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Enhancement effect in photon-stimulated ion desorption for benzene adsorbed on silicon surfaces observed using angle-dependent technique

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Abstract:

We have investigated photon-stimulated ion desorption from deuterated benzene (C_6D_6) adsorbed on Si(100) and Si(111) surfaces following C 1s core excitation. Using time-of-flight mass spectrometry combined with angle dependent technique, we measured the dependences of mass-spectra of desorption ions on photon energies and on incident angle (θ) of synchrotron beam. We have found the ion yields for adsorbate-derived fragments of CD^+ and CD_2^+ are enhanced in very small angles of incident x-rays. Moreover, molecular orientation effect appeared in excitation energy dependences of D^+ ions from the Si(100) and Si(111) surfaces; that is, ion yield spectra measured at $\theta=10°$ are different from that at $\theta=65°$. Furthermore, it was found that desorption ion yields increase greatly with decreasing incident angles. The angular dependences are consistently similar for all ion species, excitation energies, and indexes of substrates. Possible desorption processes are described on the basis of the observations.

1. Introduction

Photon-stimulated ion desorption (PSID) using synchrotron radiation (SR) has so far been investigated for a variety of surfaces [1]. This is because it has potential to give electronic and structural information with chemical selectivity and surface sensitivity. On the other hand, the polarization angle dependent NEXAFS (near-edge x-ray absorption fine structure) spectroscopy has been successfully applied to the derivation of precise orientation of molecules and functional groups on surfaces or in solids [2].

Even in the matured PSID technique, however, some fundamental properties such as dependences of ion yields on incident angles of x-rays are still ambiguous. Indeed, most of all previous researches were conducted with a fixed incident angle, except for few investigations including a first work by Treichler et al in 1985 [3]. They incorporated angle-dependent NEXAFS technique with PSID using rotatable quadrupole mass spectrometry. It was shown that excitation energy spectra of desorption ion yields are in fact dependent dramatically on incident angles in CO chemisorbed on Ru(001), pioneering how to elucidate the symmetry of double excitations. Recently, studies using the angle-dependent desorption technique have been reported for materials including multilayered molecules [4] and self-assembled monolayer molecules [5], where dominant interaction would be of inter-molecular. Only few papers, however, have been reported for monomolecular-layers, where main interaction is of adsorbate-substrate, although it is intriguing to see how desorption depends on molecular configuration on surfaces.

In this paper, we present ion yields dependent on incident angles of x-ray photons in carbon-1s core excitation edge for C_6D_6 adsorbed on Si(100) and Si(111) surfaces. Using a rotatable time-of-flight mass-spectrometer (TOF-MS), we measured the desorption mass-patterns in a variety of incident angles of photons. On the basis of angle-dependent data, possible desorption processes are discussed.

2. Experimental

The experiments were performed at the beamline 13C of the Photon Factory [6]. The energy resolution of the photon was about 0.2 eV at 285 eV. The details of experimental setup have been described elsewhere [7]. Briefly, the incident-angle dependences of TOF spectra for desorption ions was measured using the rotatable-TOF-MS [7] with microchannel-plate at the end of TOF tube using pulsed synchrotron radiation. TOF spectra were measured using time-to-amplitude converter (TAC) and a pulse-height-analyzer (PHA). The TOF detector was ca. 30 mm distant from the sample surfaces and was normal direction to the surfaces. The spot size of the photon beam on the sample was ca. 2mm square in the normal incidence. The horizontal length of the spot size changes by a factor of $\sim L(\theta=90^{o})/\sin(\theta)$, where θ is incident angle and $L(\theta=90^{o})$ means the length in the normal incidence, i.e., ca. 2mm, in a similar manner to conventional NEXAFS measurements. Using a high precision sample manipulator (VG Co.), the sample position was carefully controlled and we avoided illuminating the sample edge or the holder; thus, any signals from the sample edge or the holder are negligible. Auger electron yield (AEY) was recorded with hemispherical electron analyzer (CLAM2; VG Co.), which monitored the intensities of the C KVV Auger peaks appearing around 260 eV originating from benzene adsorbates. All spectra were normalized to the incident photon flux monitored with a gold-coated W mesh and pre-edge intensities around 280 eV. The base pressure of the chamber was $\leq 7\times10^{-8}$ Pa.

The Si(100) and Si(111) crystals (Shin-Etsu, Co.), p-type (B-doped) ~10 $\Omega^{\cdot}cm^{-1}$ resistivity, were cleaned by cycles of Ar^+ sputtering and annealing. Free contamination of carbons on the surfaces was confirmed by XPS and NEXAFS analysis. Commercial C_6D_6 (Wako Chem. Co., chemical purity >99.9%, degree of deuteration, 99.6 %) was used after degassed. Typically 1000L of C_6D_6 was exposed to the Si crystals. All measurements were carried out at room temperature.

3. Results and discussion

3-1. Time-of-flight mass spectra measured with varied incident angles of x-ray beam

Figure 1 shows TOF mass-spectra measured for C_6D_6 adsorbed on Si(100) and Si(111) surfaces with 5, 10, and 65° incident angles (θ) of x-ray photons below the C 1s absorption edge (hν=~279 eV) [Fig. 1 (a) and (c)] and on the C $1s\rightarrow\sigma^*_{C\text{–}C}$ resonance (hν=~292.0 eV) [Fig. 1 (b) and (d)]. All signals were normalized by both of incident photon flux and accumulation time. H^+, D^+, CD^+, CD_2^+, and F^+ desorption ions are observed, where H^+ and F^+ ions are always detected from Si substrates [8]; while, D^+, CD^+, and CD_2^+ originate from adsorbed C_6D_6. In Fig. 1, all signals are also normalized to the yields of H^+ ions to compare desorption mass patterns among incident angles. Here, the most interesting finding is that in smallest incident angle of 5°, relative desorption yields of CD^+ and CD_2^+ are enhanced, compared with large incident angles of 10° ~ 65°.

The enhancement effect was significant in the Si(100) surface, but the similar trend was observed in the Si(111) surface. Furthermore, this effect was also observed in other excitations; that is, on C $1s\rightarrow\pi^*_{C=C}$ (hν=~285 eV) and C $1s\rightarrow\sigma^*_{C\text{–}D}$ (hν=~288 eV) resonances, as well as C 1s→continuum (hν=~311 eV). In addition, this effect was also seen in the both Si(100) and Si(111) substrates. The following two facts are noteworthy:

1.- The enhanced species (CD^+ and CD_2^+) are derived from the adsorbate molecule.

2.- This enhancement effect was not very significant in the photon energies below the C 1s absorption edge, as shown in Fig. 1 (a) and (c).

These two facts strongly suggest that C 1s core-excitation of adsorbed benzene is a key trigger which induces the enhancement of CD^+ and CD_2^+ desorption yields in the very small incident angles.

3-2. NEXAFS spectra measured with varied incident angles of x-ray beam

Carbon 1s edge NEXAFS spectra were measured by recording carbon KVV Auger electron yields (AEY) as a function of photon energies, which correspond to x-ray absorption spectra for adsorbed benzene. Figure 2 (bottom) shows the AEY spectra measured in θ=10° and 65° for the Si(100) and Si(111). The assignments are based on the previous report [9]; that is, resonances from C 1s core level into $\pi^*_{C=C}$ [285.0 eV], σ^*_{C-D} [287.7eV], σ^*_{C-C} [292.2 eV], and $\sigma^*_{C=C}$ [298.6 eV] unoccupied orbitals.

For the both Si(100) and Si(111) surfaces, the $\pi^*_{C=C}$ resonance was observed, meaning the existence of C=C double bond in the adsorbates. The spectra for the C_6D_6-Si(100) and -Si(111) are qualitatively similar to the previously published NEXAFS spectra for benzene (C_6H_6) adsorbed on the Si(100) [9] and Si(111) [10] surfaces. The π^* peak area in Fig. 2 do not depend significantly on incident angles within the experimental errors, suggesting that π orbitals, or double bonds, are randomly oriented; that is, a substantial amount of carbon planes perpendicular to the surfaces exist in addition to the parallel planes. If benzene chemisorbs on the Si(100)-2×1 [9] or on the Si(111)-7×7 [10] reconstructed surfaces at room temperature, it leads to 1,4-cyclohexadiene-like structure with di-σ-bonds and shows that the NEXAFS spectra depend on polarization angles, indicating that the carbon ring planes tend to be parallel to the surfaces [9, 10]. Accordingly, the angular *independent* NEXAFS shown in Fig. 2 can probably be ascribed to the fact that the Si surfaces were not reconstructed such as Si(100)-2×1 or Si(111)-7×7, and/or that the surfaces had many step edges and thus were not atomically flat. Another possibility is that benzene molecules might have reacted with Si dangling bonds into Si–C($_6$D$_5$) and Si–D, which was shown to occur in the Si(111)-2×1 surface [11].

We tentatively assumed that the configuration of our samples is a mixture of dissociative chemisorbates (C_6D_5) and those similar to cyclohexa-diene or -monoene: these are not oriented due to atomically non-flat Si surfaces. Even if benzene planes were not oriented, it is rather favorable for the purpose of the present study. This is because it became possible to select the orientation of molecules in excitation by changing polarization angles.

3-3. X-ray energy dependences of desorption ion yields measured with varied incident angles

Figure 2 shows photon energy dependences of D^+, CD^+, and CD_2^+ desorption yields for C_6D_6 adsorbed on Si(100) and Si(111) surfaces at the C 1s excitation region. All spectra were normalized to the pre-edge values around 280 eV. Qualitative conclusion is that energy dependences showed various spectral shapes depending on fragment species. Desorption mechanism is discussed based on the x-ray energy dependences of desorption probabilities, which are defined as ion yields divided by

AEY, as shown in Figure 3.

D^+ desorption probabilities in the $\sigma^*_{C–D}$ resonance are enhanced for both incident angles and for both the Si(100) and Si(111) surfaces. This enhancement has been explained in terms of selective dissociation of C–D bond due to electron occupation into unoccupied orbital of strong anti-bonding $\sigma^*_{C–D}$ [12, 13]. At higher excited states around energies from ~292 eV ($\sigma^*_{C–C}$) to ~300eV (near $\sigma^*_{C=C}$), the D^+ probabilities are also somewhat enhanced, suggesting that these excited states are also antibonding along C–D bond.

In the $\pi^*_{C=C}$ resonance, the D^+ desorption probabilities from the both surfaces at $\theta=10°$ are suppressed, which is seen as negative swing at the $\pi^*_{C=C}$ in Fig. 3 (a) and (c); in contrast, the D^+ probabilities at 65° are not very suppressed in the $\pi^*_{C=C}$. The suppression at $\theta=10°$ can be understood due to the non-bonding character of the $\pi^*_{C=C}$ orbital concerning the C–D bonding: this is because the electron occupation to the $\pi^*_{C=C}$ orbital reduces the effective Coulomb repulsion between multiple holes in Auger-final-states [13].

However, the non-bonding character of the $\pi^*_{C=C}$ orbital only is not enough reason to explain why D^+ desorption probabilities at $\theta=65°$ are not very suppressed. The higher probabilities at 65° can be understood in terms of the direction of C–D bonds in $\pi^*_{C=C}$ excited molecules (the orientation effect of neutralization in ion desorption). In $\theta=10°$, molecules with C–D bonds directed mostly parallel to the surface are selectively excited; thus, D^+ fragments originating from such excited molecules pass through closer to the substrate than in $\theta=65°$ and are effectively charge-neutralized. In $\theta=65°$, however, molecules with C–D bonds tilted more upwards are selectively excited. Thus, neutralization effect becomes less significant.

The results demonstrate that the neutralization of fragment ions depends on the orientation of excited molecules. This is most probably due to the fact that charge/electron transfer interaction between adsorbate and substrate depends on molecular orientation. Finally, it should be noted that the orientation effect observed for D^+ desorption is consistent for the both Si(100) and Si(111) surfaces.

In Fig. 3 (top), the desorption probabilities for CD_2^+ are enhanced at the $\sigma^*_{C–C}$ resonance and at higher energies from ~295 eV to ~305 eV including $\sigma^*_{C=C}$ excitation, regardless of angles or substrates. This enhancement is simply understood as due to the fact that C–C bond breaking is enhanced by the antibonding character of $\sigma^*_{C–C}$ and $\sigma^*_{C=C}$ unoccupied orbitals, in the analogous manner with the interpretation of D^+ enhancement following the $\sigma^*_{C–D}$ excitation.

In the both surfaces, the desorption probabilities for CD_2^+ ions at θ=10° are suppressed at the $\pi^*_{C=C}$, which is seen as negative swing in Fig. 3 (a) and (c); in contrast, the CD_2^+ yields at 65° are not very suppressed at the $\pi^*_{C=C}$. This finding is very similar to that observed for D^+ desorption and can also be explained by a similar manner to that given to D^+ suppression following the $\pi^*_{C=C}$ excitation. Again, the results can be explained by a combination of two effects; that is, less antibonding character of the $\pi^*_{C=C}$ orbital and the direction of C=C bonds in the excited molecules (orientation effect of neutralization in ion desorption).

We might had better to speculate that CD_2^+ species are derived from rearrangement of deuterium atoms in excited molecules before desorption takes place, considering that substantial amount of CH_2^+ and CH_3^+ fragments are produced by 70 eV electron impact (EI) of gas phase benzene (C_6H_6) via rearrangement of hydrogen atoms [14].

Although the desorption probabilities for CD^+ ions show a little enhancement at the $\sigma^*_{C\text{–}D}$ resonance in Fig. 3 (middle), the overall profiles of CD^+ yields are very different from the AEY spectra as evident in Fig. 2 (a)-(d) (middle), regardless of incident angles or substrates. All CD^+ spectra consistently represent similar features: resonances characteristic of molecule are no longer very prominent. The *independences* on photon energies of this energy region (280–315 eV) are characteristic of Si 2p absorption spectra of silicon substrates [15]. The following two explanations are possible for this finding:

1. – The *independences* is due to x-ray induced electron stimulated desorption (XESD) [16]; that is, fragment desorption may be induced by collision excitation of secondary electrons generated through inelastic scattering of Si 2p photoelectrons and/or Si LVV Auger electrons.

2. – The *independence* is due to the fact that Si 2p core-excitation of silicon atoms at the top surface, which are directly bonded to carbon atoms of adsorbates, induces the CD^+ desorption.

The incident angular dependences discussed in Sec. 3-3 suggest that photo-absorption by adsorbates lying at the top surface layers is a key process in ion desorption consistently for all species of D^+, CD^+, and CD_2^+. Thus, we assume that the mechanism

2 is more suitable for CD^+ desorption. In this sense, we speculate that CD_2^+ and CD^+ fragments originate from carbon atoms farther from and bonded to silicon atoms of the substrate, respectively. This speculation agrees with the fact that yields of CD_2^+ are much higher than those of CD^+; also, this is reasonable because fragment ions originally bonded to Si atoms should be effectively neutralized more than those not bonded to Si atoms.

3-4. Dependences of desorption ion yields as a function of x-ray incident angles

To clarify the incident angle dependence more quantitatively, we measured the desorption ion yields (integrated peak area) as a function of the incident angles (θ). Figure 4 shows those for the pre-edge (hν=~279 eV), $\sigma^{\square *}_{CC}$ (hν=~292 eV), and ionization continuum (hν=~311 eV) excitations. As evident in Fig. 4, ion yields depend significantly on incident angles. D^+, CD^+ and CD_2^+-yields showed all similar angular dependences in most of all excitations. Here, yields for $\sigma*^{\square}_{CC}$ excitation are higher than those of pre-edge, except for CD^+ ions, indicating that C 1s core-excitation plays important role in the desorption. In addition, angular dependences of $\pi^*_{C=C}$ (hν = ~285 eV) and $\sigma^{\square *}_{CD}$ excitations (hν = ~288 eV) (not shown) were similar to those of $\sigma^{\square *}_{CC}$ excitation. Furthermore, similar dependences were observed for Si(100) and Si(111) surfaces. Characters of angular dependences are briefed as follows,

1.- Ion yields steeply increase in small angles.

2.- Ion yields gradually decrease or approach constants in large angles.

It should also be noted that even if the same number of photons are impinged into the surfaces, ion yields are greatly changed. Thus, intuitive inspection suggests that absorption of photons by benzene adsorbates lying at the top surface layers must be a key process for ion desorption; that is, bulk excitation does not contribute significantly to desorption.

4. Summary

The present paper demonstrates that the developed rotatable TOF-MS can provide novel information concerning the relations between fragment ion desorption and incident angles of x-ray photons. Following facts have been found.

1.- Ion yields for adsorbate-derived fragments are enhanced in very small angles of incident x-rays for the both Si surfaces.

2.- Molecular orientation effect appeared in excitation energy dependences of D^+ and CD_2^+ ions for the both Si surfaces.

3.- The desorption yields of fragment ions represent steep rise in small incident angles. Similar tendencies are consistently observed for all ion species, excitation energies, and Millar indexes of substrates.

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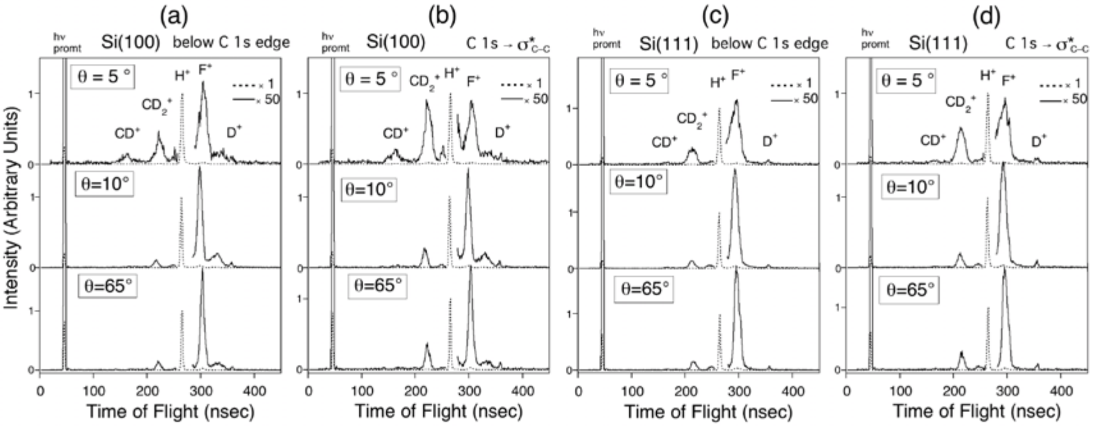

Fig.1 Time-of-flight mass spectra measured with 5, 10, and 65° incident angles of x-ray photons for C_6D_6 adsorbed on Si(100) [left; (a) and (b)] and Si(111) [right; (c) and (d)]. (a) and (c) Excitation energy was pre-edge (hν = ~279 eV). (b) and (d) Excitation was tuned to C $1s\rightarrow\sigma^*_{C\text{–}C}$ resonance (hν=~292 eV). Broken (- - - - -) and solid (———) lines represent original and 50 times enlarged spectra, respectively. The incident angle, θ, is the same as the one between surface normal axis and electric field vector of synchrotron radiation.

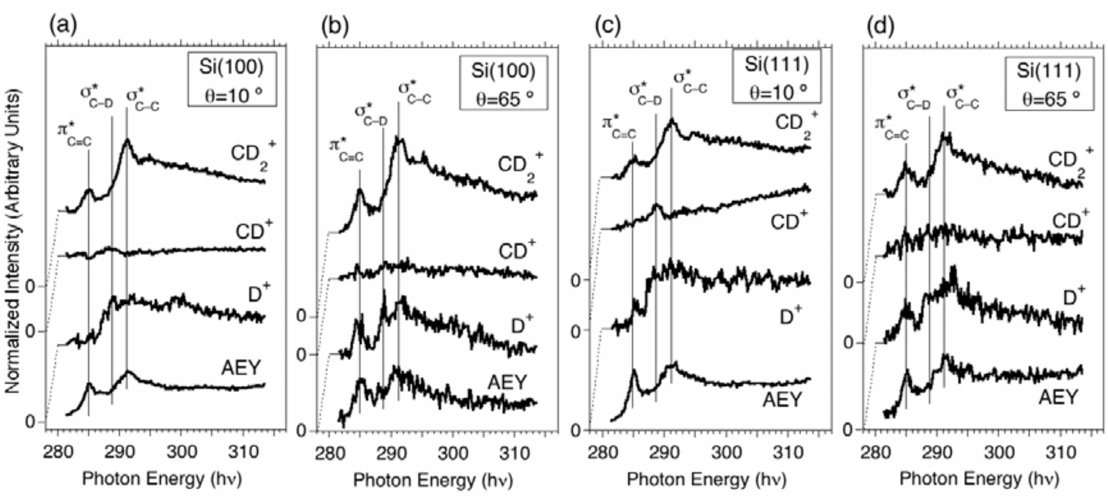

Fig. 2 Photon energy dependences of D^+, -CD^+, and -CD_2^+- desorption ion yields and Auger electron yields (AEY) for C_6D_6 adsorbed on Si(100) (left) and Si(111) (right) surfaces at the C K-edge. All spectra were normalized to the pre edge around 280 eV. (a) θ=10º and Si(100), (b) θ=65º and Si(100), (c) θ=10º and Si(111), and (d) θ=65º and Si(111).

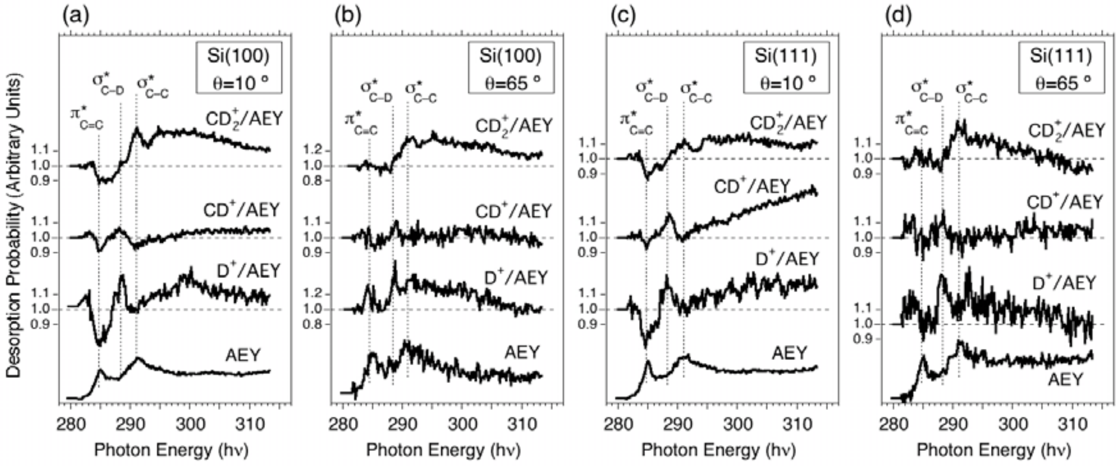

Fig. 3 Photon energy dependences of D$^+$, -CD$^+$, and -CD$_2$$^+$- ion desorption probabilities [defined as ion yields divided by Auger electron yields (AEY)], along with AEYs, for C_6D_6 adsorbed on Si(100) (left) and Si(111) (right) surfaces at the C K-edge. All spectra were normalized to the pre edge around 280 eV. (a) θ =10º and Si(100), (b) θ =65º and Si(100), (c) θ =10º and Si(111), and (d) θ =65º and Si(111).

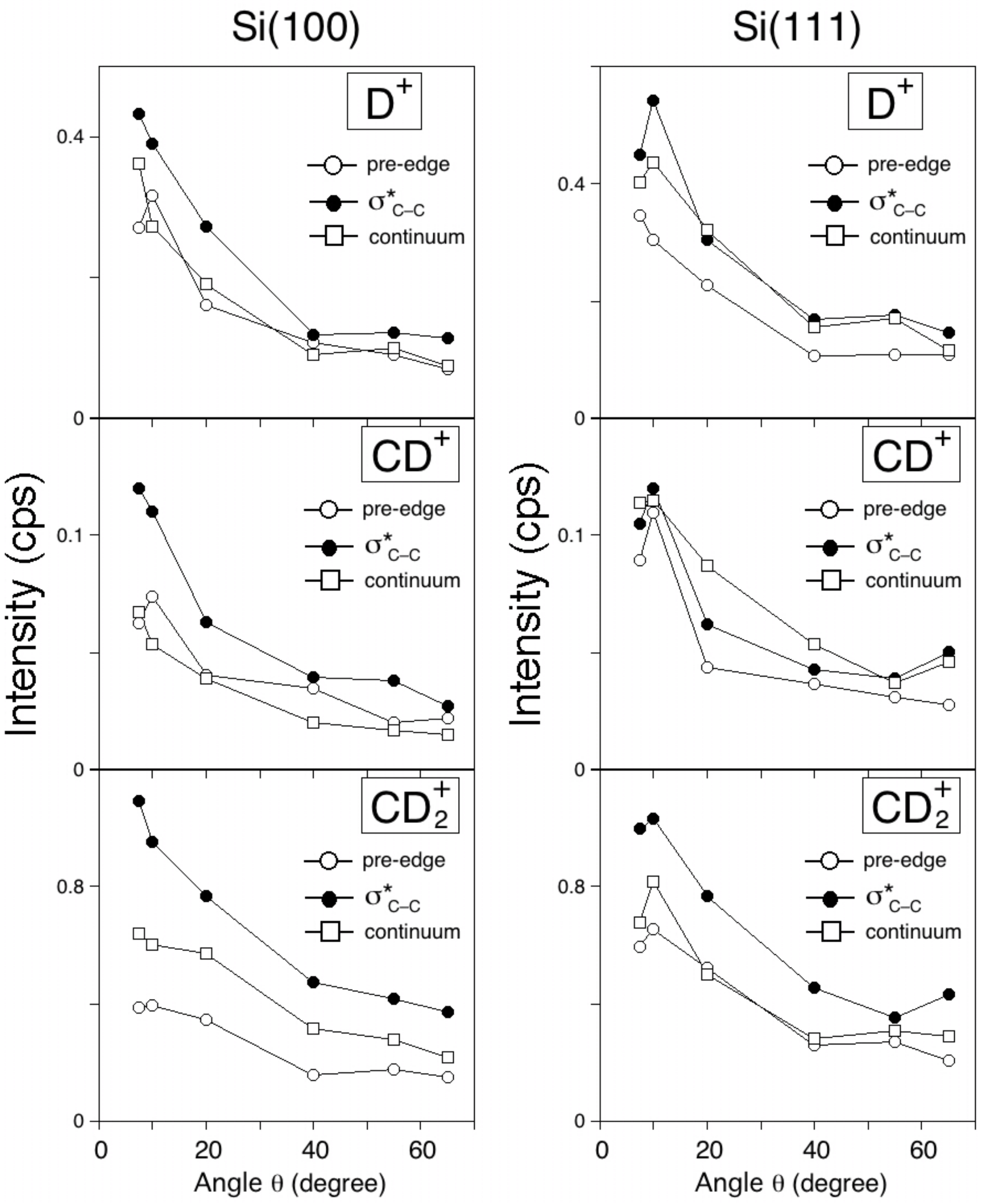

Fig. 4 Dependences of D$^+$, -CD$^+$, and -CD$_2^+$- desorption ion yields on incident angles (θ) of photon beam for C_6D_6 adsorbed on Si(100) (left) and Si(111) (right) surfaces. Ion yields measured with the excitations of energies blow the C K-edge (hν=~279 eV), on resonance C 1s→σ^*_{C-C} (hν=~292 eV), and in the continuum (hν=~311 eV) are plotted.