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Photoelectron spectroscopy on the charge reorganization energy and small polaron binding energy of molecular film

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ABSTRACT

Understanding of electron-phonon coupling as well as intermolecular interaction is required to discuss the mobility of charge carrier in functional molecular solids. This article summarizes recent progress in direct measurements of valence hole-vibration coupling in ultrathin films of organic semiconductors by using ultraviolet photoelectron spectroscopy (UPS). The experimental study of hole-vibration coupling of the highest occupied molecular orbital (HOMO) state in ordered monolayer film by UPS is essential to comprehend hole-hopping transport and small-polaron related transport in organic semiconductors. Only careful measurements can attain the high-resolution spectra and provide key parameters in hole-transport dynamics, namely the charge reorganization energy and small polaron binding energy. Analyses methods of the UPS HOMO fine feature and resulting charge reorganization energy and small polaron binding energy are described for pentacene and perfluoropentacene films. Difference between thin-film and gas-phase results is discussed by using newly measured high-quality gas-phase spectra of pentacene. Methodology for achieving high-resolution UPS measurements for molecular films is also described.

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1. Introduction

Organic semiconductors are molecular solids with specific charge transport properties due to weak intermolecular interaction [1,2]. A key character to find the semiconductive property in a molecular solid is recognized that (i) an electron (hole) is localized at each molecular site as described by a molecular orbital (MO) picture, however (ii) it is in part delocalized in the molecular solid and spills into other materials at the interface even if they contact by weak electronic coupling. The former feature (i) gives some advantages when fabricating molecular devices, because molecular characteristics in gas phase may be conserved in condensed phase by weak intermolecular interaction. As seen in the present progress of organic electronics, one can estimate qualitatively the device performance in accordance to the individual molecular property and can even synthesize a molecular material with a desired function. On the other hand, the latter feature (ii) is indispensable to realize solid-state devices that use charge transport property and

thus very important target to cut deeply into mechanisms of charge transport throughout the device and origins of their elementary steps. Unfortunately, however, origin of the charge transport property is far from being adequately understood [3,4].

To reveal charge transport characteristic of organic materials quantum mechanically/quantum chemically, the precise experiments on the electronic structure not only of gas phase and/or solid phase (single crystal, thin film etc.), but also at various interfaces in devices, including organic-organic and organic-inorganic (metal/semiconductor) contacts are demanded. Requirements of the electronic structure investigation come from at least two motivations. First, the energy-level alignment (ELA) at the interface between different materials plays a key role in charge injection/ejection to another interface material by overcoming the interface barrier height, or by charge (exciton) separation/recombination processes at the interface. The charge injection barrier dominates the transporting charge-carrier concentration (n) in the electrical conductivity. The ELA is described by measuring the binding energy (BE, E_b) from Fermi level (E_F) and/or ionization energy (IE, E_i) by ultraviolet photoelectron spectrum (UPS).

Second, the carrier dynamics related phenomena give also important bases to discuss charge transport property, which is

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related to the charge mobility μ . The hopping mobility is given by the band shape and intensity in the UPS and band mobility is evaluated by the energy-band dispersion in the angle-resolved UPS.

Charge-transfer processes and carrier dynamics in organic solids have been widely studied in various fields. Detailed theoretical descriptions can be found in several reviews [5–9]. According to general microscopic models, total mobility can be expressed as the sum of two contributions, *i.e.*, (i) coherent conduction that dominates band transport at low temperatures and (ii) incoherent conduction that becomes dominant by charge hopping at high temperatures. Important subjects still to be understood are related to molecular and lattice vibrations (phonons) and their coupling to a charge carrier. The electron-phonon interaction depends on the molecular structure and their packing motif and therefore it can impact both molecular site energies and transfer integrals. The overall strength of electron-phonon coupling observed in highly-resolved UPS is given by the relaxation energy between neutral and ionized states, and the reorganization energy associated. In this short review, we describe a recent development in direct measurements of (local) electron-phonon coupling (HOMO hole-molecular vibration coupling) for large functional molecular materials, which will shed light on the incoherent charge hopping property [3,4].

2. How to realize fine feature measurement

As organic molecules consist of light elements, the intramolecular vibration energy is much larger than energies of lattice phonons, and molecular vibrations with larger energies (~ 100 meV) contribute more to reorganization energy (λ). This means that we do not need an ultimate-resolution electron-spectrometer system for measurement in this level of the study. The principal drawback for obtaining high-resolution UPS is that spectral broadening due to film structure is much larger than the vibration energy, *i.e.*, inhomogeneity of molecular film and energy-band dispersion dominates the observed spectral-line width. We thus need to minimize such broadening in UPS. The non-uniform structure of the thin film introduces serious dependence on the position of the ionization energy, which originates from the site dependence of the electronic states and the relaxation energy (polarization energy) between in the final state upon ionization [10,11]. Furthermore, electronic interaction for adsorbed molecule and substrate should be minimized to reduce the appearance of new interface states with different binding energies.

Fig. 1 shows HeI UPS taken for various phases of pentacene (PEN). The spectra for gas-phase (from ref [12]), monolayer (ML) films, amorphous film, and crystal films are compared. The E_b is measured from the Fermi level of the substrate, and the IE is from the vacuum level. In panel (a), the gas-phase spectrum is well reproduced by theoretical calculation instead of vibration satellites. In panel (b), the monolayer (0.3 nm film on HOPG) spectra, where the electron is emitted from flat-lying film, seem to correspond to the gas-phase one at least for top seven orbitals (all are π states), indicating the electronic structure is not largely modified by intermolecular and molecule – substrate interactions. In panel (e), the spectra correspond to those of the amorphous phase, since there is no clear angular distribution of features. Valence bands are broadened comparing with gas-phase spectrum. In panels (c) and (d), the situation is rather complicated. In the spectrum for 10nm-pentacene prepared on HOPG (panel (c)), forming an oriented polycrystalline film (long molecule axis parallel to the surface) [13], the highest-occupied molecular orbital (HOMO) band peak does not correspond to the gas-phase position if one makes spectrum alignment at other deeper-lying states. In the spectrum for 20nm-pentacene prepared on SiO₂ (panel (d)), showing ordered polycrystalline film (long molecule axis

perpendicular to the surface) [14–17], additional feature is appeared at the gap between HOMO and HOMO-1(H-1). These large changes in the HOMO band shape are caused by forming energy-band dispersion for well-stacked polycrystalline samples [18,19]. To describe more precisely, the results of angle-resolved UPS (ARUPS) are useful to understand the band shape [13–19]. When we look the spectra in the details very carefully, the figure in a survey view also tells important physics both on the initial state and final state effects in the UPS, which would be (i) the polarization energy depends on the orbital distribution and (ii) the one-electron approximation does not work for energy level calculations of molecular solids [20,21]. The impact of electronic relaxation is also crucial to understand the charge transport in molecular solids. Upon electron(hole) hopping, for example, the remaining electrons response to the hopping electrons (hole). Effects of such a dynamic relaxation should appear in the photoelectron spectrum and can be discussed by a time-dependent many-particle picture, which is beyond the scope of this review.

The origin of the UPS bandwidth for organic solids was discussed extensively until the end of the 70s [22–24]. After the work done by Salaneck *et al.*, [23], the UPS bandwidth of the HOMO state in organic films was considered to have been mainly dominated by the dependence of relaxation (polarization) energy [24] on the site/depth, since it yielded a broadened UPS feature with a full-width-at-half maximum (FWHM) of $> \sim 0.4$ eV. As a result, it was considered that intermolecular energy-band dispersion could not be measured, since the dispersion width may be smaller than the spectral bandwidth due to the dependence of relaxation (polarization) energy [3] on the site/depth. Nowadays, the measurement of band dispersion on an organic material has been successfully achieved in many systems [3], and very recently even for very small band dispersion in a range of a few-tens meV was observed by Yamane *et al.* for phthalocyanine (Pc) films, which thanks to development in the measurement technique and the sample preparation [25,26]. Unfortunately, the measurement of electron(hole)-phonon(vibration) coupling in organic thin films has also been believed to be impossible, although the possibility of molecular vibration contributing to the width of the HOMO band in UPS has been suggested by taking into consideration of the excellent one-to-one correspondence of the valence-band features to those in gas-phase [27], and evidence was found for a tetracene film in an early work on UPS by N. Ueno. [28]. Therefore, gas-phase UPS spectra, where hole-vibration coupling is resolved for HOMO, have been used in theoretical studies of hole-hopping mobility [5,6]. However, there is a serious problem in using the gas-phase spectrum, since the molecules are in more thermally excited states due to the evaporation at higher temperature. We need to measure HOMO hole-vibration coupling at lower temperatures using thin films or adsorbed molecules to discuss hopping mobility.

In Fig. 2, the high-resolution HeI UPS of HOMO taken for various phases of PEN are presented. The spectra for gas-phase, monolayer films [29], amorphous film [18,19], and crystal film [18,19] are measured by using the same apparatus (Omicron HIS13 UV lamp with polarizer and VG-CLAM4 analyzer). In the gas spectrum, a very sharp HOMO band is observed and hole-vibration coupling is detected at the high-binding energy side with asymmetric feature. Note that the line shape of gas-phase UPS depends on the instruments as well as the temperature of molecules. Deposition of low-vapor pressure molecules on electrodes of electron analyzer system may cause serious problems on the line shape as seen in Fig. 2. Coropceanu *et al.*, reported a spectrum which shows a larger tail shape in the high-kinetic energy side [12], while our newly measured gas-phase UPS is free from it. The high-kinetic-energy tail feature by Coropceanu *et al.* [12] might be produced by an instrumental artifact. The details of a newly constructed gas-UPS apparatus will be described in elsewhere.

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