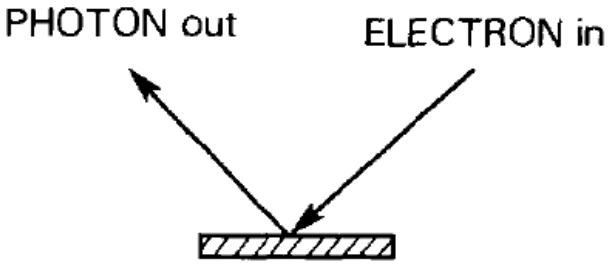
*B*remsstrahlung *I*sochromat *S*pectroscopy. (*BIS*)

A special case of *I*nverse *P*hoto *E*lectron *S*pectroscopy (IPES)



Joseph. J (CY06D035)
Kuppan. B (CY06D022)
Santanu Roy (CY07D008)

Bharathwaj. S (CY05C005)
Ramachandran. E (CY05C15)

CY 653 – Electron Spectroscopy
28 – March – 2007, Wednesday.

Concept…

- What is IPES? BIS?
- Comparing and contrasting PES with IPES…
  - Energy levels (dig. next page)
  - How are they different?
  - Equations
- In reality…

- Detectors
  - Crystal Monochromator – X Ray photons. Disadvantage.
  - Dose's Detector.

Diagram with equations…

- PES:
  - $h\nu = E_f - E_i$,
  - $-E_i = h\nu - E_{kin} - \varphi$
  - $E_f = E_{kin} + \varphi$
  - Since $-E_i = E_B$;
  - $E_B = h\nu - E_{kin} - \varphi$
- IPES
  - $h\nu = E_i - E_f$
  - $E_f = -h\nu + E_{kin} + \varphi$
  - $E_i = E_{kin} + \varphi$
  - Since $E_f = -E_B$;
  - $-E_B = -h\nu + E_{kin} + \varphi$

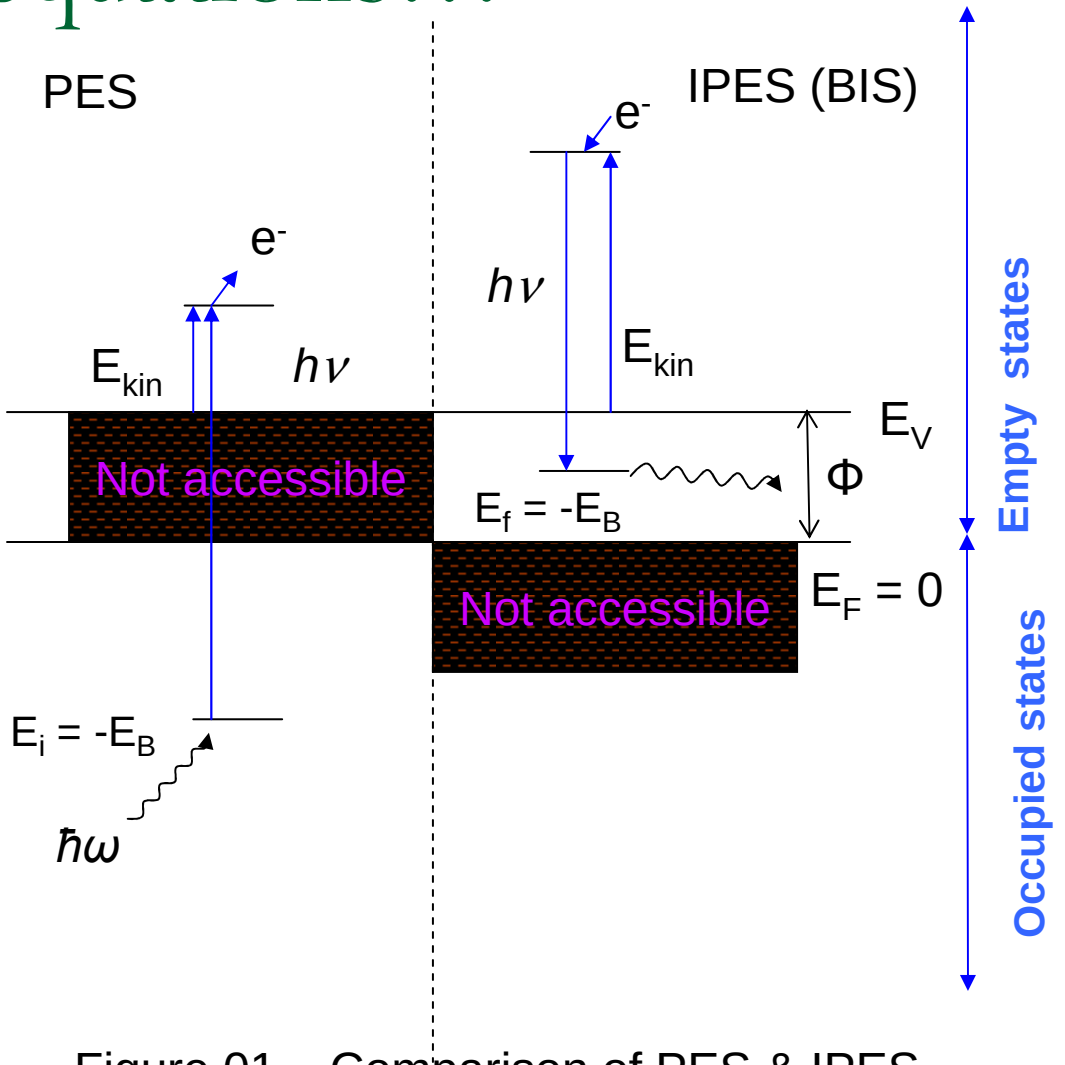


Figure 01 – Comparison of PES & IPES

Dose Detector

- Geiger Müller counter, with stainless steel tube of 20mm diameter, with stainless steel electrode, filled with about 100mbar of multiplier gas, Argon. Few crystals of I_2 act as the detecting agent.
  - $X \rightarrow X^+ + e^-$; X = He / Ar.
  - $I_2 + h\nu \rightarrow I_2^+ + e^-$
- The entrance window of the proportional counter is a 2mm thick CaF2 crystal, transparency cut-off ~ 10.2 eV.

- Transmission window – 9.7±0.40 eV.
- Sensitivity enhancement – using a mirror to collect the radiation (as used in the k-resolved measurements)

- Photo-multiplier, with KBr evaporated on the first dynode in combination with CaF_2 window. 9.9±0.3 eV.
- Grating monochromators – use of SrF_2, shifts to 9.5±0.3 eV. Resolution enhancement.

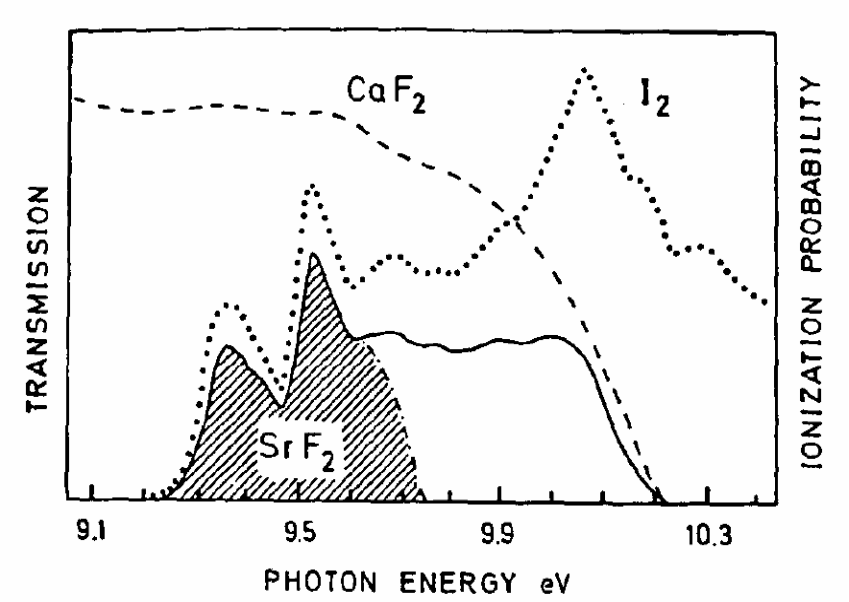


Figure 02 - Transmission spectra of CaF_2, SrF_2, Absorption of I_2, Convolution curve.

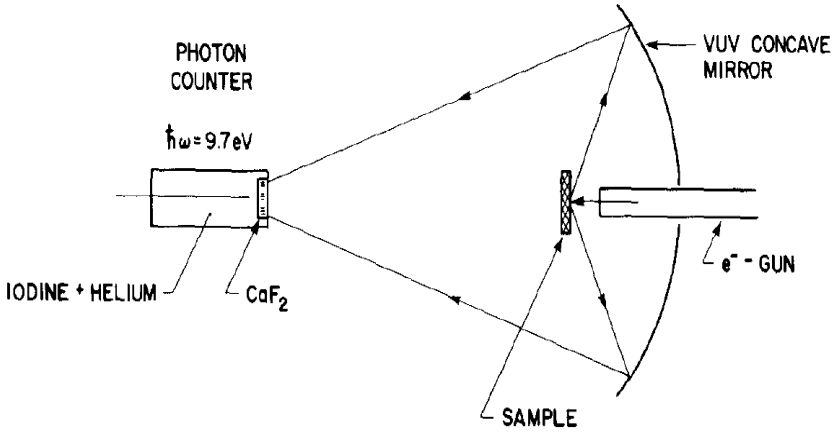


Figure 03 – Arrangement for the experimental setup for *IPES* using GM counter. (Dose Detector)

F.J. Himpsel, *Surface Science Reports*, **12** (1990), 1 – 48.

Applications

- Surface State energy determination.
- Bulk Band Structure determination.
- Adsorbed Molecules study.

SURFACE STATE Studies…

- Define *surface state & image potential*. Physical interpretation. Lies between E_f & E_v, thus is probed by BIS.
- Determination of SS energy using BIS. Copper (100) covered with CO.

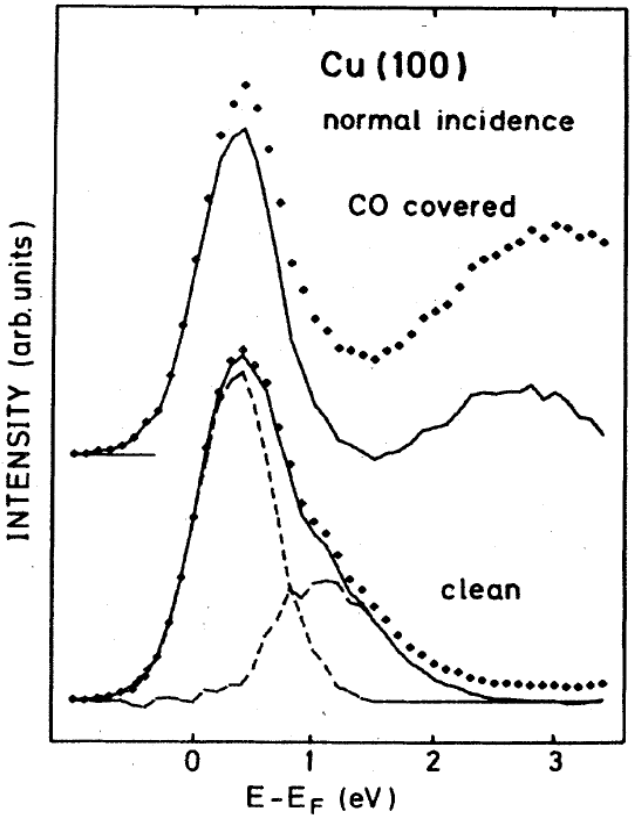


Figure 04 – BIS of Cu (100), clean (bottom) and CO adsorbed (top).

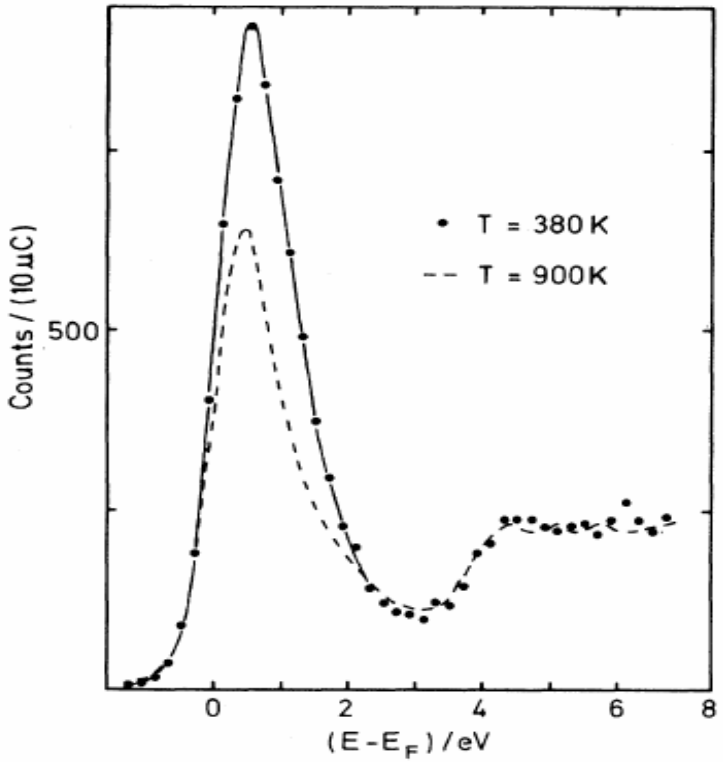


Figure 05 – Temperature dependence of BIS. (Debye-Waller Effect)

A. Goldman et. al., *Physical Review B*, **32**, (1985), 1971 – 1980.

Dose et. al., *Physical Review Letters,* **52**, (1984), 1919 – 1921.

- 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, $E_v - E_1 = 0.85$ eV in vacuum.
- Cu (100) covered with c(2X2) overlayer of Cl, Pt (111) covered with K.
- Observe the change in φ in both the cases.

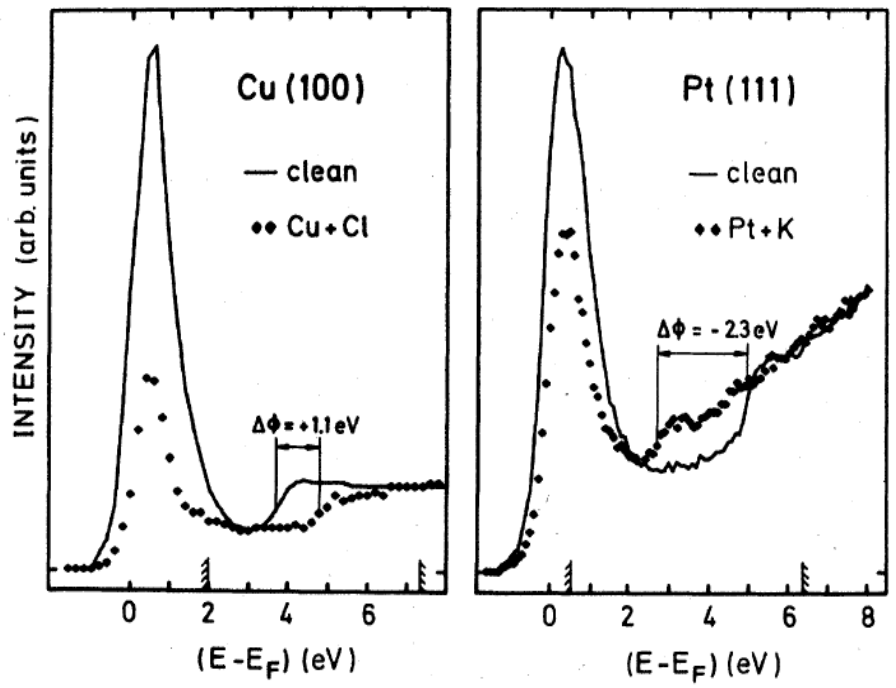


Figure 06 – Effect of work function change on the energy of the barrier induced surface state.

Image Potentials of few metals (E_B, E_1) 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. Between 0.4 – 0.85 eV is observed in general.

A. Goldman et. al., *Physical Review B*, **32**, (1985), 1971 – 1980.

Bulk Band Structures.

- Time constraint.
- Complementary to PES, used to check the accuracy of the assumed position of the unoccupied bands.
- The figure shows the results of band mapping performed in Ge by combination of PES & IPES. Two sets complement each other, in addition the theoretical plot too seems to agree with the experimental data.

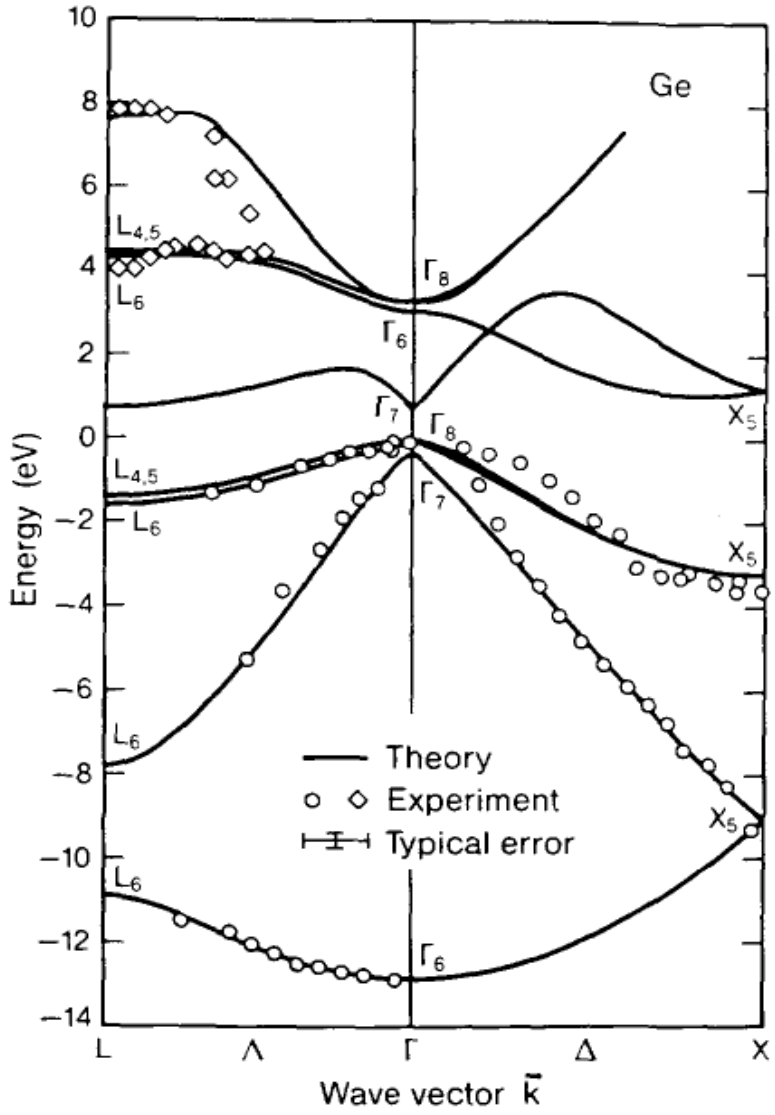


Figure 07 – Band Structure for Ge. Data for PES & IPES are combined to check the theoretical band structure.

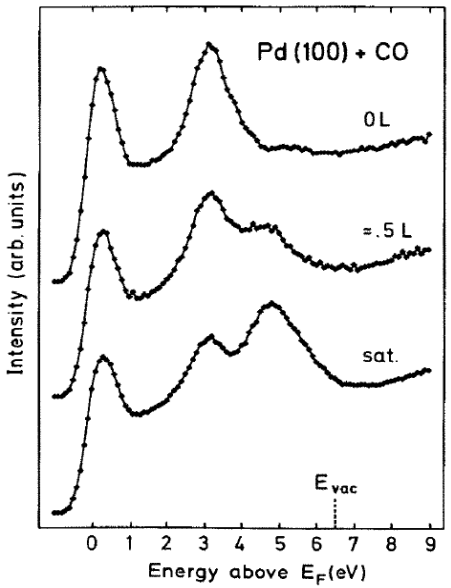
F.J. Himpsel, *Surface Science Reports*, **12** (1990), 1 – 48.

Adsorbed Molecules.

- Pd coated with CO & NO. (Why Pd??)
- A case in point is the anti-bonding orbitals of molecules adsorbed on substrate surfaces. $(\sigma_g\ 2s)^2\ (\sigma_u\ 2s)^2\ (\sigma_g\ 2p)^2\ (\pi_g\ 2p)^4$ for CO. NO has $(\pi_g\ 2p)^1$. I.E for CO ~ 14 eV, NO ~ 9.3 eV.
- Chemisorption of CO & NO on Pd. Back donation from the metal to the adsorbed species. 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 less tightly bound than that of NO which can be inferred from the figure.

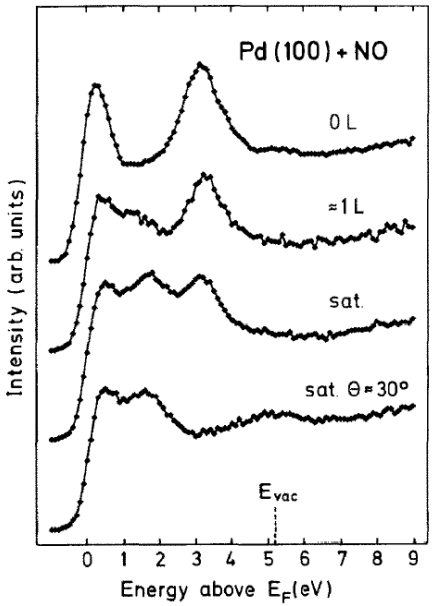
Pd(100) – CO & NO…

- Metal peaks are left largely unaltered. These findings have implications for the stability of intra-atomic bonds in the chemisorptive state. In NO the 2 π* level can be easily filled, thus exhibits greater tendency towards chemisorption.



←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



J. Rogozik et. al., *Surface Science Letters,* **143**, (1984), L653 – L658.

- Correlation energy determination. Pd(111) adsorbed with NO.
- IPES of Ni(001) with N_2, CO & NO.

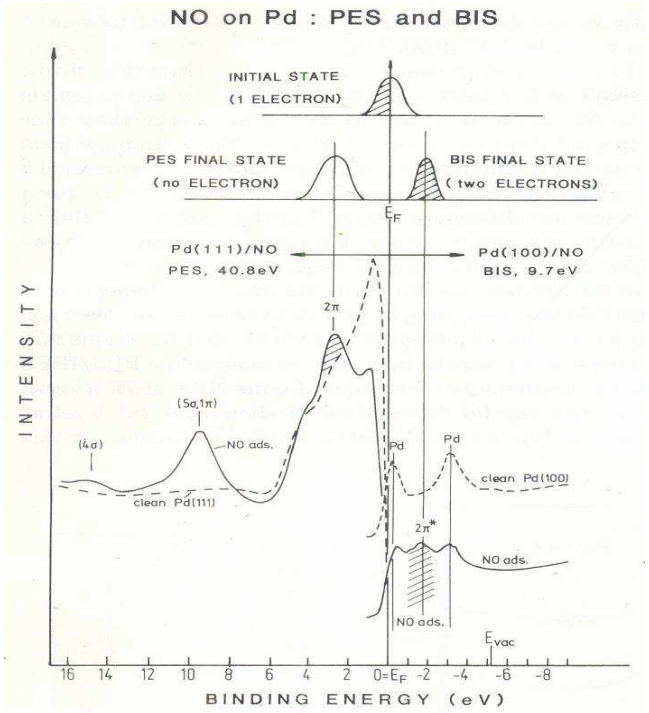


Figure 10 – (Left) PES of Pd(111) Clean & NO adsorbed. (Right) BIS. The * is left off in PES as the hybridisation with Pd makes NO lose its anti-bonding nature.

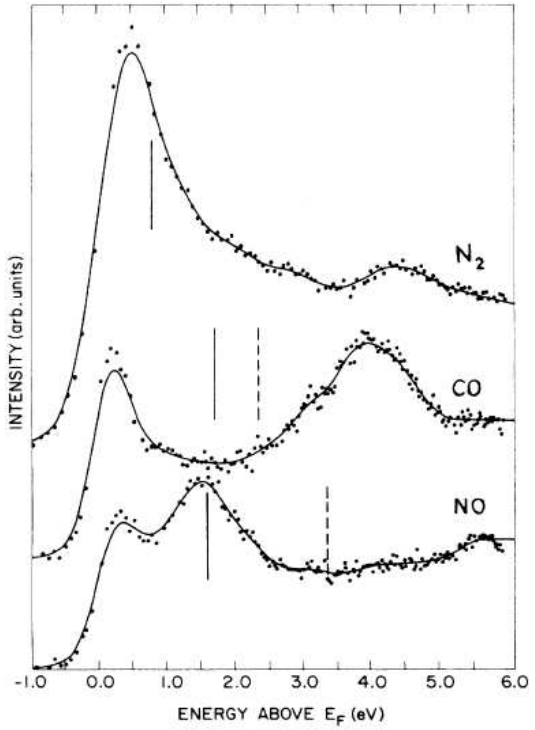
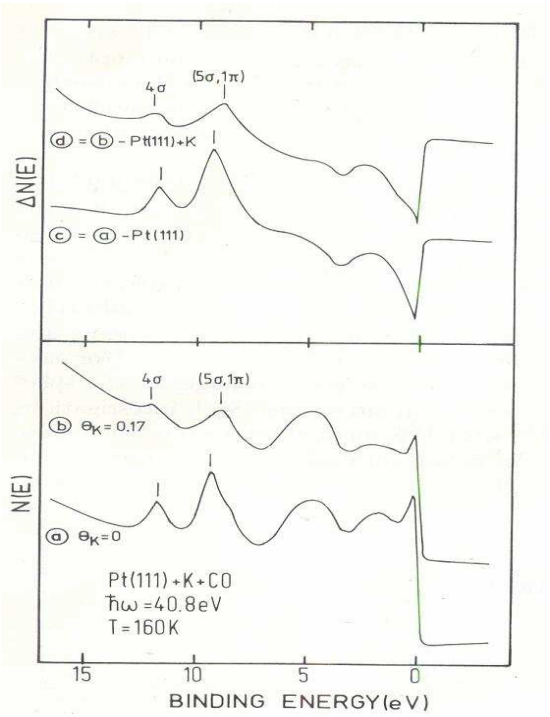


Figure 11 - 2π* orbital observed by IPES for N2, CO, NO adsorbed on Ni (001)

P.D. Johnson & S.L. Hulbert, *Physical Review B,* **35 (18)**, (1987), 9427

PES & IPES together…

- Catalysis by alkali metal on the adsorption of CO on Pt(111)



←Figure 12 PES of

Bottom a → Pt(111) + CO

Bottom b → Pt(111) + K + CO

Top c→ Spec. a minus Pt(111)

Top d→ Spec. b minus Pt + K

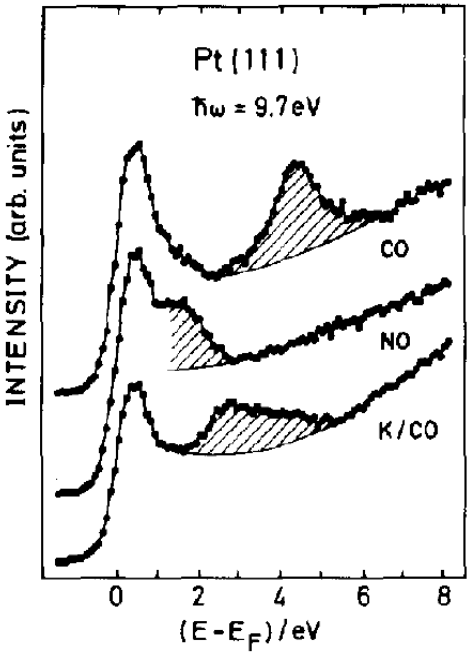


Figure 13 - BIS of CO, NO & → K/CO on Pt (111). The co-adsorption of K lowers the CO orbitals drastically.

Much information is not seen in PES, however BIS gives valuable information that there is a significant back donation which strengthens the Pt-CO bond and weakens the C-O bond (IR evidence).

V. Dose, *Surface Science Reports,* **5**, (1985), 337 – 378.

Conclusion…

BIS, IPES in general, is a vital 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.

Thank You!!