

## Element- and Orientation-Selective Photo-Fragmentation using Polarized Synchrotron Radiation

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### Introduction

Due to intra-atomic nature of inner-shell excitation, chemical bonds can be broken in the vicinity of excited atoms in molecules. The phenomenon of such a "site-specific fragmentation" has attracted intensive attention, thus investigated for many substances in the gas phase. Furthermore, such a fragmentation is more likely to take place on surfaces. This is because less energetic excited states that end in less selective fragmentation are mostly deactivated by interaction with substrates. However, a question arises how such a specific fragmentation pathway is modified depending on molecular orientation at surfaces. To elucidate it we measured the dependence of the photon-stimulated ion-desorption (PSID) yield spectra on the polarization angle.

### Experimental

The experiments were performed at BL11A and 13C stations. The dependence of fragment-ion yields on photon incidence angles were measured using a rotatable time-of-flight mass-spectrometer (TOF-MS) that was developed in our group. TOF-MS measurements were done using pulsed soft X-rays during the single bunched operation. Polarization NEXAFS was measured by total electron yield (TEY) method. Thin layers of sample molecules were grown on a cleaned Si(100) or gold substrate cooled by liquid nitrogen. Fluorinated graphite was prepared by implantation of F<sup>+</sup> ions into highly oriented pyrolytic graphite (HOPG).

### Results and discussion

Monolayers of H<sub>2</sub>O/Si(100,111) and C<sub>6</sub>H<sub>6</sub>/Si(100,111); multilayers of HCOOH[1], C<sub>6</sub>H<sub>6</sub>[2], HCOND<sub>2</sub>[3], C<sub>6</sub>H<sub>5</sub>F, C<sub>6</sub>D<sub>5</sub>Cl, CO<sub>2</sub>; self-assembling monolayer films, HS(CH<sub>2</sub>)<sub>15</sub>COOCH<sub>3</sub>/Au[4,5]; and fluorinated graphite were investigated using the rotatable TOF-MS. Significant polarization dependence of fragment yields was observed for all systems and insights into site-specific fragmentation and desorption were obtained. We summarize findings as follows:

(1) A core-hole resonance enhances the fragmentation

occurring at the core-hole site, while it does not enhance the fragmentation at a site far from the core-hole.

(2) Polarization dependence is observed for the fragments that include core-excited atom or nearest neighboring atom of it; however, no polarization dependence is seen for the fragments that originate at a site far from a core hole.

(3) The degrees of polarization dependence and yield enhancement depend on substances.

As an example of the facts (1) and (2), the polarization dependencies of relative desorption probabilities for H<sup>+</sup> (Fig.1-(a)) and for F<sup>+</sup> (Fig.1-(b)) from condensed C<sub>6</sub>H<sub>5</sub>F are given. Desorption probability is defined as desorption ion yields divided by total electron yields. Probabilities relative to that of continuum state are displayed. F1s→σ\*<sub>C-F</sub> resonance enhances F<sup>+</sup>-yields, while it does not enhance H<sup>+</sup>-yields. F<sup>+</sup>-yields depend on polarization, while H<sup>+</sup>-yields do not. Observed orientation effect indicates that molecules with C-F axis standing upward more produce F<sup>+</sup>-fragments than those with C-F axis parallel to the surface. Fragments such as H<sup>+</sup> from C<sub>6</sub>H<sub>5</sub>F at F1s region and F<sup>+</sup> at C1s region (not shown) show no polarization dependence. We explain these fragments are indirectly caused by collision of secondary electrons such as Auger electrons.

As an example of the fact (3), a comparison of the polarization dependence between C<sub>6</sub>H<sub>5</sub>F and HCOOH is given. Orientation effect for HCOOH is stronger than that for C<sub>6</sub>H<sub>5</sub>F. This is attributed to higher branching ratio of direct dissociation for HCOOH.

### References

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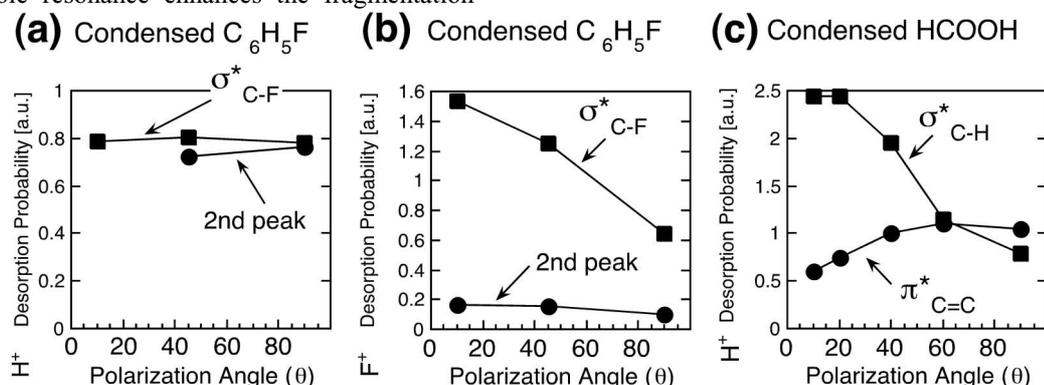


Fig. 1 Polarization-angle dependence of the desorption probabilities of fragment ions. (a) H<sup>+</sup> by F 1s excitation of condensed C<sub>6</sub>H<sub>5</sub>F, (b) F<sup>+</sup> by F 1s excitation of condensed C<sub>6</sub>H<sub>5</sub>F, (c) H<sup>+</sup> by C 1s excitation of condensed HCOOH.