

Bremsstrahlung Isochromat Spectroscopy (BIS)

*A Special Case of Inverse
PhotoElectron Spectroscopy (IPES)*



ELECTRON SPECTROSCOPY (CY – 653)

Quiz II – Seminar

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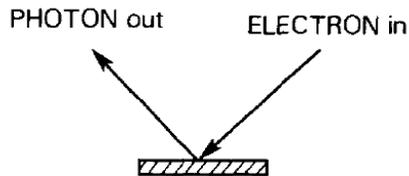
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Bremsstrahlung Isochromate Spectroscopy (BIS)

Introduction

Bremsstrahlung, is a composite word in German made of “Brems” meaning “brake” & “Strahlung” meaning “radiation”. “Iso” “same” & “Chromos” “color”. Tending to meaning that the resonance spectroscopy that is done using very high energy radiation. It is a well known fact that PES can be performed in the reverse mode, i.e. by sending electrons of varying energy onto the sample and detecting the photons produced by them. This technique of sending the “electron” in and detecting the “photon” out process is termed as *Inverse PhotoElectron Spectroscopy (IPES)*.



In simple words, it's an electron in photon out process. It must be noted that photons of all energies are detected in this technique. However if only photons of one particular energy are detected, as is done generally, the technique is termed as *Bremsstrahlung Isochromate Spectroscopy (BIS)*.

Complementary nature of PES & IPES:

The figure below demonstrates the complementary nature of PES & IPES. The energies are referenced to the Fermi level E_F .

PES:

$$\begin{aligned}h\nu &= E_f - E_i, \\- E_i &= h\nu - E_{kin} - \phi \\E_f &= E_{kin} + \phi \\ \text{Since } - E_i &= EB; \\EB &= h\nu - E_{kin} - \phi\end{aligned}$$

IPES

$$\begin{aligned}h\nu &= E_i - E_f \\E_f &= -h\nu + E_{kin} + \phi \\E_i &= E_{kin} + \phi \\ \text{Since } E_f &= -EB; \\- EB &= -h\nu + E_{kin} + \phi\end{aligned}$$

It might initially seem that PES measures an initial state energy while IPES the final state, however is misleading, both spectroscopies measure only the final state.

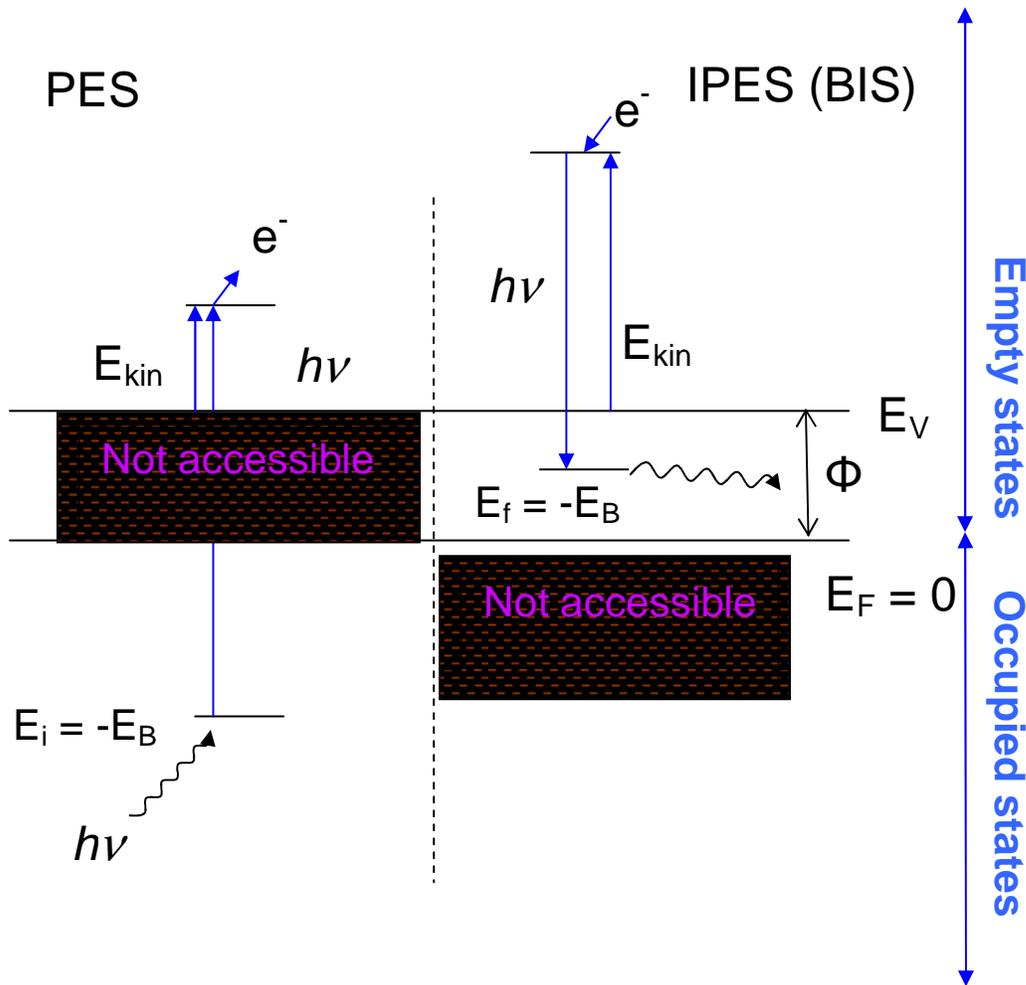


Figure 01 - Comparison of PES & IPES

IPES probes the “empty” energy levels, thus detects the level above E_F . PES probes, occupied levels, i.e. below E_F and above E_V . Thus IPES is a very vital technique to probe the region between E_F and E_V .

The serious research in IPES began around the 1960, when X-rays as photons to be detected using crystal monochromator. This however had a disadvantage that quite high fluxes of electrons had to be employed, that in turn put more restrictions on the samples used and also on the exposure time of these samples to the radiation. Dose’s discovery of a gas proportional counter solved this problem, which had a very high efficiency for the detection of photons of 9.7 eV.

The Dose’s detector is a Geiger Müller counter, with stainless steel tube of 20 mm diameter, with stainless steel electrode, filled with about 100 mbar of multiplier gas, Argon. Few crystals of I_2 act as the detecting agent, which produce iodine vapor in the cell, the threshold for this being 9.23 eV. The entrance window of the proportional counter is a 2mm thick CaF_2 crystal, transparency cut-off ~ 10.2 eV (Figure 02 gives a cross-section of this). The combination of photo-ionization cross-section of I_2 and CaF_2

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detects in the range 9.7 ± 0.40 eV. The sensitivity can also be enhanced by using a mirror to collect the radiation as shown in figure 03.

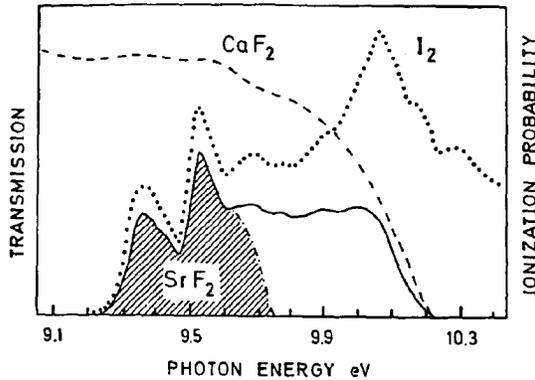


Figure 02 - Transmission spectra of CaF_2 , SrF_2 , Absorption of I_2 , Convolution curve.

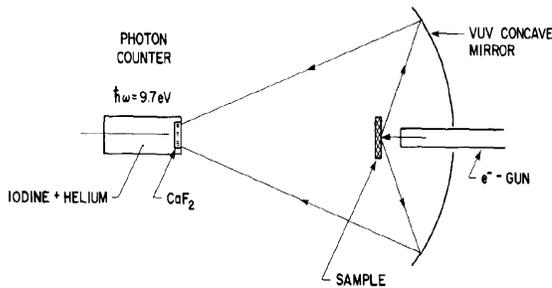


Figure 03 – Arrangement for the experimental setup for *IPES* using GM counter. (Dose Detector)

More such innovations followed in the form of detectors where a photo-multiplier was used to detect the photons. As the photo-multiplier is made of a series of electrodes with increasing potential down the cell, the electrons produced by the impinging photon intensity is increased, each electrode called as the DYNODE. Range of 9.9 ± 0.3 eV was obtained using a KBr evaporated on the first dynode in combination with CaF_2 window. Grating monochromators were also used to increase the resolution. However the use of SrF_2 instead of CaF_2 provided a two fold increase in the resolution of detection as the frequency window gets more narrowed down, 9.5 ± 0.3 eV. This can be very well understood from figure 02 as the area of the $\text{SrF}_2 + \text{I}_2$ is almost half of that of $\text{CaF}_2 + \text{I}_2$. The threshold for CaF_2 transmission being 10.2 eV, SrF_2 being 9.75 eV.

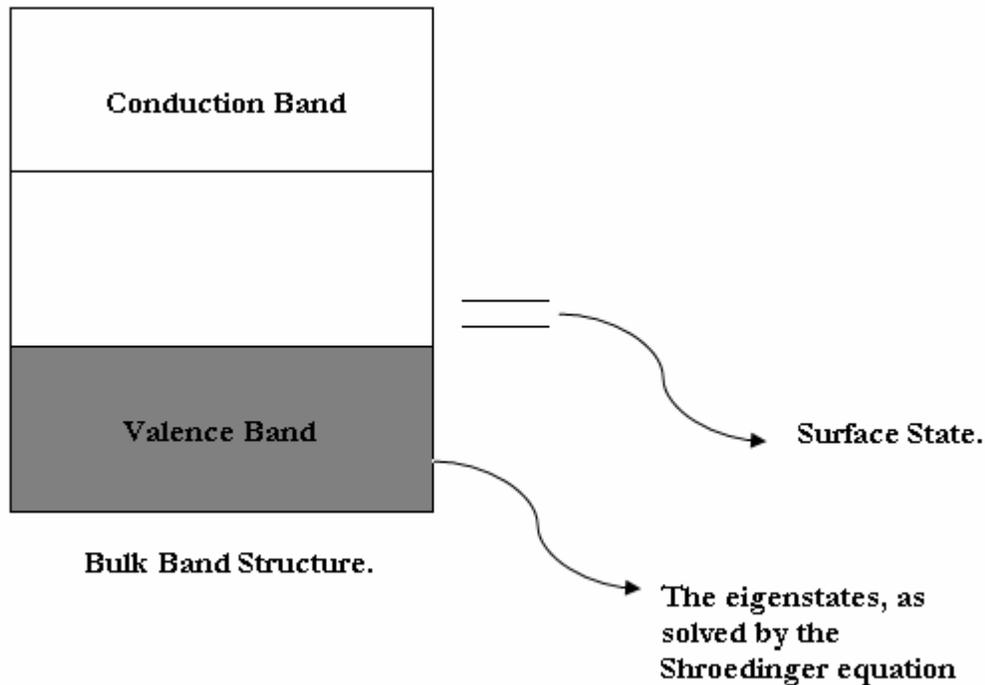
Applications of BIS have been in three major fields:

1. Determination of surface states energies in a system.
2. Elucidation of the bulk band structure.
3. Interaction of adsorbed molecules on a surface.

Beginning with the first application, namely the determination of surface states energies in a system, we first need to know what a surface state means. Before that, a bulk band structure for a metal is known. Now, these correspond to the 2D projection of the density of states of the energy levels that are calculated using the Shroedinger equation. However due to distortions (or any impurities) the energy level of the atom will be “off” this band,

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either lying above or below the valence band. An illustration below shows a bulk band structure with surface states above the valence band.



Every atom in the lattice has its own "image". Once this is been used to calculate the energy values of the atom, we get an image potential, which once again lies anywhere above or below the valence band. Since this surface state rests between the E_F and E_V levels its best probed by IPES. As an example the Cu(100) was probed under two conditions, one in the clean state and the other adsorbed with the CO.

The clean spectrum is dominated by an asymmetric peak near E_F which can be resolved into two peaks as shown. The dotted trace in the figure show the experimental points and the smooth curve gives the data with the background subtracted. Resolving the peak gives a broad peak at around E_F and a shoulder nearby 1.1 eV. The main peak has been interpreted as a direct transition in the bulk band structure while the shoulder is due to the surface state. Covering the surface with CO causes the surface state to disappear while the direct transition is hardly changed.

A more extended spectrum is shown in figure 05 from the Cu (100) surface at a higher temperature ($T = 900\text{K}$). In these spectra an additional structure at a E_B of -4 eV is seen, interpreted as the image potential state expected at 0.55 eV less than E_V . Confirmation of this assignment comes from the temperature dependence of the intensity of this state, with the main peak reducing in intensity due to Debye - Waller effect, where intensity is proportional to $\exp(-2W)$, W being a function proportional to T . Thus with increase in T , the intensity reduces.

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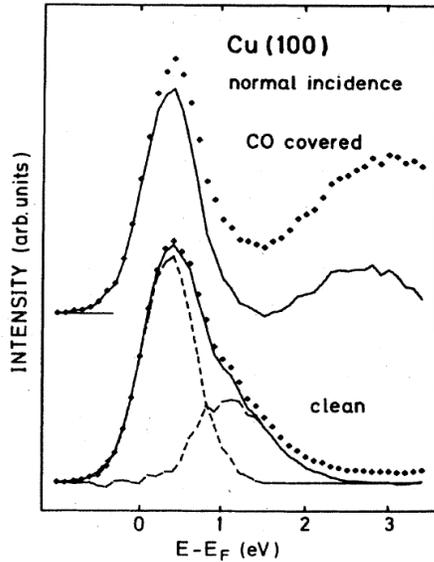


Figure 04 – BIS of Cu (100), clean (bottom) and CO adsorbed (top).

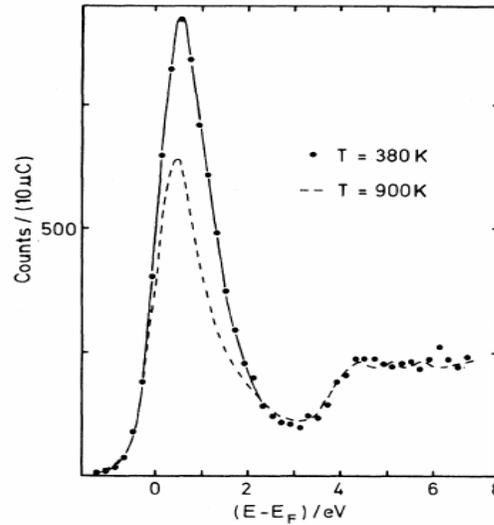


Figure 05 – Temperature dependence of BIS. (Debye-Waller Effect)

Observing an image-potential or barrier induced surface state comes from the fact that the state is pinned to the vacuum energy, as predicted by,

$$E_v - E_n = \frac{0.85}{\left(n + \frac{1}{2} - \frac{\epsilon}{2}\right)^2} \text{ eV, where } n = 0, 1, 2, \dots, \epsilon \text{ the permittivity of the medium,}$$

equal to one for vacuum. This thus reduces to $E_v - E_1 = 0.85 \text{ eV}$.

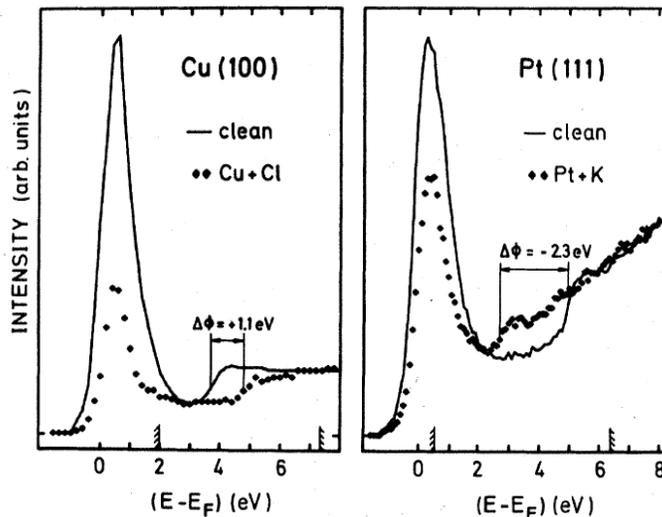


Figure 06 – Effect of work function change on the energy of the barrier induced surface state.

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The spectrum of clean Cu(100) is compared to that of the one coated with c(2X2) overlayer of Cl for which the work function is increased by 1.1 eV, the surface barrier state increases in energy as indeed it should as it is pinned to the vacuum level as predicted by the above equation. Conversely for Pt (111) the adsorption of K lowers the work function, as seen above.

A compilation of image Potentials of few metals (E_B) in eV; Au(100) – 0.63, Ag(100) – 0.5, Cu(100) – 0.6, Ni(100) – 0.4, Sb(100) – 0.76, Ni (111) – 0.6. This shows that binding energies fall in a narrow range between 0.4 – 0.85 eV in general.

Now, moving on to the next application of elucidating the bulk band structures, usually the sample needs to be probed for a reasonable amount of time as in BIS we will be monitoring only one of the energy, and there are other transitions too that occur. However an optimum time must be reached as more exposure can lead to damage of the sample, which is not inherent to this technique, thus the information attainable is restricted. It must be noted that PES measurements gives a well defined values for the unoccupied bands, IPES has been used mostly to check the accuracy of the assumed position of the unoccupied bands.

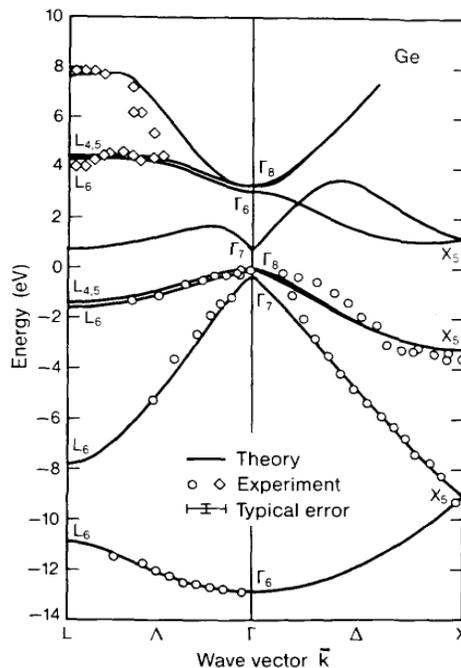


Figure 07 – Band Structure for Ge. Data for PES & IPES are combined to check the theoretical prediction of the band structure.

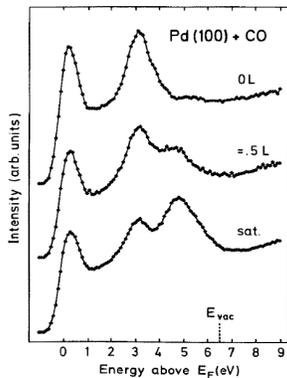
The above figure (07) is an example where band mapping was performed for Germanium by combination of PES & IPES. It can be realized that the two techniques compliment each other quite nicely in addition to the concurrence with the theoretical prediction.

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Finally, utilizing BIS to study the interaction of adsorbed molecules on a surface is a significant application. By its very nature IPES is suited well for the study of energy levels between E_F & E_V . A case in point is the anti-bonding orbital of molecules adsorbed on substrate surfaces, the discussion here is presented by comparing the IPES data for CO & NO adsorbed on Pd. Pd is chosen as the substrate because it induces very little NO decomposition.

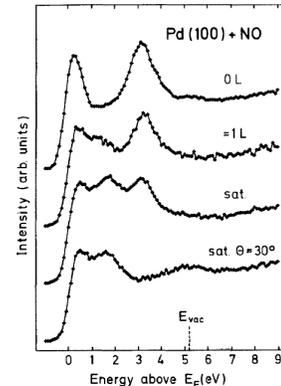
The electronic configuration being, $(\sigma_g 2s)^2 (\sigma_u 2s)^2 (\sigma_g 2p)^2 (\pi_g 2p)^4$ for CO. NO has $(\pi_g 2p)^1$. The nature of the respective orbital being bonding or anti-bonding can be deduced from the symmetry labels. The smallest ionization energy of CO gas is the $(\pi_g 2p)^4$ photoionization of 14 eV, whereas that of NO being 9.3 eV $((\pi_g 2p)^1)$.

Chemisorption of CO & NO are studies on Pd. One must invoke the concept of back donation of electrons from the metal to the adsorbed species that is CO / NO. This leads to a lowering of the energy levels and sometimes even occupation of the levels that are not occupied in the gas phase. The $2\pi^*$ level of CO can be less tightly bound than that of NO which can be inferred from the figure shown below.



← Figure 08 - BIS of CO on Pd(100)
Observe around 4.5 eV

Figure 09 - BIS of CO on Pd(100) →
Observe around 1.5 eV



The clean Pd(100) shows a two peaked IPES. Adsorption of CO / NO adds a further peak, but leaves the metal signal largely unaltered. The NO signal is nearer the Fermi energy than that of CO, as is to be expected from the above discussion, which in turn reflect the stability of the intra-atomic bond of the molecule in the chemisorbed state. In NO the $2\pi^*$ state can be easily filled by back donation from the metal because it is at E_F , thus NO exhibits greater tendency to get chemisorbed than CO.

Another interesting observation is made looking at the PES & IPES of Pd(100)/NO (Fig. 10). The 2π level is seen in both the cases!! The E_B in PES & IPES being 2.5 eV & -1.5 eV respectively. This is puzzling due to the fact that, it can either be observed in PES or in IPES. This can be understood as follows. In the initial state, the level is half occupied and is thus pinned to the E_F . In PES this electron is removed and one observes the 2π hole state at 2.5 eV below the Fermi energy level. Conversely a 2 electron $2\pi^*$ level is observed in the BIS. This shows the correlation energy of the 2π & $2\pi^*$ levels, which happens to be ~ 4 eV, compared to the 9.5 in the neutral isolated gaseous state.

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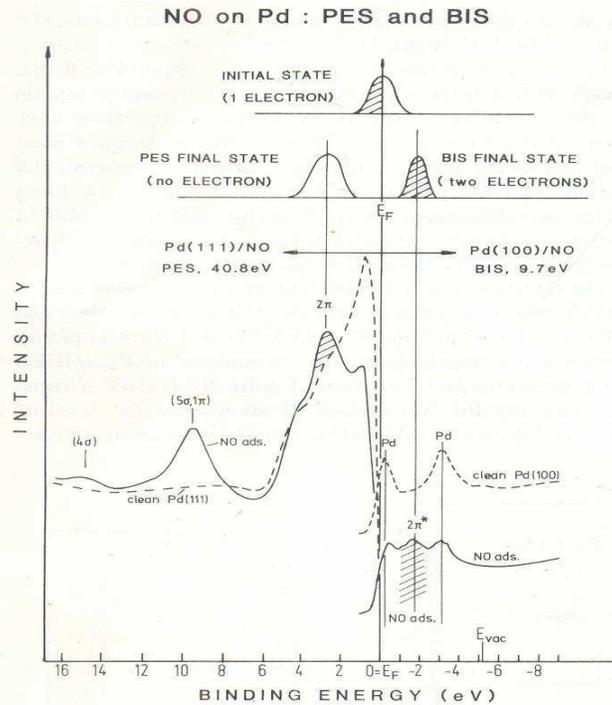


Figure 10 – (Left) PES of Pd(111) Clean & NO adsorbed. (Right) BIS. The * is left off in PES as the hybridisation with Pd makes NO lose its anti-bonding nature.

The following spectrum shows the BIS of adsorption of N_2 , being an isoelectronic species with CO, the hump (other than the parent peak) indicating the 2π level in each case.

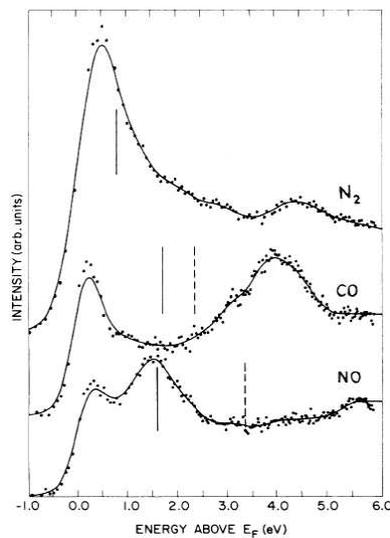


Figure 11 - $2\pi^*$ orbital observed by IPES for N_2 , CO, NO adsorbed on Ni (001)

The unoccupied or partly occupied orbitals are sensitive to small changes in the electronic structure and in the geometry. In doing IPES measurements changes in the spectra can be seen originating from these small alterations. However in PES one probes the tightly bound occupied orbitals.

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Lastly, considering the promotion of adsorption of CO over Pt by alkali metals is considered, alkali metal considered being K.

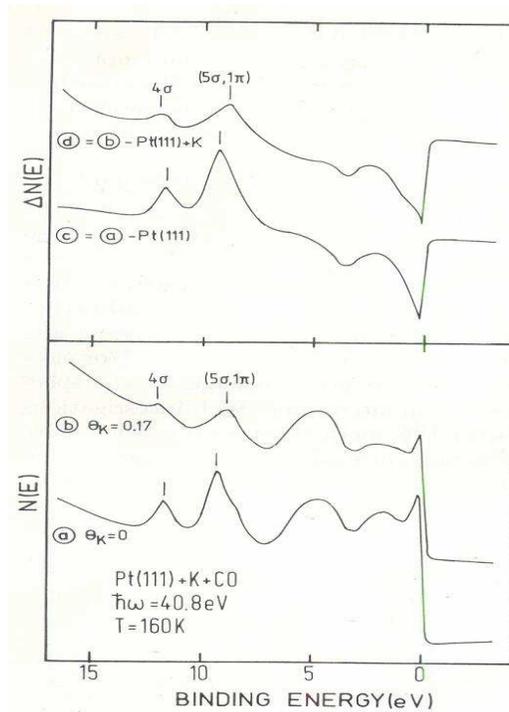


Figure 12 PES of:

'a' Pt(111) + CO

'b' Pt(111) + K + CO

'c' Spec. a minus Pt(111)

'd' Spec. b minus Pt + K

The above figure shows He II spectra of this system. Curve 'a' shows a HeII spectrum of CO on Pt(111). Below the Pt - d band, one sees the two-peaked structure created by the adsorption of CO, representing the photoionization from the 4σ & $(1\pi, 5\sigma)$ orbitals. The spectrum with an additional small coverage of K (17%), trace b, which hardly reveals and change at all. The changes become slightly more evident if the Pt contributions to the spectra are subtracted, as done in 'c' and 'd'. It can now be seen that covering Pt surface with small amounts of the promoter K, the 4σ & $(1\pi, 5\sigma)$ splitting increases. However since the PES contains initial and final state effect the interpretation of the spectra is not straightforward.

For comparison, (figure 13) the BIS of CO on Pt and Pt + K is also shown, the shaded areas indicating the contributions due to the ligand CO. (NO shown for the sake of comparison). It is apparent that the adsorption of the promoter K on the surface lowers the energy of CO anti-bonding $2\pi^*$ orbital considerably. This implies that the back donation of charge into the CO $2\pi^*$ orbital by the K co-adsorption, which strengthens the Pt-C bond, in turn reducing the C-O, detected by using IR. Thus in comparing one realizes immediately the considerable advantages of IPES over PES for studying the chemical bond.

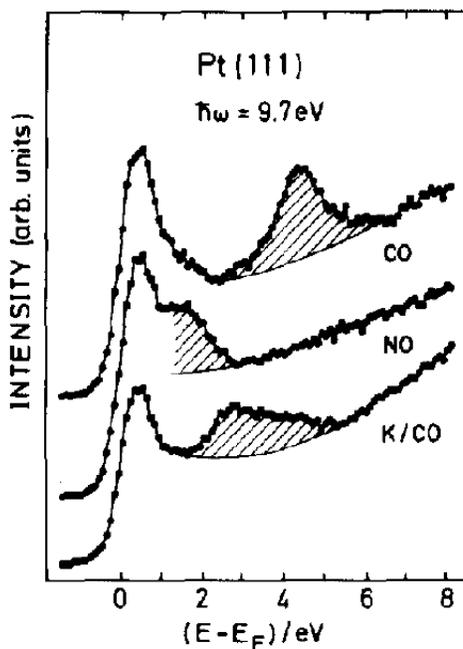


Figure 13 - BIS of CO, NO & K/CO on Pt (111). The co-adsorption of K lowers the CO orbital drastically

Concluding BIS is a technique to probe the surface state of the metal, for the elucidation of the bulk band structure of a metal (in conjunction with PES), helps in achieving a good insight of understanding the interactions between adsorbed molecules and surfaces (chemical bonds).

References:

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