VIII-V Studies of Electronic Structure of Organic Thin Films

Electronic structures of organic film surface and organic/inorganic interface are expected to play an important role in organic-device properties. It is important to clarify the characteristics of not only occupied states but also unoccupied states for organic thin films, since the device properties such as the efficiency of the electron and/or the hole injection depend on the position and/or the distribution of these electronic states. We have investigated the electronic structure of organic film surface and organic/inorganic interface using surface sensitive spectroscopies such as photoelectron spectroscopy and near-edge x-ray absorption fine structure (NEXAFS). To help the assignment of NEXAFS spectra, we use the photon energy dependence of photon-stimulated ion desorption, since the chemical bond scission by inner-shell excitation depends on the electronic configuration of the excited state.

VIII-V-1 Photodegradation of Poly(Tetrafluoroethylene) and Poly(Vinylidene Fluoride) Thin Films by Inner Shell Excitation

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Ion time-of-flight (TOF) mass spectra of poly(tetrafluoroethylene) (PTFE) and poly(vinylidene fluoride) (PVDF) thin films near fluorine and carbon *K*-edges were observed. For PTFE thin films peaks corresponding to F^+, CF^+, and CF_3^+ appeared, while for PVDF F^+ and H^+ were mainly observed. They indicate that for PTFE the polymer chain (C–C bonds) as well as C–F bonds are broken by irradiation of photons near fluorine and carbon *K*-edges, while for PVDF the bond scission occurs mainly at the C–F and C–H bond. In Figures 1 (a), (b), and (c) partial ion yield (PIY) spectra of F^+, CF^+ and CF_3^+ for PTFE thin films are compared with total electron yield (TEY) near the fluorine *K* absorption edge. PIY spectra of F^+, CF^+ and CF_3^+ are different from the TEY spectrum. The intense PIY feature of F^+ appears at $h\nu$ = 689 eV corresponding to the transition from F1*s* to σ(C–F)*. The PIY intensity of F^+ at $h\nu$ = 689 eV is much stronger than at $h\nu$ = 693 eV corresponding to the transition from F1*s* to σ(C–C)*, while the TEY intensity at $h\nu$ = 689 eV is slightly stronger than that at $h\nu$ = 693 eV. That is, the C–F bond scission by irradiation of photons at $h\nu$ = 689 eV (F1*s* → σ(C–F)*) is expected to occur more effectively than at $h\nu$ = 693 eV(F1*s* → σ(C–C)*). For the case of PVDF, the intense PIY feature of F^+ appears at the transition from F1*s* to σ(C–F)*. The excitation from fluorine 1*s* to σ(C–F)* is specially efficient for F^+ ion production for both PTFE and PVDF.

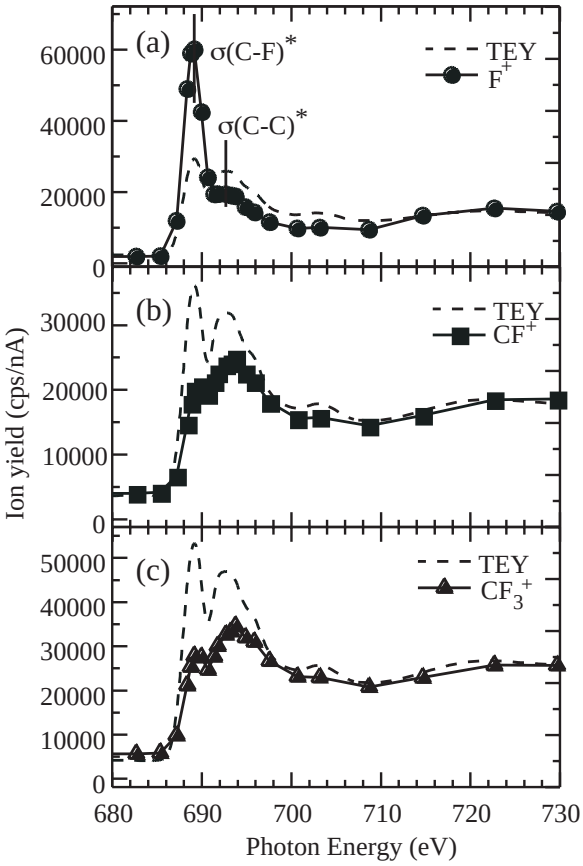

Figure 1. PIY spectra of (a) F^+, (b) CF^+ and (c) CF_3^+ for PTFE thin film near the fluorine *K* absorption edge. TEY spectra (broken curve) are also shown for comparison. TEY spectra are renormalized at $h\nu$ = 682.5 eV and at $h\nu$ = 730 eV to fit PIY intensities.

VIII-V-2 Excited States of Perfluorinated Oligo(p-phenylene) by Inner-Shell Excitation

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Ion time-of-flight (TOF) mass spectra and near edge x-ray absorption fine structure (NEXAFS) spectra of

perfluorinated oligo(*p*-phenylene) (PF-8P) films near fluorine (F) and carbon (C) *K*-edges were observed. In ion TOF mass spectra near F and C *K*-edges, F^+, CF^+, and CF_3^+ were intensely observed. It indicates that C–C bonds of phenyl ring as well as C–F bonds are broken by irradiation of photons near F and C *K*-edges. Partial ion yield (PIY) spectra of PF-8P show clear $h\nu$ dependence near F and C *K*-edges. Especially, near F *K*-edge, the PIY spectra of F^+ increases remarkably at $h\nu$ = 689.2 eV, which corresponds to the lowest peak in NEXAFS. The lowest peak in the NEXAFS near fluorine *K*-edge is assigned to the transition from F1*s* to σ(C–F)*. Furthermore, from the analysis of PIY spectra of PF-8P near carbon K-edge, the peak at $h\nu$ = 289.5 eV is ascribed to the transition from C1*s* to σ(C–F)*.