then I also have a C-O-C oxygen. And, as we have already discussed the C-O-C oxygen is having a higher binding energy that something you expect and then you can also now assign their energy, and by looking at the energy shift compared to a molecule which is basically in the gas phase. You can kind of not in the gas phase you can by just comparing a molecule, which is not in the film you can also basically compare what is the energy shift. But you also see that in in the case of dimethyl PTCDA, so you do have only one peak that is corresponding to the C double bond O. So, this is basically the C double bond O and then you see just one resonance. But now interesting thing is that this molecule both of them having a very particular resonance which is marked here as a pi-pi star resonance. So, it is a new electronic state that is coming up when the molecules are actually packing like in a stacked manner. So, the molecule is a planar molecule so when you pack the molecule like above each other and when they actually just grow like this, or they would be basically growing like that, but what so ever the packing is basically kind of a pi-pi interaction, then you would see this kind of resonance which is very very particular when molecules are actually packing in this kind of fashion. So, this is quite something that you observe for molecules that are having large pi electron cloud. And when they interact like that you see this kind of resonance, which is typically an electronic state and this is a transition that happens between the pi-to-pi star. So, the interesting thing here is that both the molecules there are no true chemical bonds between the molecule in the thin film itself. But there is only some kind of weak pi-pi interactions and that is what you would basically find just due to the fact that you have this pi-pi star kind of resonance and that is an indication. So, that is showing that both the molecules are actually just kind of having a Vander Waals interaction through their pi-pi electrons in the molecules. So, this is quite nice, so you can kind of understand what is going on in the molecular film in terms of their interaction, intermolecular interaction. So, that is what you would gain in the XPS. But now I can also do something interesting with this kind of molecular film, what is in this particular example I have chosen is that the same molecule.

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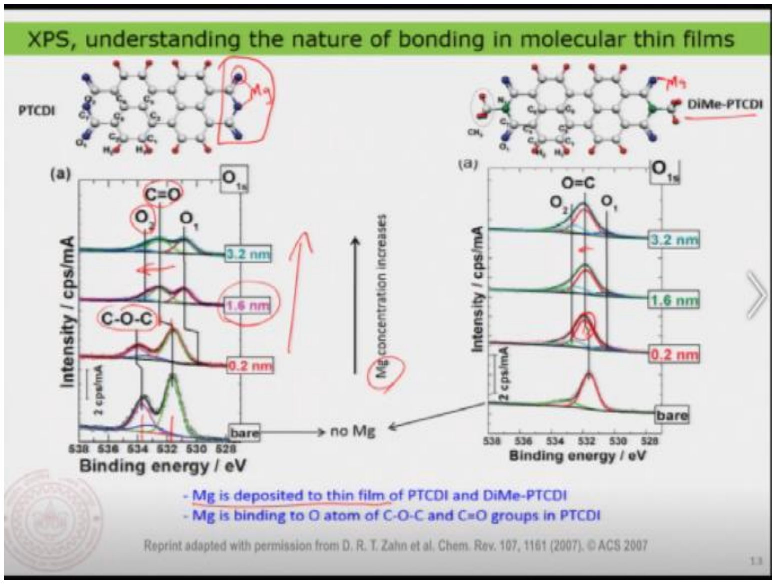

XPS, understanding the nature of bonding in molecular thin films

- Mg is deposited to thin film of PTCDI and DiMe-PTCDI
- Mg is binding to O atom of C-O-C and C=O groups in PTCDI

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But you take now the film and then dope this film with magnesium, so that is like kind of a metal that you are adding inside in order to kind of increase, the transport property. I will show you in a greater detail in an upcoming example something of this kind which is basically discussing about the about the importance of doping in a molecular metal. But this is not that important right now in the context. But what I want to show you here is that the magnesium concentration is basically increasing as you increase the as you go along this direction and what you are seeing is in the case of PTCDI. So, I would expect definitely two peaks that; is corresponding to the C-O- C oxygen and also the carbonyl oxygen. So, that is something I see. But now when I increase the concentration of the magnesium, what you see clearly is after a certain coverage so, this is somewhat in terms of coverage you have to see. Is that the C-O-C resonance is almost absent and then the C double bond O resonance is being actually shifted to a higher binding energy. So, that is what your observation is. So, this clearly indicates that the magnesium that you are doping must be going somewhere here, close to the C-O-C oxygen and also to the carbonyl oxygen. So, that means the magnesium is somewhat getting coordinated to this particular position. So, how do I see that? Because I see that the resonance corresponding to the C-O-C is almost vanished or maybe shifted downwards and that is what is written here with the O2. And, also you can see the carbonyl peak is basically just getting shifted also to the lower energy. So, that means also this oxygen is getting a bit more oxidized than its nascent state. This is quite interesting. So, now with this kind of spectrum I can clearly understand what is basically just going on at this kind of interface which is basically where I am doping the magnesium into the film itself. So, that means the molecules are now getting partly connected by the magnesium atom. So, this is quite interesting you can also do the same experiment with the dimethyl PTCDI. So, there you also see something interesting but quite different from what you have seen in the PTCDI case, because you can see here the magnitude of shift of the CO resonance in the case of PTCDI, and the magnitude here is very very very small. That is indicating somewhat, the magnesium is actually just going here but it is not as nicely occupying to this space as you have seen in the case of the PTCDI. So, that is actually due to the fact that you have this bulky methyl group nearby, so the magnesium is not really going and occupying there. But of course, what is happening is definitely at the site of oxygen the magnesium is somewhat interacting. But the interaction is very very weak because, you can see the shift is very small compared to this one because here the shift is basically very large. So, you can read out from the energy which is already giving you the bonding scheme inside. So, this analysis eventually gives me an indication about the bonding scheme of the molecular adsorbates inside the self-assembly of the molecules. So, now in general, so what I have here is actually a thin film of the PTCDIs and dimethyl PTCDI, and what I have basically just done is I have added magnesium to dope basically the surface, the film. And then we have actually just looked at the way the magnesium is actually interacting with the molecule. So, you now see that with this technique XPS you can basically make a clear understanding about what is going on within the film. So, in terms of the molecule-molecule interaction, the molecule-surface interaction because that is also the reason why I have discussed with you the case of carbon monoxide on different surfaces. You have seen there we can even understand the interaction of the molecule with the surface, and this is of course a case where I am talking about a thicker film, therefore it is unimportant about the molecule surface influence that is also something we have actually also seen in the case of UPS if you recollect for this molecule. We have also done something like a thickness or the coverage dependent, the thickness dependent experiment, there you already have seen that after about a certain number of layers you do not see any more the influence of the surface. You know so that is also something you have seen. So, that means as a combination of UPS and XPS you can understand basically the entire conduct, entire valence band, and also the core band. So, the valence band is important for us and to understand because that is the electrons which is actually responsible for the reactivity of a molecule, or when it comes to a charged transport, those are the electrons that are basically going to be getting transported because, that is the one with the lower binding energy.

But the electrons that are lying deep inside the core band is something which is also having that nice chemical information about how the interaction between the molecules, and also, the interaction between the surfaces is going on. So, with XPS we can therefore by looking at the oxidation state we can clearly understand the interface and also the chemical structure. So, that is the thing about the photoelectron spectroscopy. So, with this lecture I am trying to conclude the two photoelectron spectroscopy methods, and in the next lecture we would be looking at the molecular material 2-dimensional molecular material. I was planning to have that lecture in this but we will be looking at in the next lecture. So, there we would be also using again the same techniques. But we would be basically just using a combination of many techniques in order to clearly understand the microscopic, electronic, chemical structure of molecular or adsorbate on surface. With this like I like to conclude this lecture. Thank you very much.