

IV-E Photoelectron Spectroscopy of Organic Solids in Vacuum Ultraviolet Region

The works of ultraviolet photoelectron spectroscopy (UPS) with synchrotron radiation light source (UVSOR-UPS) of advanced organic materials have been proceeded to find their quantitative electronic structures and also to analyze their structures of assemblies.

IV-E-1 Angle-Resolved Photoemission Spectra of ω -(*n*-pyrrolyl) Alkanethiol Self-Assembled Monolayers: Possible Assemblies of Substituent Pyrrole

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Angle resolved ultraviolet photoelectron spectra (ARUPS) on pyrrolyl-SAMs on polycrystalline Ag were measured by using synchrotron radiation. We found the π bands originated from the substituent pyrrole which are distinguishably observed from the bands of alkyl backbone. Since the π bands are available for the cue to probe the surface structures of pyrrole, we calculated the photoelectron angular distributions of them for the model structures obtained by molecular dynamics (MD) calculations. We revealed that two surface structures of pyrrole, face-stacked and herringbone structures, are possible for pyrrolyl-SAMs on Ag(111) and the herringbone structure is energetically favored.

The calculated photoelectron angular distributions can clearly distinguish between the face-stacked and herringbone structures of surface pyrrole, and give information on the orientation of pyrrole, the direction of pyrrolyl facing axis, and symmetry of the surrounding molecules. The ARUPS measurement for pyrrolyl-SAMs is promising for quantitative determinations of surface structures and now in progress.

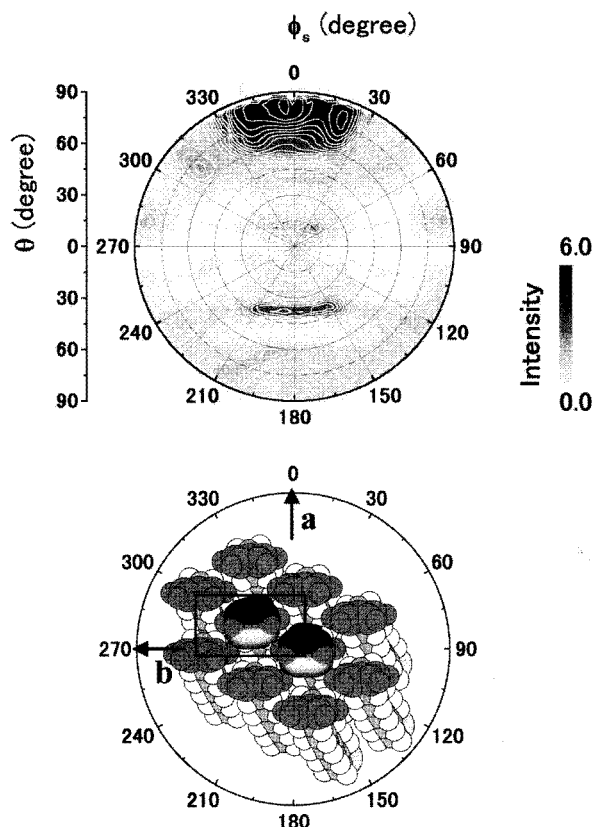


Figure 1. Calculated photoelectron angular distribution of π state within the single-scattering approximation. The photoelectron intensity is displayed by shading by the two-dimensional mapping with θ and ϕ_s . The illustration shows the face-stacked structure of pyrrolyl-SAMs obtained by MD calculation.

IV-E-2 Structure of Copper- and H₂-Phthalocyanine Thin Films on MoS₂ Studied by Angle-Resolved Ultraviolet Photoelectron Spectroscopy and Low Energy Electron Diffraction

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Angle-resolved ultraviolet photoelectron spectra (ARUPS) of copper phthalocyanine (CuPc) and metal-free phthalocyanine (H₂Pc) films (thickness from monolayer to 50–80 Å) on cleaved MoS₂ substrates were measured using monochromatic synchrotron radiation. Observed take-off angle (θ) and azimuthal angle (ϕ) dependencies of the top π band intensity were

analyzed quantitatively by the single-scattering approximation theory combined with molecular orbital calculations. The analysis indicated that the molecules lie flat on the MoS₂ surface in monolayer films of CuPc and H₂Pc. The azimuthal orientation of the molecules (angle between molecular axis and surface crystal axis of MoS₂), was found to be about -7° , -37° , or -67° for both monolayer films of CuPc and H₂Pc. In the azimuthal orientation, the analyses indicated that there are only molecules with counterclockwise rotation, although both clockwise and counterclockwise rotations are expected. From the low energy electron diffraction, the two-dimensional lattice structure of the monolayer film was obtained. On the basis of these two kinds of experimental results, the full structure of the monolayer film, the two-dimensional lattice and the molecular orientation at the lattice points, was determined. Furthermore, for the thick films it is found from the analyses of ARUPS that CuPc and H₂Pc molecules tilt about 10° from the surface plane.

IV-E-3 Electronic Structure of Poly (1,10-Phenanthroline-3,8-diyl) and Its K-doped State Studied by Photoelectron Spectroscopy

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[*J. Chem. Phys.* **110**, 2552 (1999)]

Ultraviolet photoelectron spectra were measured using synchrotron radiation for thin films of poly(1,10-

phenanthroline-3,8-diyl) (PPhen) and its potassium-doped state. Upon potassium doping of PPhen, two new states, which could be assigned to bipolaron bands, appear in the originally empty energy gap. The electronic structure of the neutral and potassium-doped states was theoretically analyzed using single-scattering approximation combined with semiempirical molecular orbital calculations.

IV-E-4 Electronic Structures of Alq₃/LiF/Al Interfaces Studied by UV Photoemission

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[*Synth. Met.* **102**, 1145 (1999)]

The electronic structure of tris (8-hydroxyquinolino) aluminum (Alq₃)/LiF/Al system was studied in relation to the enhancement of electron-injection efficiency by the insertion of LiF insulating layer at Alq₃/Al contact, using UV photoemission spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS), and metastable atom electron spectroscopy (MAES). The observed energy separation between the HOMO of Alq₃ and the Fermi level of Al substrate increased from 2.7 eV to 3.0 eV by inserting 0.5 nm thick LiF layer. This result indicates that the LiF layer induces the decrease of the electron injection barrier. We also found extra states probably caused by the interaction at the Alq₃/Al interface. The spectral intensity of this extra state decreased with increasing LiF thickness, and vanished at 0.5 nm.

IV-F Electrical Conduction and its Related Properties of Organic Solid

To expand the research field of molecular conductors, we always consider to find a new category. One of them is three components organic semiconductors, conductors and superconductors. In this section, we present the works of three components organic superconductors based on C₆₀.

IV-F-1 Three Component Organic Superconductors: Intercalation of KH into C₆₀

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We have prepared (KH)₃C₆₀ as an initial composition by direct reaction of potassium hydride (KH) to C₆₀. (KH)₃C₆₀ had higher T_c (19.5 K) and larger lattice constant (14.351 Å), compared with K₃C₆₀ prepared by doping of potassium metal. The expanded lattice constant is suggestive of the intercalation of hydrogen. The evidence of the inclusion of hydrogen was given by mass-analyzed thermal desorption experiment. We have also prepared (NaH)_{4-x}(KH)_xC₆₀ to study the substitutional effect of KH to (NaH)₄C₆₀. It was found that the superconducting phase is stabilized by

substitution of only a few percent KH as seen in (NaH)_{3.9}(KH)_{0.1}C₆₀.

IV-F-2 Hydrogen Intercalation in Potassium-C₆₀

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Solid state ¹H NMR of (KH)₃C₆₀ was measured in the temperature range between -80 and 60°C . A doublet spectrum composed of main peak at -7.0 ppm and shoulder peak at ~ 0 ppm was observed at room temperature. The negative chemical shift of the main peak indicates that hydrogen in (KH)₃C₆₀ exists as a hydride-like ion. The 60°C spectrum became singlet at -5.8 ppm due to motional narrowing.