

Site-specific ion desorption of fluorinated phthalocyanine

Koji. K. Okudaira^{1*}, Eiichi Kobayashi², Kazuhiko Mase², Nobuo Ueno¹

¹Faculty of Engineering, Chiba University, 1-33 Yayoi-cyo, Inage-ku, Chiba 263-8522, Japan

²KEK-PF, Tsukuba, Ibaraki 305-0801, Japan

Introduction

Site-specific chemical bond scission by inner-shell excitation using synchrotron radiation is a promising approach to the control of chemical bond scission, since inner shell excitation is highly localized on specific atoms in molecules. To clarify the mechanism of ion desorption induced by inner-shell excitation, the Auger-electron photo-ion coincidence (AEPICO) method is a powerful tool because it can be used to measure ion desorption yields for a selected core excitation or a selected subsequent Auger transition. [1]

Recently, for fluorinated copper phthalocyanine ($F_{16}CuPc$), selective F^+ desorption occurs by the irradiation of photons corresponding to the transition from F 1s to $\sigma(C-F)^*$ [2]. In this report we described an ion desorption mechanism of $F_{16}CuPc$ by using Auger and AEPICO spectroscopies.

Experimental

Experiments were performed at the beamline 13C at the Photon Factory, Institute of Materials Structure Science. AEPICO spectra were measured by using the EICO apparatus, which is composed of a coaxially symmetric mirror electron energy analyzer and a polar-angle-resolved compact time-of-flight ion mass spectrometer with four concentric anodes. TEY and TIY, Auger, AEPICO spectra were observed at the incidence angle of the photons of 84° (grazing incidence). TIY and TEY were normalized to the incident photon flux recorded as the photocurrent at the photon-flux monitor consisting of a gold-evaporated mesh. All measurements were performed at room temperature.

Results and discussion

Figure 1 shows AEPICO F^+ signal intensities as a function of the E_k (AEPICO yield spectra) at $h\nu=691.4$ eV (the transition from F 1s to $\sigma(C-F)^*$) and 695.8 eV. At these photon energies F 1s NEXAFS spectra show large peaks. On the other hand, in the total ion yield spectra the large peak appears only at $h\nu = 691.4$ eV. In the AEPICO yield spectra at $h\nu=691.4$ eV and 695.8 eV, two peaks appear at $E_k=645-650$ eV and 620-625 eV. At $h\nu=691.4$ eV, the intensity of the larger E_k peak is remarkably high. The E_k position of this peak in AEPICO yield spectra is about 2 eV larger than that of corresponding Auger peak. On the other hand, at $h\nu=695.8$ eV, the AEPICO yield is small and the shift is not observed. The AEPICO peak shift to the Auger peak indicates that the mechanism of the high F^+ desorption at $h\nu = 691.4$ eV is related to the spectator-Auger process.

To estimate the contribution of spectator-Auger process, we compare AEPICO yield spectra with the difference Auger spectra, because the difference Auger spectra correspond to the spectator-Auger component. As seen in Fig.1, the intense peak positions of the AEPICO yield spectrum at $h\nu=691.4$ eV is in good agreement with that of the corresponding difference Auger spectrum. A possible explanation of selective F^+ desorption at $h\nu=691.4$ eV is that the desorption is intermediated by spectator-Auger processes.[1] At the final states of spectator-Auger process C-F bonds are more repulsive than those at the normal Auger final states, because $\sigma(C-F)^*$ has a C-F antibonding character. The intense F^+ desorption at the transition F 1s to $\sigma(C-F)^*$ by spectator-Auger process is more effective than that by the normal-Auger process.

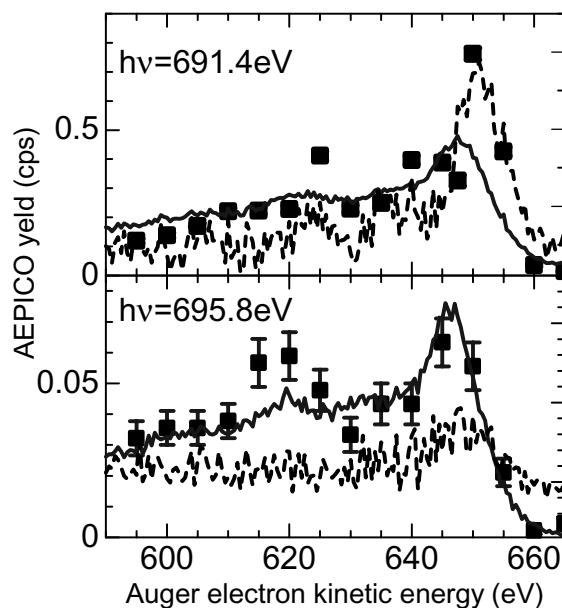


Fig 1 F^+ AEPICO spectra at $h\nu=691.4$ eV and $h\nu=695.8$ eV. The solid lines represent the Auger spectra in arbitrary units. The broken lines represent the difference Auger spectra in arbitrary units.

References

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* okudaira@faculty.chiba-u.jp