

Mechanism of state-specific enhancement in photon-stimulated desorption as studied using a polarization-dependent technique

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Introduction

We have incorporated photon-stimulated ion-desorption (PSID) technique with polarization spectroscopy around NEXAFS (near-edge x-ray absorption fine structure) region. We believe it will give insights into orientation nature at top-most layers if desorption mechanism is fully understood[1]. However, there are still only few data of polarization-angle dependence of PSID spectra. Here we studied the angle-dependent PSID from condensed deuterated chlorobenzene (C₆D₅Cl)[2]. This system is interesting because it extends to 2*p*-edge excitation from 1*s*-edges studied so far, also because we can compare the angle dependences between core excitations of different elements, i.e. carbon and chlorine.

Experimental

The experiments were performed at BL11A station. The dependence of fragment-ion yields on photon incidence angles were measured using a rotatable time-of-flight mass-spectrometer (R-TOF-MS) that was developed in our laboratory. TOF measurements were done using pulsed soft X-rays during the single bunched operation. Polarization-dependence of NEXAFS was measured by recording sample drain current as total electron yields (TEY). The sample was prepared by depositing thick deuterated chlorobenzene onto a sputter-cleaned Si(100) wafer at 80K.

Results and discussion

Figure 1 compares the chlorine 2*p*-edge (a) Cl⁺-PSID- and (b) TEY-NEXAFS spectra of condensed C₆D₅Cl for various polarization angles θ. According to the gaseous ISEELS study, resonances A and B are respectively due to Cl 2*p*_{3/2} → π* (b₁) and Cl 2*p*_{1/2} → π* (b₁).

It is noteworthy that Cl⁺ desorption yields in resonances A and B depend on polarization angles, while TEY show no significant angle dependence. Assuming 2*p*-d(π*) transitions, we speculate the following two transitions are plausible for the A, B resonances taking into account photo-selection rule for C_{2v} symmetry.

$$\text{Cl } 2p_x \rightarrow d_{xz} \pi^* \text{ with } M_z \dots (1),$$

$$\text{Cl } 2p_z \rightarrow d_{xz} \pi^* \text{ with } M_x \dots (2),$$

where M_z and M_x refer to transition moments with C-Cl axis and perpendicular to benzene plane, respectively.

Here we rule out the possibility (1). For the transition (1), all C-Cl bonds have to be parallel to the surface when normal incidence (E//surface, E: electric vector of the light). But, this is not the case considering that strong enhancement of ion desorption is observed at normal incidence. The transition (2) is reasonable because all C-Cl bonds should be close to parallel to the surface when grazing incidence (E⊥surface), while parts of C-Cl bonds are upwards when normal incidence and have a possibility to end in enhanced desorption.

We measured and compared similar angle dependent data for

D⁺- and Cl⁺-desorption at C 1*s* and Cl 2*s* edges and found the following intriguing tendencies: (i) marked angular dependences are observed only when resonant enhancement in desorption is observed; (ii) the excitation of molecules with standing upward C-Cl (or C-D) bond leads to more efficient desorption (Orientation effect).

To explain the orientation effect, we assume first that ultra-fast dissociation (UFD) is involved in the desorption mechanism; and second that the charge-neutralization rate of desorbing ions decays exponentially with a normal distance from the surface. Figure 2 displays the desorption sequence proposed for our system. According to UFD, C-Cl (or C-D) bond is presumably elongated and Cl atoms (or D atoms) migrate a substantial distance within the lifetime of the core-hole states owing to anti-bonding nature of unoccupied orbitals. Therefore, the ion survival rate depends on the surface normal projection of the elongation. This view fits with the observed angular dependences.

[1] T. Sekiguchi et al., J.Elect.Spect. **144/147**, 437 (2005).

[2] T. Sekiguchi et al., Surf.Sci.(2005) in press.

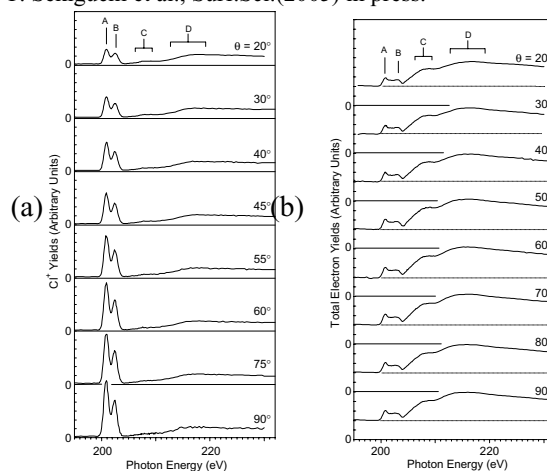


Fig. 1 Cl 2*p*-edge (a)Cl⁺- and (b)TEY- NEXAFS spectra of solid C₆D₅Cl for various polarization angles (θ). "θ" shows the incidence angles of X-ray beam. The E vector of polarized light and the surface normal has an angle of θ.

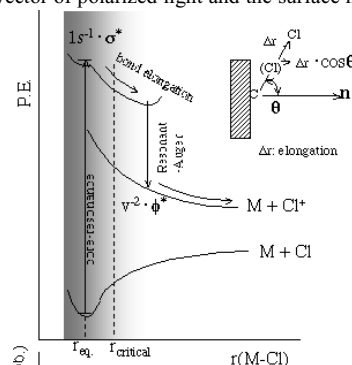


Fig.2 Desorption mechanism proposed for observed angular dependence of fragment-ion desorption.

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