Bremsstrahlung Isochromat Spectroscopy. (BIS)
A special case of Inverse Photo Electron Spectroscopy (IPES)

PHOTON out  ELECTRON in

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CY 653 – Electron Spectroscopy
Concept...

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

- Detectors
  - Dose’s Detector.
Diagram with equations...

- **PES:**
  - $\hbar \nu = E_f - E_i$,
  - $-E_i = \hbar \nu - E_{\text{kin}} - \varphi$
  - $E_f = E_{\text{kin}} + \varphi$
  - Since $-E_i = E_B$;
  - $E_B = \hbar \nu - E_{\text{kin}} - \varphi$

- **IPES**
  - $\hbar \nu = E_i - E_f$
  - $E_f = -\hbar \nu + E_{\text{kin}} + \varphi$
  - $E_i = E_{\text{kin}} + \varphi$
  - Since $E_f = -E_B$;
  - $-E_B = -\hbar \nu + E_{\text{kin}} + \varphi$

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.
  - $X \rightarrow X^+ + e^{-} ; X = \text{He} / \text{Ar}$.
  - $I_2 + h\nu \rightarrow I_2^+ + e^{-}$

- The entrance window of the proportional counter is a 2mm thick CaF2 crystal, transparency cut-off $\sim 10.2$ 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)

Applications

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

- Define *surface state* & *image potential*. Physical interpretation. Lies between $E_i$ & $E_v$, 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)


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 $\varphi$ in both the cases.

![Figure 06 – Effect of work function change on the energy of the barrier induced surface state.](image)

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.

**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.

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 \(\sim 14\) eV, NO \(\sim 9.3\) 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.
Metal peaks are left largely unaltered. These findings have implications for the stability of intra-atomic bonds in the chemisorptive state. In NO the $2\pi^*$ 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

- Correlation energy determination. Pd(111) adsorbed with NO.
- IPES of Ni(001) with N₂, 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)

PES & IPES together…

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

Figure 12 PES of
Bottom a $\rightarrow$ Pt(111) + CO
Bottom b $\rightarrow$ Pt(111) + K + CO
Top c $\rightarrow$ Spec. a minus Pt(111)
Top d $\rightarrow$ 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).

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!!