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K-shell dependent bond dissociation of core-excited *p*-fluorobenzyl SAM

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Introduction

Core-electron excitations have quite unique nature differently from valence excitations because of special localization of core electrons. So, ionic dissociation induced by resonant core excitations also reveals characteristic phenomena, in particular site-selective ionic dissociation is one of noteworthy characteristics. So far, we have found that such selective bond breaking can occur on organic surfaces, especially for ester compounds like PMMA thin films and ester-terminated self-assembled monolayers (SAMs) [1].

In this study, near-edge X-ray absorption fine structure (NEXAFS) and the following ionic dissociation were spectroscopically investigated for p-fluorobenzyl type SAMs (*p*-$FC_6H_4CH_2S$/Au; *p*FPh SAMs) in which strong C-F bond scission was expected under the equivalent core model (Z+1 approximation).

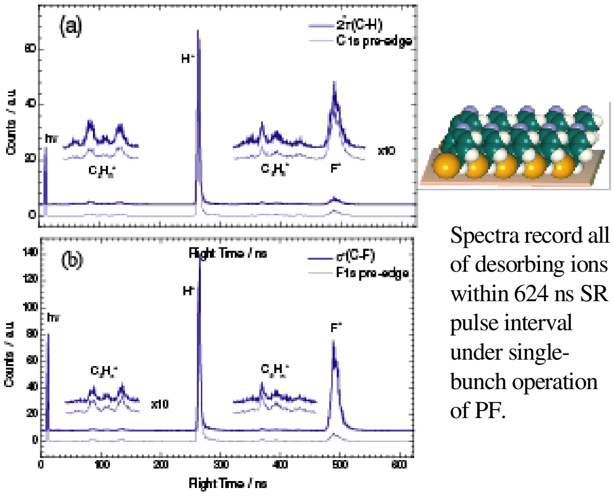
Experimental

NEXAFS and time-of flight (TOF) measurements were carried out at the beamline BL7A, whose details were described elsewhere [2]. Partial ion yield spectra (PIY) were measured by detecting ions selected by TOF ion mass spectrometer under single-bunch operation of PF.

Results and Discussion

NEXAFS spectra of *p*FPh SAMs indicate fine structure mainly originating from phenyl rings in the C K-edge, and C-F bonding in the F K-edge. Fig. 1 shows TOF spectra measured at both C and F K-edges. In the case of *p*FPh SAMs of which main skeletons are composed by phenyl rings, main desorption specie in both C1s off-resonant and resonant core-excitations (Fig. 1(a)) is the H^+ ion and the other species like CH_n^+/$C_2H_n^+$ ions are significantly reduced in compared with functional alkane thiol SAMs [1]. On the other hand, in F K-edge (Fig. 1(b)), the resonant excitation to the σ^*(C-F) antibonding orbital significantly enhances C-F bond dissociation.

PIY spectra of *p*FPh SAMs measured in C and F K-edges are indicated in Fig. 2. Spectra indicate mainly three characteristic features. (i) F^+ desorption shows enhancement of C-F bond dissociation in excitations to C-F related antibonding orbitals in both K-edges. (ii) $C_2H_n^+$ and $C_3H_n^+$ ions desorb selectively in the C1s excitation to the 2π*(C-H) where electronic state probably changes due to fluorination. (iii) In the F K-edge, the enhancement of C-F bond scission (F^+ desorption) is very strong as expected from the equivalent core model. On the other hand, all of the other measured ions indicate structureless profiles and no excited state dependence. This is a quite interesting phenomenon indicating the locality of the core-electron excitation.



Spectra record all of desorbing ions within 624 ns SR pulse interval under single-bunch operation of PF.

Fig. 1. TOF spectra of *p*FPh SAMs measured in (a) C K and (b) F K-edges.

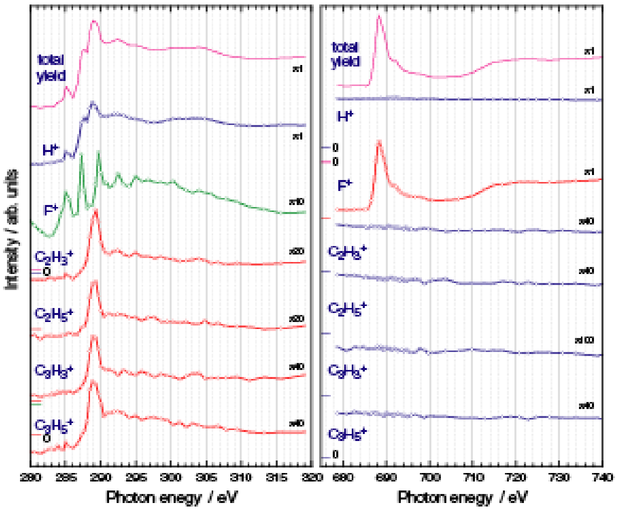


Fig. 2. PIY spectra of *p*FPh SAMs measured in (a) C K and (b) F K-edges.

References

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