O 82: Focus Session: Unoccupied States by Inverse Photoemission III

The Other Half of the Picture: 50 Years of Direct Access to Unoccupied States by Inverse Photoemission

In 1981, J. Pendry evaluated the experimental access to electron states in solids: "Currently only half of the picture can be seen with photoemission. Inverse photoemission provides the other half." A complete picture of electron states needs both occupied and unoccupied states in order to describe, understand, and finally tailor macroscopic material properties. In 1976, V. Dose had submitted a first paper on Bremsstrahlung Isochromat Spectroscopy in the VUV range: "The physics involved may be most simply described as an inverse photoelectric effect." The first experiments provided surface-sensitive information on the density of unoccupied states. Later, momentum and spin resolution were added to investigate the spin-dependent E(k) dispersion of unoccupied electron states. During five decades, the technique was further developed by several groups worldwide to enhance the intensity and improve the resolution in energy, momentum, and spin. A wealth of information was gained about metals, semiconductors, ultrathin films as well as adsorbate systems. The experimental studies were accompanied by several theoretical approaches, which are able to accurately describe the unoccupied electronic structure and model the inverse photoemission process. In 2012, H. Yoshida extended the energy range to the near-UV range (low-energy inverse photoemission), which is especially suited to study organic samples due to a lower damage risk caused by the exciting electron beam.

Current research fields for inverse photoemission are, e.g., spin textures of exchange- and/or spin-orbit-induced influenced systems and topological insulators, gap structures in transition metal dichalcogenides, LUMO levels in semiconductors for photovoltaic applications, electronic structure of atomic-layer and quantum materials. This focus session will highlight recent advances obtained by inverse photoemission in different fields and material systems. Also, it will bring together researchers from different areas for addressing current trends and future applications of inverse photoemission from experimental as well as theoretical perspective.

Organized by Markus Donath, Fabian Schöttke and Peter Krüger (U Münster).

Time: Thursday 10:30–12:30 Location: WILL/A317

Invited Talk O 82.1 Thu 10:30 WILL/A317

Low-energy inverse photoelectron spectroscopy (LEIPS): probing unoccupied states and conduction band structure in functional materials — •Hiroyuki Yoshida — Chiba University, Chiba, Japan

We developed low-energy inverse photoelectron spectroscopy (LEIPS) in 2012 [1] to enable damage-free probing of functional materials such as organic semiconductors, polymers and hybrid perovskites. By reducing the incident electron energy below the damage threshold (about 5 eV), LEIPS allows damage-free measurements while simplifying operation and improving energy resolution. By incorporating an electron energy analyzer [2], we achieved an energy resolution of 98 meV. LEIPS enables determination of electron affinity with an uncertainty of 0.1 eV. These precise values provide access to key parameters including band gaps, exciton binding energies, polarization energies, and electron injection barriers. The technique has been commercialized, and more than 100 systems are now in operation worldwide. We further developed angle-resolved LEIPS (AR-LEIPS) [3], enabling for the first time direct observation of conduction band structure in organic semiconductors [4]. The measured band structures yield insight into electron-phonon coupling and polaron formation relevant to carrier transport. [1] Chem. Phys. Lett. 539-540, 180 (2012). [2] Rev. Sci. Instrum. 94, 043908 (2023). [3] Rev. Sci. Instrum. 94, 063903 (2023). [4] Nat. Mater. 21, 910 (2022).

Invited Talk O 82.2 Thu 11:00 WILL/A317

Enhanced Sensitivity in Low-Energy Inverse Photoemission Spectroscopy with an Off-Axis Parabolic Mirror for Efficient Light Collection — •Yongsup Park[1,2], Jong-Am Hong[1], Kyu-Myung Lee[1], and Min-Jae Maeng[1] — [1]Dept. of Physics, Kyung Hee University, Seoul, Republic of Korea — [2]Dept. of Information Display, Kyung Hee University, Seoul, Republic of Korea

Inverse photoemission spectroscopy (IPES) is a powerful tool for studying unoccupied electronic states but suffers from low sensitivity due to the low photon emission probability during free electron transitions. To improve sensitivity via better photon collection, an off-axis parabolic (OAP) mirror was designed and built for low-energy IPES (LEIPS). Optical simulations showed the OAP mirror raised photon collection efficiency from 3.06% to 63.3%, confirmed experimentally through LUMO spectra of C60 thin films. The OAP mirror-LEIPS system was applied to study energy level alignment (ELA) of pentacene films on substrates with different work functions (WF). By measuring HOMO and LUMO levels, the changes in transport gaps and the ELA with respect to the Fermi level were analyzed. Pentacene showed n-type behavior on low WF substrate (Cs2CO3) and p-type on high WF substrate (ITO). This OAP mirror-enhanced LEIPS system significantly shortened experiment times, enabling efficient and reliable measurements.

O 82.3 Thu 11:30 WILL/A317

Development of angle resolved low energy inverse photoelectron spectroscopy for conduction band structure measurements of functional materials — •yuki kashimoto[1], satoshi ideta[1], haruki sato[1], keita kawamura[1], hibiki orio[1], and hiroyuki yoshida[1,2] — [1]chiba university, chiba, japan — [2]chiba university MCRC, chiba, japan

Understanding the energy band structure is essential for clarifying charge-transport behavior in solids. Although angle-resolved inverse photoelectron spectroscopy (ARIPES) can measure conduction bands, it is unsuitable for emerging materials such as organic semiconductors due to their narrow bandwidths and electron irradiation damage. Low-energy inverse photoelectron spectroscopy (LEIPS)[1] overcame these issues by reducing the electron kinetic energy. In this study, we advanced LEIPS and enabled band-structure measurements by introducing angle-resolved detection. Stray electric and magnetic fields were suppressed, and a dedicated low angular spread, energy-scannable electron source was implemented. This enabled angle-resolved LEIPS (AR-LEIPS) with 0.23 eV energy resolution and 0.94 nm^{-1} momentum resolution[2]. Using AR-LEIPS, we determined the conduction band structure of pentacene, the first such measurement for an organic semiconductor[3] and revealed the conduction-band dispersion of the photovoltaic perovskite $CH_3NH_3PbI_3$. [1] H.Yoshida, Chem. Phys. Lett. 539-540, 180 (2012). [2]Y.Kashimoto, H.Yoshida et al, Rev. Sci. Instrum. 94, 063903 (2023) [3] H. Sato, H. Yoshida et al, Nature Mat. 21,910 (2022).

O 82.4 Thu 11:45 WILL/A317

Observation of conduction band structure of conductive polymer PBTTT — •Taichi Suruga[1], Shunichiro Ito[2], Taishi Takenobu[2], and Hiroyuki Yoshida[1,3] — [1]Chiba University, Chiba, Japan — [2]Nagoya University, Nagoya, Japan — [3]Chiba University MCRC, Chiba, Japan

The most fundamental information regarding the electron transport mechanism of these polymers is the conduction-band structure. However, until now, we did not have the appropriate methods to measure it. In 2020, we developed angle-resolved low-energy inverse photoelectron spectroscopy (ARLEIPS) [1] and successfully measured the conduction band structure of small-molecule organic semiconductors for the first time [2]. In this study, we applied ARLEIPS to a conductive polymer. Fabricating crystalline thin films with well-aligned molecular orientation is essential for the ARLEIPS measurement. We fabricated thin films using the blade-coating method [3]. Using ARLEIPS, we observed the conduction-band structure of a conductive polymer, PBTTT-C14 [4,5], in oriented films. As predicted by the DFT calculations, the bands split into two and exhibited large dispersion along the Γ-Z direction. These results demonstrate the first observation of conduction-band in a conductive polymer. [1] Y. Kashimoto, H. Yoshida et al., Rev. Sci. Instrum, 94, 043908 (2023) [2] H. Sato, H. Ishii, H. Yoshida et al., Nat. Mater. 21, 910 (2022). [3] D. Delongchamp et al., ACS Nano. 3, 780 (2009). [4] H. Tanaka, K. Kanahashi, T. Takenobu et al., Sci. Adv., 6, eaay8065 (2020) [5] S. Ito, H. Tanaka, T. Takenobu et al., Appl. Phys. Express 18, 021002 (2025)

O 82.5 Thu 12:00 WILL/A317

Effects of Crystallization on the Electronic Structure of Discrete Oligomers — •Alexander Ehm[1], Rukiya Matsidik[2], Michael Sommer[2], and Dietrich R. T. Zahn[1] — [1]Semiconductor Physics and Research Center for Materials, Architectures and Integration of Nanomembranes (MAIN), TU Chemnitz, Chemnitz, Germany — [2]Polymer Chemistry, TU Chemnitz, Chemnitz, Germany

Recently, organic photovoltaic cell efficiency surpassed the 20 % landmark, thanks to the development and improved crystallinity of non-fullerene acceptor (NFA) molecules and suitable polymer donors [1]. Low exciton binding energies (EBE), measured by the difference of the transport gap and the optical bandgap, were attributed as key factors in such improvements [2].

Photoemission and low-energy inverse photoemission spectroscopy (PES and LEIPES) in combination directly measure the transport gap. However, challenges are posed by their surface sensitivity in conjunction with the solution processing, low conductivity and radiation sensitivity of thin films of large organic molecules.

Here, we address strategies to avoid surface contamination and charging effects, while investigating the interfacial electronic structure of conjugated discrete oligomer films [3] spin-coated on Ag substrates. Their thermal crystallization reduced their bulk EBE to < 0.1 eV.

[1] F. Furlan, N. Gasparini, Nat. Mater. 24, 336 (2025)
[2] A. Sugie *et al.*, J. Phys. Chem. Lett. 14, 11412 (2023)
[3] R. Matsidik *et al.*, J. Am. Chem. Soc. 145, 8430 (2023)

O 82.6 Thu 12:15 WILL/A317

Development of near-ambient-pressure low-energy inverse photoelectron spectroscopy enabling measurement under the water vapor pressure — •Mihiro Kubo[1], Gaku Yokogawa[1], Hitoshi Tomizuka[2], and Hiroyuki Yoshida[1] — [1]Chiba University, Chiba, Japan — [2]TOYAMA Co., Ltd., Kanagawa, Japan

Inverse photoemission spectroscopy has evolved over fifty years, providing essential insight into the unoccupied electronic structure. In 2012, Dr. Yoshida developed low-energy inverse photoelectron spectroscopy (LEIPS[1]). This technique enables the measurement of organic materials without damaging the sample by reducing the kinetic energy below 5 eV, their typical damage threshold. To further extend the applicability of LEIPS, we are developing near-ambient-pressure LEIPS (NAP-LEIPS) capable of measurement under the vapor pressure of water (10^3 Pa). NAP-LEIPS will allow measurements of volatile samples, biomaterials, and catalysis with the introduction of reactive gases. To realize NAP-LEIPS, we use an electron gun with a yttria-coated disc cathode and an electrostatic energy analyzer. Because the electron source operates at pressures better than 10^{-5} Pa, a differential pumping system is installed between the electron source chamber and the main chamber (10^3 Pa). Electrons travel about 300 mm through the differential pumping section using an electrostatic transfer lens. Photons emitted from the sample are focused by a mirror, passed through a band-pass optical filter, and detected with a photomultiplier tube. The apparatus has been constructed and is currently in the start-up phase. [1] H. Yoshida, Chem. Phys. Lett. 539-540, 180 (2012).