The role of tin in surface bonding of CO to Pt(111)

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Abstract

We have used synchrotron radiation based photoelectron spectroscopy to study tin induced modifications in surface bonding of CO to Pt(111). Tin can form both so-called surface alloys, where tin replaces surface platinum atoms and ordered adatom structures where tin stays on top of the surface. The alloy is formed after annealing to 600 °C. The results from Pt(111) are in excellent agreement with previous literature, with CO binding in top site and in bridge site. On Pt(111)-Sn alloys we observe the same species, but with a reduced bridge site emission. Tin does not take direct part in the chemical bond to CO, but it influences the nearby Pt. On the overlayer structure we observe that CO binds directly to tin. Thus we conclude that the form of tin on the surface plays an important role in the surface chemistry of CO to tin modified Pt surfaces.
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Introduction

The importance of catalysts to produce chemicals or to clean exhaust gas cannot be over accentuated. It is indeed one of the corner stones in our society. In order to tailor a catalyst for a particular reaction a detailed picture of those reactions are needed on the molecular level. Surface science experiments on model systems coupled with detailed theoretical modelling are one viable route to a deeper understanding on how surface structure and composition influence the outcome of a reaction.

In this work the bonding of CO to well-ordered Pt(111) (1x1), Pt(111)-Sn (2x2) and (√3x√3) surface alloys and to Pt(111)-Sn adatom structures has been studied using X-ray photoelectron spectroscopy (XPS) of the C1s, Pt4f, Sn4d and O1s core levels. The experimental work was performed at Materialfysik at KTH-Electrum in Kista and at the national Swedish synchrotron radiation laboratory MAXLAB in Lund.

First I will present a few different models describing bonding of CO to metal surfaces, followed by a description of CO-oxidation, the influence of alloying other elements into a metal surface, the experimental set-up and presentation of the results and conclusions.
Bonding of CO to metal surfaces, a short review

Bonding of CO to metal surfaces has been studied for long times. This is motivated by the need to remove CO from exhaust gas. It has been noted that CO binds with different strength to different metals. This result is nicely summarized in Fig. 1a. (from [i]). One can see that the bond strength of CO to different metals decreases when going from left to right in the periodic table. On the right hand side the bond is weak and CO is easily desorbed from the surface at moderate temperatures. On the left hand side the interaction is so strong that CO can dissociate into C and O, see for example [ii].

There is also a structural dependence; the bond strength is different on different surface terminations on the same materials. This is shown in Figure 1b (also from [i]).

Figure 1; from I. Toyoshima, G.A. Somorjai, Cat. Rev. Sci. Eng. 19 (1979) 105.

a) the heats of adsorption of CO and O\textsubscript{2} over different transition metals,
b) the heats of adsorption for CO over different transition metals and their different surfaces
The reason for these variations can be found in the chemical bond between CO and metals. CO is isoelectronic, it has five $\sigma$-type orbitals and one $\pi$-type orbital fully occupied. We divide the chemical bond into $\pi$ and $\sigma$ interactions. These chemical bonds are strongly coupled. A re-distribution in the $\pi$ electronic structure will affect the distribution in the $\sigma$ electronic structure, because they are coupled through the interactions between electrons. Figure 2 depicts the construction of the molecular orbitals in CO from the atomic orbitals in C and O. The highest occupied orbital (HOMO) is $5\sigma$ and has contributions from C2p only, the lowest unoccupied molecular orbital (LUMO) $2\pi$ is composed of C2p and O2p.

![Diagram of molecular orbitals in CO](image)

**Figure 2.** Schematic picture of which atomic orbitals contributes to different molecular orbitals in CO.(from reference iii )
In surface science, the so called Blyholder model is generally spread among surface scientists. It was originally a way to explain the interactions between CO and metal surfaces [iv]. The term “Blyholder model” has normally become associated with a frontier orbital description, involving a donation from the 5σ orbital and a backdonation into the empty 2π* orbital. The frontier orbital model has explained vibrational shifts induced upon adsorption and provides a simple scheme for the bonding, which helps understanding many interactions. A more elaborated theory was presented by Föhlisch et al [v] which includes all molecular orbitals. There are two strong contributions to the bonding between the metal and CO; from the σ-d and the π-d interactions. Although they are both strong, they are opposite (σ is net-repulsive and π is net-attractive [v]) and it is the balance between the σ and π interactions that determines the bond strength and the heat of adsorption of CO on different metals and also explains why it is usually small in comparison to the internal C-O bond.

In the “Hammer-Nörskov” model [vi], the d-band centre determines the position of the molecular orbitals compared to the Fermi level. This is schematically described in Fig. 3, including only the frontier orbitals contribution to the surface chemical bond. The 5σ is located below the Fermi level and 2π* is located above the Fermi level. The interaction of these orbitals with the Pt s,p band broadens the molecular orbitals. They are also pulled down in energy, determined by the surface potential. Obviously, the interaction can pull the 2π* orbital below the Fermi level and consequently allow for charge injection into this state. The 2π* orbital is anti-bonding for the CO, thus more electrons will weaken the CO bond. Further, the interaction (hybridization) with the Pt d-band splits the σ and π states into bonding and anti-bonding contributions. According to Hammer and Nörskov, it is the Pt-d to 2π* interaction that is more important. The amount of charge in the 2π* is critically determined by the Fermi level and the position of the d-band. With less d-electrons (to the left in the periodic table) the d-band moves up with respect to the Fermi level and the molecular orbitals follows, the anti-bonding states are emptied and the bond strength increases, in agreement with Fig 1.

Different sites on the metal surface will have different d-band widths and d-band positions [vi], in addition the geometry at the adsorption site determines the geometric overlap of the metal d-states and molecular orbitals and thus the bond strength.
Figure 3. Development of CO molecular orbitals in the free molecule and after interaction with the metal electrons. From reference vi.

CO-oxidation

In order to oxidize CO to CO$_2$ one adsorbed CO has to react with one adsorbed O. They are typically sitting in different sites and in order to meet they have to migrate over the surface. The mobility of the adsorbed species on the surface is determined by the energy barriers they encounter on their way. It is thus important to understand how and why these molecules/atoms bind to a surface and which energies are involved.

In a paper by Dupont et al [vii] isolated adsorption of CO and O has been considered first to reveal the competitive structures. Once the competitive sites have been determined, co-adsorption between CO and O has been considered. Among the possible reaction pathways reported for CO oxidation on Pt(111), two different mechanisms have been retained. The reaction between co-adsorbed CO and O$_2$ and the reaction between adsorbed CO and dissociated O. On PtSn surfaces, CO adsorption on tin is not stable. Among the energy contributions of PtSn alloy surfaces toward CO oxidation, a correlation is evidenced between the decrease of the barrier and the strengthening of the interaction energy between CO and O moieties. Along the reaction pathways, a CO$_2$ is obtained on all the surfaces. The oxidation pathways reveal a lowering of the activation energy barrier and an asymmetric structure for the transition states on PtSn surfaces. The promoter effect of tin has been elucidated with an energetic model which links the activation barrier and the variations of the re-bonding energy summed over the separate adsorbed reactants and of the interaction energy between CO and O moieties. On all the surfaces, a mechanism involving chemisorbed CO$_2$ surface intermediate.
Surface alloying, modifying the electronic structure

One way to tune the surface bond and to modify the energy barriers is to add another element to the catalyst material, for example by alloying. Modifying a clean surface by deposition of a metallic additive leads to different structures depending on the growth mode. Two-dimensional overlayers or three-dimensional islands can be obtained. Alloying might also be observed depending on the deposition / annealing temperature.

Tin modified platinum catalysts are of big interest in heterogeneous catalysis, affecting selectivity in hydrogenation and oxidation reactions. Platinum-tin surface alloys have received some attention with respect to the selective hydrogenation of α, β-unsaturated aldehydes [viii, ix]. The Pt(111)-Sn (√3x√3) surface alloy is one of the most commonly studied surfaces in this system and it has been found that the selective activation of unsaturated functionalities is sensitive to the Sn:Pt ratio [x, xi].

The Sn/Pt(111) system has the advantage of presenting several surface structures, depending on the initial tin coverage and the annealing temperature, see figure 4, which is a surface phase diagram of the Pt(111)-Sn system. For an initial Sn coverage below 0.6 ML and substrate below 450 K, T. Paffet reported the formation of ordered overlayers [xii]. The LEED pattern observed goes from a (√3x√3)R30º for the lowest coverage to a c(4x2) pattern at 0.6 ML.
Formation of the surface alloy requires sample annealing at temperatures above 450K. The main interest of having a surface alloy lies in the possibility to vary the surface chemical composition while the surface structure remains more or less unchanged. Two ordered surface alloys can be formed, both formed by selective substitution of Pt-surface atom by a Sn atom; at ¼ ML coverage a (2x2) structure is observed and at 1/3 ML a (√3x√3) is seen. The model in figure 5 shows the resulting structure and also two possible overlayer structures with the same LEED patterns.

In LEED and XPD, it appears that in both surface alloys the tin atoms are incorporated into the first Platinum layer. On this particular surface the atomic structure is modified very little; tin atoms are 0.22 Å higher than Pt, but the electronic structure changes. In a theoretical study by Rodriguez et al [xiii], a Sn(5s,5p) -> Pt(6s,6p) charge transfer was suggested together with a Pt5d – Pt(6s,6p) rehybridisation. Recent theory show that tin induces a negative polarisation of Pt and down shifts the d-band centre [xiv]. Experimentally it has also been shown that the local density of states on Pt is reduced [xv], which modifies the donating as well as accepting capacity of Pt, thus the bond strength of CO on Pt.
Figure 5. Some structures on Pt(111)-Sn. To the left overlayer structures with Sn atoms on top of the Pt surface and to the right surface alloys with tin in the platinum surface. From [Error! Bookmark not defined.]

The purpose of our experiment

With this study we want to compare how alloyed and adatom tin influences the bonding of CO to Pt(111). We have used synchrotron radiation based photoelectron spectroscopy which is very sensitive to difference in the electronic structure and bond geometry.
Photoelectron spectroscopy (PES)

Photoelectron spectroscopy is a powerful technique in physics and chemistry. The technique is based on photoelectric effect as mentioned above. Albert Einstein first explained this in 1905. A photon with the energy $h\nu$ penetrates the surface of a material, and is absorbed by an electron with binding energy $E_B$, which then emerges from the surface with a kinetic energy $E_k$. The kinetic energy is related to the binding energy through $E_k = h\nu - E_B - \phi$, where $\phi$ is the work function of the sample. The basic idea of PES is to analyse the kinetic energy of the emitted electrons and to determine their binding energies.

Photoemission is quantum mechanically described as a one-step process, where the electron is taken from its ground state inside the material and deposited at the detector. The photoemission can for clarity be described in a three step model:
- In step one, excitation from an initial state, an electron is excited by absorbing a photon $h\nu$ in a process where both energy and crystal momentum are conserved.
- In step two, transportation to the crystal surface, the electron propagates from the excitation volume to the sample surface.
- In step three, escape through the surface into vacuum, the electron may escape from the material into the vacuum if its kinetic energy $(h\nu - E_B)$ is higher than the vacuum level energy $E_V$.

PES can probe two kinds of electronic states: the core and the valence band levels. Core level binding energies are first of all element-specific, so we can identify which atoms are present on the surface. Secondly they are sensitive to the chemical environment such as adsorption, breaking of the bulk crystal structure and reconstructions which induces binding-energy shifts for the core electrons of the surface atoms compared to the bulk atoms. Although the core levels are not directly involved in the formation of chemical bonds, they are sensitive to the bonding environment around an atom, which corresponds to a specific distribution of charges, screening the positive charge of the nucleus in the region occupied by the core electron. The energy of the core electron is determined by its interaction with the screened charge of the nucleus, therefore the chemical environment of an atom can induce changes in the core level binding energy. The shifts in energy between the core levels of free atoms and chemically bound atoms are called chemical shifts. Core level binding-energy shifts can be divided into initial state and final state effects. The initial state effect includes
chemical shifts. The final state effect includes screening and relaxation shifts that occur after the core level has been ionised.

The principle of the photoelectron spectroscopy process is schematically represented in the figure 6. Photoelectron spectroscopy is a photon-in and electron out process. An electron is excited from its previous level to a higher level.

![Figure 6. Schematic description of the photoemission process.](image)

The XPS set-up

XPS experiments were done both in Kista, using a Mg Kα source from Omicron Nanotechnology and a VSW hemispherical electron analyser, and at MAXLAB in Lund using synchrotron radiation from an undulator beamline and a Scienta electron spectrometer. Synchrotron radiation based research is performed on both the MAX I (550 MeV), the MAX II (1.5 GeV) and the MAX III (700 MeV) storage rings. The synchrotron radiation from the three storage rings covers the wave-length range from the far infrared through the UV, VUV, soft x-ray up to the hard x-ray range using radiation from bending magnets or insertion devices. Among the techniques used at these beamlines are infra-red spectroscopy and microscopy, VUV and soft x-ray electron spectroscopy and microscopy, soft x-ray magnetic
circular dichroism, x-ray fluorescence, x-ray absorption spectroscopy and a wide range of different x-ray diffraction and scattering techniques.

The preliminary experiments in Kista were done to calibrate the evaporator and to learn how to prepare the surface. However, the resolution and sensitivity of that system is not good enough for detailed investigations. Furthermore, with synchrotron radiation we can change the photon energy and thus change the sensitivity.

A picture of MAXLAB is shown in Figure 7 with the three rings indicated. The red arrow indicates where beamline I511 is located.

![Figure 7. Overview of MAXLAB, from MAXLAB home page](image)

The beamline is mounted on the MAX-II storage ring as shown in the figure above. Beamline I511 is an undulator based VUV, soft X-ray beamline aimed at high resolution High Pressure X-ray Photoemission Spectroscopy (HP-XPS), X-ray Absorption Spectroscopy (XAS), and X-ray Emission Spectroscopy (XES). The beamline has two branch lines, I511-1 and I511-3, utilizing a common undulator a monochromator with a flip-mirror placed immediately after the exit slit to direct the radiation alternately into these two stations. The I511-1 experimental station (HP-XPS) is equipped with analyzers for XPS and XAS on surfaces under near-ambient pressure conditions.
In the ring electrons orbit at 1.5 GeV energy. When these high-energy electrons are accelerated by a magnetic field they emit synchrotron radiation. The wavelengths emitted depend on the magnetic field and the electron kinetic energy. The undulator, shown in Figure 8, is an array of magnets, which generates a wave like motion of the electrons. At each turn they emit radiation and if they are put on proper distances the emission from each bend can interfere constructively to achieve very high intensities. The light is also polarized in the plane.

Figure 8. An undulator, from www-xfel.spring8.or.jp
The light is thereafter guided to a monochromator, shown in Figure 9, which only lets a narrow wavelength interval pass through the exit slit. Mirrors guide the monochromatic light to the sample where photoemission takes place.

Figure 9. The inside of a SX-700 monochromator, from www.bessy.de

Figure 10. The outside of a SX-700 monochromator, from www.maxlab.lu.se
In the photoemission chamber the light hits the sample and the electrons are emitted into the analyzer, shown in Figure 11. The electrons are directed by lenses to the entrance slit of the hemisphere. In the hemispherical part a voltage is applied between the inner and outer hemisphere which bends the electron path. Different kinetic energies are bent differently so only those electrons with the “right” energy will hit the detector.

**Figure 11.** The inside of a hemispherical energy analyzer, from Hans Lüth, “Surfaces, interfaces and thin films” Springer Verlag

**Figure 12.** The outside of a R4000 Scienta analyzer, from VG-Scienta Broschure
Extracting detailed information from curve fitting analysis

In order to extract chemical and physical characteristics from the core level spectrum, a detailed analysis is necessary. Typically an experimental spectrum is numerically fit using one or several components. Each component represents a group of atoms on the surface with a specific environment that results in a specific binding energy. The intensity of each peak is related to the relative amounts of that particular atom in the surface. The intensity is also influenced by the so-called, photoionisation cross-section, the probability that a photon will be absorbed an en electron being emitted. The number of peaks or components included in the fit is determined by the experimental line shape, and how well the components reproduce the spectrum. If one component is not sufficient, another has to be added and so on.

The width of the core level peaks results from several factors. A broadening mechanism comes from the limited lifetime of the hole left behind by the photoemitted electron. The lifetime is determined by the effectiveness of the relaxation processes. Short lifetime leads to broad peaks and can therefore limit the use of surface core level spectroscopy. The line shape is Lorentzian for this broadening ($W_L$). A second important source of broadening comes from the sudden change in core-potential with the emission of the photoelectron. This shakes up phonons, due to different bonding of the atom to the environment in the ground state and the ionised state. Recent studies have revealed that on metals, the phonon broadening is often small and difficult to separate from the instrumental broadening. Also limited experimental resolution and defects will contribute to this Gaussian shaped ($W_G$) broadening.

Background intensity is also present, in addition to the core level peaks. This is the result of photoelectrons suffering energy losses due to inelastic scattering events and also due to secondary electrons created in the process. The cross-section for scattering is small at high $E_k$ and the trouble with fitting of the background can usually be avoided by choosing high enough photon energy. The background can be exponential, linear or integrated.
Surface preparation and evaporator calibration

The Pt(111) surface was prepared by sputter-annealing cycles. Sputtering was done using 1000 eV Ar\(^+\) ions accelerated towards the surface. After sputtering the surface was re-ordered by annealing at 700 °C. To remove residual carbon, the sample was annealed in O\(_2\)-atmosphere (2\(\times\)10\(^{-6}\) mbar) at 550 °C for 10 minutes.

Sn was evaporated from a tungsten filament-coil on to which tin had been melted. The evaporator was calibrated using a quartz-crystal monitor (QCM). This is a quartz-crystal that is set to vibrate at its resonance frequency. When something is deposited onto the surface the eigen frequency changes, and the weight of the deposited material can be measured.

CO exposures were done using a precision leak valve. The pressure during CO-dosing was 1\(\times\)10\(^{-7}\) Torr. The total dose is given in units of Langmuir (L) where 1 L = 10\(^{-6}\) Torr\cdotsec. Here 1 L is reached after 10 seconds at 10\(^{-7}\) Torr. The surface was saturated with CO at 10 L.

Surface order and LEED

In surface science, LEED is one of the most used techniques to characterise clean surfaces and overlayers. In a typical LEED experiment, a beam of mono-energetic electrons, in the range 20-500 eV is backscattered from a crystal surface. The wavelength of these electrons (about 1 Å at 100 eV) is of the order of the inter-atomic distances in crystal lattices. So the electron waves interfere when scattered by individual lattice points. The backscattered electrons are detected on a fluorescent screen (see Fig. 13) where a diffraction pattern is observed. The spot size is inversely proportional to the domain size on the surface. So increased surface order is reflected by a decreased spot size and background intensity on the LEED screen.

Figure 13. The LEED set-up
Results

Pt4f7/2 core level spectra recorded from different preparations are presented in Fig 14. On the clean surface, a surface shifted component (S) is resolved on the low binding energy side [xvi,xvii,xviii]. The surface shift (ΔES) is 0.39 eV in good agreement with literature [xviii]. The intensity of S corresponds to the top monolayer of Pt atoms on this surface. After deposition of ca 1/3 ML of tin on the surface, S is weaker, but the shift is the same. In the Pt(111)-Sn (√3x√3) the surface shift, ΔES1 is 0.25 eV, and the intensity is higher again. When the tin is just deposited it binds as shown in the left part of figure 5 each tin atom binds to three Pt. For those Pt that bind to Sn the surface shift is changed and the intensity of S is reduced. When the surface is heated and ordered in (√3x√3) the tin replaces platinum in the top layer and there are more Pt-atoms on the surface. The smaller surface shift is because the electronic structure in the alloy is different than on the clean Pt(111) surface.

Figure 14 Pt4f7/2 spectra from three different surface preparations.
Figure 15 shows four Pt4f spectra from Pt(111) after different CO-doses. The surface peak S is reduced and new peaks appear on the left side of the spectrum. At 15 L CO the bulk peak is weaker and original surface peak is also reduced dramatically from 53.7% (1 monolayer) to 16.3% which means that large amount of the surface Pt are not bound to CO. Pt atoms binding to CO are shifted to higher binding energy, C2 at 0.31 eV and C1 at 1.02 eV, with respect to the bulk component. These shifted components are related to CO in top site (C1) and CO in bridge site (C2) [xvii]. The different shifts can be explained from the larger impact a CO will have on one single Pt (top) compared to one CO for two platinum atoms (bridge). The relative intensities of these components are 32.2% (C2) and 17.4% (C1), which means that there are almost equal amounts of bridge bonded CO and top site CO. It is usually believed that ca 0.5 ML is needed to saturate the surface [xix]. Not all Pt are bound to CO. This is because the lateral dipole repulsion between adsorbed CO.

![Pt4f/2 spectra from Pt(111) with different amounts of CO.](image)

Figure 15 Pt4f/2 spectra from Pt(111) with different amounts of CO.
C1s spectra from CO on Pt(111) has two components, the one at higher binding energy is from top site CO and the one at lower binding energy is from bridge bonded CO. The top site is first occupied at low coverage and at higher coverage the bridge site is populated. The top site peak looks broader, with some weak structure on the high binding energy side. This is due to excitation of CO-vibrations by the emitted electron. The bridge bonded peak has also a weak structure on the high binding energy side. It is also due to vibrational excitations.

The difference in binding energy is determined by the difference in electron density around the C atom; in the bridge site C binds to two Pt and is closer to the surface and the surface electrons, this gives a chemical shift to lower binding energy.
Figure 17 Pt4f7/2 spectra from Pt(111)-Sn (√3x√3) with different amounts of CO.

Figure 17 is a set of Pt4f7/2 spectra recorded from the Pt(111)-Sn (√3x√3) surface at different CO doses. The initial surface shifted component is strongly reduced. Two new components, C1 and C2, with similar origin as on Pt(111) appear after CO dosing. The CO induced chemical shifts are, C2 at 0.35 eV and C1 at 1.06 eV, with respect to the bulk component. The C2/B intensity is almost the same as on Pt(111)-CO, indicating that the amount of bridge bonded CO is similar. C1, on the other hand, is much weaker than on Pt(111) (~0.15 ML). There is also a higher amount of surface Pt not affected by CO, as compared to Pt(111).
Sn 4d core level spectra recorded using 125 eV photon energy are shown in figure 18, from the (√3x√3) surface before and after CO dosing to saturation. There is only one component in the spectra. There is no change in shape but only a small shift of 100 meV to higher binding energy upon CO adsorption. In a previous study of croton aldehyde adsorption on Pt(111)-Sn (√3x√3), a similar 100 meV shift to higher binding energy was observed, due to Sn-O coordination [xviii]. Thus, it cannot be excluded that Sn takes part in the bond to the adsorbate, although not through a strong direct chemisorption bond.

Figure 18: Sn 4d spectra recorded from the Pt(111)-Sn (√3x√3) surface with and without CO.
When the surface is not heated properly after deposition the tin is not incorporated in the top layer, it stays as adatoms on top of the Pt surface. This affects the surface reactivity.

Figure 19: Pt4f$_{7/2}$ spectra recorded from Pt(111)-Sn without heating with and without CO, compared to the CO saturated Pt(111) surface (top).

Figure 19 shows two Pt4f spectra from the Pt(111) with deposited and not annealed Sn and with CO. The initial surface shifted component is reduced compared to the clean Pt(111) surface, as shown in figure 14 previously. CO adsorption reduces the surface shifted intensity even further. Instead a new component appears at higher binding energy. The shift agrees with top site bonded CO as discussed above. There is also bridge bonded CO, but less than on the Pt(111) surface. This is because tin blocks the Pt atoms and top site is the most accessible.

On the well prepared Pt(111)-Sn ($\sqrt{3}$x$\sqrt{3}$) surface alloy tin is not directly involved in the chemical bonding to CO. On other surfaces with “non-alloyed” tin on the surface it is a little bit different. In figure 20 Sn4d spectra from some different PtSn surfaces are presented. At low coverage after too low heating both alloyed tin and tin adatoms exist on the surface. The adatoms have a lower binding energy. After CO adsorption this component disappears. The adatoms react. But the alloy peak does not change. At room temperature (RT) deposition
without annealing the adatom peak is much stronger than the alloy peak. After CO exposure
the adatom peak shifts to higher binding energy, by 0.3 eV. This is similar to the Pt4f shift
from bridge bonded CO. Thus, one could suggest that CO binds to tin in bridge position. But
the chemical shift is not necessarily the same for all atoms, so the results are not conclusive. It
is clear though, that Sn is reactive towards CO, when not alloyed.

Figure 20: Sn4d spectra from different Pt(111)-Sn surfaces with and without CO.
Figure 21: C 1s spectra recorded from the Pt(111) and Pt(111)-Sn (√3x√3) surfaces with CO.
Figure 21 presents C1s spectra recorded at 398 eV photon energy from the CO dosed Pt(111) and Pt(111)-Sn surfaces. There are two components; from top site CO and from bridge bonded CO as before. Addition of a small amount of tin and annealing generates a weak additional (2x2) structure. The peaks broaden a little bit. Additional tin results in a mixed (2x2) and (\(\sqrt{3}\times\sqrt{3}\)) structure, with a C1s spectrum that looks very similar. However, when the surface turns into purely (\(\sqrt{3}\times\sqrt{3}\)) the spectrum changes and only the top site CO signal is left. The spectrum is essentially the same for CO on the Sn-adatom layer; only top site CO. These results show that in the alloy tin blocks the bridge sites in agreement with previous findings [xv]. It also presents new results; the adatom tin structure allows top site CO, that binds to Sn (as shown before by the Sn4d spectrum). It is thus clear that the form of tin is important; is it an alloy or is it an adatom structure.

O1s spectra were recorded at 640 eV photon energy. They are presented in figure 22 show two components; \(O_t\) and \(O_b\) at 532.7 eV and 531.0 eV, respectively. The assignment follows that from Björneholm et al [xvii]. The relative intensity on Pt(111) is higher for \(O_t\) than \(O_b\), also in agreement with Björneholm. Again the top site related component is reduced when tin is present on the surface, and the width of \(O_b\) increases slightly. There is no sign of atomic oxygen in the spectra, the expected core level binding energy is 529.4 eV on Pt(111) [xvii] and 529.5 eV on Rh(111) [xx].

![O1s spectra recorded from two CO saturated surfaces.](image)

**Figure 22**: O1s spectra recorded from two CO saturated surfaces.
Summary and conclusions

We have used photoelectron spectroscopy to study tin induced modifications in the surface bonding of CO to Pt(111). The results from Pt(111) are in excellent agreement with previous literature, with CO binding in top site and in bridge site. On Pt(111)-Sn alloys we observe the same species, but with a reduced bridge site emission. Tin does not take direct part in the chemical bond to CO, it influences the nearby Pt.

As-deposited tin stays on top of the surface and forms an adatom structure. We observe CO adsorption directly to tin. Thus we conclude that the form of tin on the surface plays an important role in the surface chemistry of CO to tin modified Pt surfaces.

References