



Principle and application of low energy inverse photoemission spectroscopy: A new method for measuring unoccupied states of organic semiconductors



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ABSTRACT

Information about the unoccupied states is crucial to both fundamental and applied physics of organic semiconductors. However, there were no available experimental methods that meet the requirement of such research. In this review, we describe a new experimental method to examine the unoccupied states, called low-energy inverse photoemission spectroscopy (LEIPS). An electron having the kinetic energy lower than the damage threshold of organic molecules is introduced to a sample film, and an emitted photon in the near-ultraviolet range is detected with high resolution and sensitivity. Unlike the previous inverse photoemission spectroscopy, the sample damage is negligible and the overall resolution is a factor of two improved to 0.25 eV. Using LEIPS, electron affinity of organic semiconductor can be determined with the same precision as photoemission spectroscopy for ionization energy. The instruments including an electron source and photon detectors as well as application to organic semiconductors are presented.

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1. Introduction

Both holes and electrons play a crucial role in electronic properties of organic semiconductors. Thus it is equally important to investigate the occupied and unoccupied states of organic solids. The occupied states have been extensively studied using photoemission spectroscopy (PES). PES is a surface sensitive technique and can be applied to organic thin films to examine the density of occupied states with reference to the Fermi and vacuum levels. A momentum resolved (k -resolution) measurement is also possible by measuring the dependencies of the energy of excitation photons or angle of emitted electron. Taking advantage of these properties of UPS, interface energy level alignments [1,2], energy band dispersion [3], and molecular orientation dependence of ionization energy [4] have been reported so far.

In contrast, little is known about the unoccupied states because of limitation of experimental technique available. Several methods have been used for the unoccupied states of organic materials, such as X-ray absorption spectroscopy, combination of ultraviolet-visible spectroscopy and PES, scanning tunneling

spectroscopy (STS), cyclic voltammetry (CV) and inverse photoemission spectroscopy (IPES) [5,6]. In principle, IPES is complementary to PES for occupied states and is only capable of quantitatively analyzing unoccupied states of solid samples with surface sensitivity and k -resolution.

Fig. 1 shows the principle of IPES. An electron having a kinetic energy E_k is introduced to a sample surface and a photon with energy $h\nu$ emitting as a result of the radiative transition to an unoccupied state is detected. The electron binding energy E_b is determined based on the energy conservation, $E_b = h\nu - E_k$. The IPES spectrum is measured either by sweeping an electron kinetic energy E_k with detecting photons at a fixed energy $h\nu$, called the isochromat mode, or by analyzing the photon energy $h\nu$ at a constant electron kinetic energy E_k , called the tunable photon energy (TPE) mode.

IPES was first applied to organic materials in 1980s [7–11]. Molecules adsorbed on single crystalline surfaces of metals were observed and the unoccupied molecular orbitals were identified by comparing with the molecular orbital calculations. Larger number of research groups started IPES around 2000 in connection with the fundamental and applied studies toward organic electronics [12–17]. However, the obtained results from IPES were disappointing. Organic samples were found to be easily degraded by the electron bombardment [18,19] and the energy resolution

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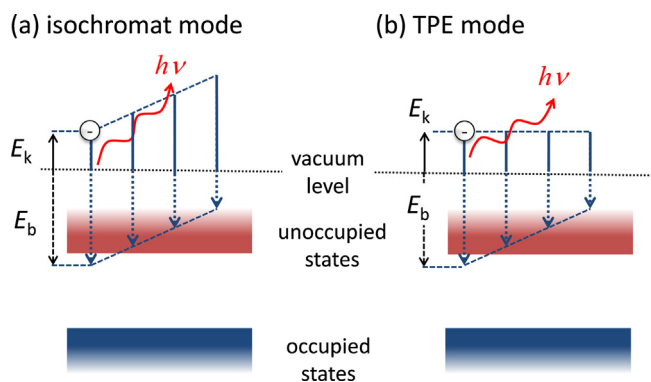


Fig. 1. Principle of inverse photoemission spectroscopy. (a) Electron kinetic energy E_k is scanned with detecting photons at a fixed energy $h\nu$ (isochromat mode). (b) Electron kinetic energy E_k is fixed and photons with various energies are analyzed using a spectrometer (TPE mode).

was as high as 0.5 eV that is substantially lower than PES [20]. In Fig. 2a compares the first and second scans of the IPES spectra of hexatriacontane ($n\text{-C}_{36}\text{H}_{74}$) at the incident electron density of $1.1 \times 10^{-3} \text{ A m}^{-2}$ [18]. The peak at 2.5 eV in the first scan shifts to 4 eV in the second scan demonstrating that the sample is seriously damaged by the electron bombardment during the measurement. Fig. 2b shows the combined UPS [21] and IPES (the energy resolution is 0.8 eV) [22] spectra of copper phthalocyanine (CuPc). Apparently, the onset region is not clear in the IPES spectrum owing to the low energy resolution.

The difficulties of IPES originate from the inherently low signal intensity. The cross section of IPES is 3 or 5 orders magnitude smaller than that of PES [23]. In order to gain a sufficient signal-to-noise ratio, an intense electron beam is introduced to a sample resulting in the sample damage. The photon is analyzed with a specially designed detector which is optimized to gain high sensitivity and lose the energy resolution [24].

Recently, we have developed low-energy inverse photoemission spectroscopy (LEIPS) [25]. This new technique have solved the issues of the previous IPES simultaneously by using electron beam having the kinetic energy lower than the damage threshold of organic materials. In this review, we present the principle, instruments, performance of LEIPS followed by several applications to the organic semiconductors.

2. Basic idea of low-energy inverse photoemission spectroscopy

IPES was first pursued in the X-ray range since 1940s (see Ref. [26]). Studies of IPES in the vacuum ultraviolet (VUV) range started with the introduction of the bandpass photon detector using the Geiger–Müller tube and optical filter in 1970s [24,27]. The iodine gas-filled Geiger–Müller serves as the high pass filter with the sensitivity beyond 9.2 eV and the optical filter of CaF_2 as low pass filter with the cut-off energy of 10 eV making a bandpass sensitivity centered at 9.7 eV with the half-width at maximum (FWHM) of 0.7 eV. This VUV photon detector has high quantum efficiency and large solid angle of the photon collection as well as is easy to construct. This work established IPES as a standard spectroscopic technique for surface science. Here, we call this experimental method as VUV-IPES. The energy resolution has been improved by changing the filled gases and the optical filters [28–34]. The Geiger–Müller tube was replaced with a solid state detector to improve the stability of operation [35–37]. Most of the IPES studies of organic materials have been conducted using the bandpass detector so as to minimize the sample damage. The disadvantage is low-flexibility of bandpass property because the bandpass sensitivity is obtained by the combination of the photon-sensitive and filter materials. The center of the passband is always around 10 eV, and the energy resolution is as high as 0.5 eV for a practical sensitivity.

For the analysis of photons in the VUV range, spectrometers have been also used [38–46]. However, these spectrometers were low in the photon detection efficiency because of the low reflectivity of gratings in the VUV range and the small solid angle of photon collection. The application to organic materials was thus limited to the highly durable molecules such as fullerenes [47,48].

Since the electron affinity of organic semiconductors mostly falls in the range between 2 and 5 eV [49,50], the energy of incident electron ranges between 5 and 15 eV when the VUV photons are detected by the bandpass photon detector. The electron beam in this energy range causes serious damage to organic samples. The damage threshold of organic materials is reported to about 5 eV [51] which corresponds to the energy of covalent bonds of organic molecules. If the energy of electron is lowered below 5 eV, the sample damage is expected to be reduced. In this case, the photon energy is estimated to be less than 5 eV, i.e., the near ultraviolet range (NUV). Basically, the NUV photons can be analyzed easier than the VUV photons leading to the higher resolution and

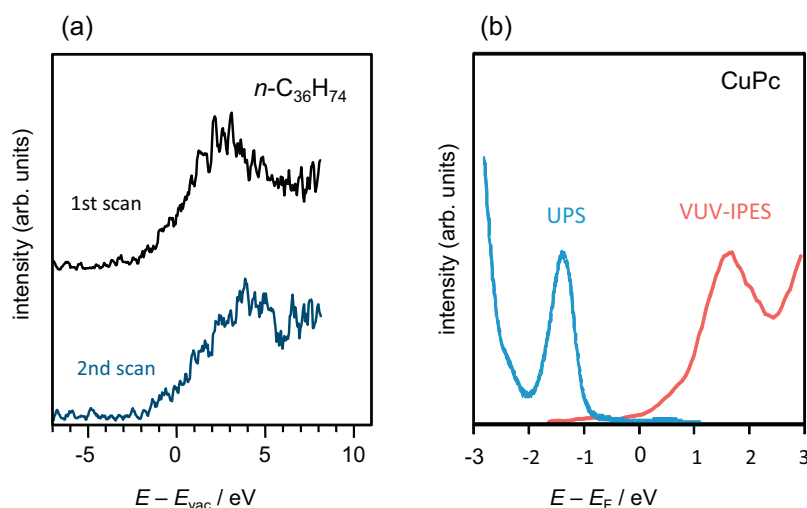


Fig. 2. Spectra of the previous IPES (VUV-IPES) demonstrating that (a) organic samples are damaged during the first scan [18], and (b) the energy resolution is substantially lower than that of ultraviolet photoemission spectroscopy (UPS) [22].

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