

Electronic Property of Functional Organic Materials

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Functional organic materials (FOM) have recently attracted considerable attention both for fundamental research and device applications because of peculiar properties not found in inorganics and small molecules. However the mechanisms and its origin of various device characteristics are still under debate. Scientific mysteries would be raised because people have believed that electronic structure of FOM would be conserved as in an isolated molecule for solid phases due to van der Waals interaction. To reveal characteristics of FOM the key investigation would be on precise experiments on the electronic structure at various interfaces, including organic–organic and organic–inorganic (metal/semiconductor) contacts. In these systems, the impacts of weak interaction on the electronic structure would be appeared as small intensity modulation of photoelectron-emission fine features depending on adsorption and aggregation on the surface. By recent development in the instrumental we can assess hidden fine structures in the electronic states, *e.g.* electron–phonon coupling, quasi-particle states, very small gap-state DOS, weak band dispersion and dynamic electronic polarization. To elucidate what really happens for the FOM at the interface upon weak interaction, an evaluation on the wave-function

spread of the electronic states would be very important because the interface states for the physisorbed systems are described to be a delocalized molecular orbital state depending on the strength of weak electronic coupling (hybridization). Seeing a modification of electron wave function upon weak electronic coupling as well as strong electron–phonon coupling is central issue on our agenda.

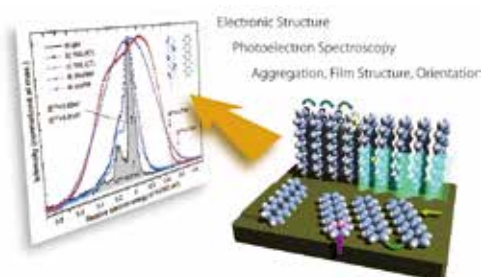


Figure 1. Scheme of a rich assortment in the structure of functional molecular materials and variety in the spectral feature of ultraviolet photoelectron spectrum (UPS) for the HOMO band taken for various structural phases (gas-phase, lying monolayers, standing monolayer, and disordered film).

Selected Publications

- F. Busolotti, S. Kera, K. Kudo, A. Kahn and N. Ueno, “Gap States in Pentacene Thin Film Induced by Inert Gas Exposure,” *Phys. Rev. Lett.* **110**, 267602 (5 pages) (2013).
- S. Duhm, Q. Xin, S. Hosoumi, H. Fukagawa, K. Sato, N. Ueno and S. Kera, “Charge Reorganization Energy and Small Polaron Binding Energy of Rubrene Thin Films by Ultraviolet Photoelectron

Spectroscopy,” *Adv. Mater.* **24**, 901–905 (2012).

- S. Kera, H. Yamane and N. Ueno, “First Principles Measurements of Charge Mobility in Organic Semiconductors: Valence Hole-Vibration Coupling in Organic Ultrathin Films,” *Prog. Surf. Sci.* **84**, 135–154 (2009).

1. Charge Reorganization Energy and Small Polaron Energy of Molecular Films¹⁾

Understanding of electron–phonon coupling as well as intermolecular interaction is required to discuss the mobility of charge carrier in functional molecular solids. We summarized 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.

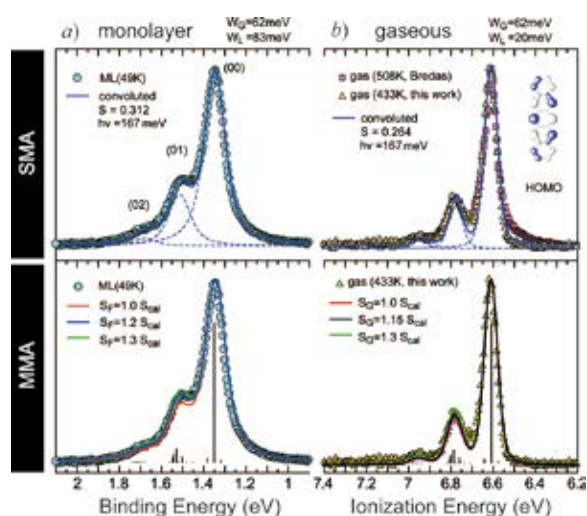


Figure 2. Comparison of HOMO band of pentacene between angle-integrated UPS for the monolayer (*a*, left panels) and gas-phase UPS (*b*, right panels). Convoluted curves by the single mode (SMA) and multimode (MMA) analyses of vibration coupling are also shown.

2. Impact of Molecular Orbital Distribution on Photoelectron Intensity²⁾

Ultraviolet photoelectron spectroscopy (UPS) is well

established technique for studying the electronic structure of surfaces and interfaces. In the detail, however, the origins of the UPS spectral features are not clearly understood even for so-called van-der Waals molecular crystals formed by weak intermolecular interaction. For molecular monolayer films prepared on a metal substrate, the spectrum is complicated much more due to orbital hybridization and charge transfer, which lead to interface states and/or broadening of spectral features. In principle, photoelectrons can give us all of important information on electronic properties in the molecular systems, when we measure precisely the molecular sample prepared very carefully.

The recent development in the theoretical evaluation of photoelectron intensity from π -electronic states delocalized over a molecule is discussed. By comparing the experimental photoelectron angular distribution (PAD) from the organic molecular assemblies with computed PAD we show that the use of the initial-state orbitals by density functional theory and the final continuum states by multiple-scattering theory (MSMO) is suited for simulations of angle-resolved UPS (ARUPS) and PAD. We demonstrate that the ARPES and PAD simulations are useful to characterize the top five π -electronic states for picene ($C_{22}H_{14}$) film.

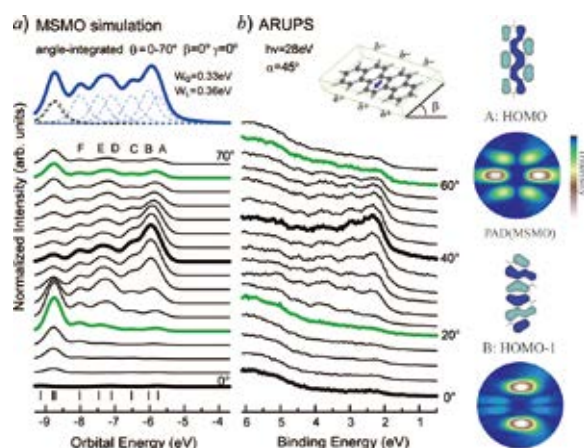


Figure 3. (a) Simulated ARUPS by MSMO calculation for an isolated picene molecule. (b) Observed take-off angle θ dependence of ARUPS of picene film (10 nm) on graphite. The molecules are assumed to be lying-flat in the film. Each spectrum is produced by convoluting Voigt function for all states. Calculated PADs of top two MO states by MSMO are shown (right).

References

- 1) S. Kera and N. Ueno, *J. Electron Spectrosc. Relat. Phenom.* **204**, 2–11 (2015).
- 2) Y. Liu, D. Ikeda, S. Nagamatsu, T. Nishi, N. Ueno and S. Kera, *J. Electron Spectrosc. Relat. Phenom.* **195**, 287–292 (2014).

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