Distinct site- and state-selective dissociation of methyl-trifluoroacetate observed in core-electron excitation at the oxygen K-edge region

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Abstract. Distinct site- and state-selective dissociation following the O1s core-excitation has been found in the gaseous molecules of methyl trifluoroacetate (MTFA). The site- and state-selective dissociation was examined by measuring the branching ratios of dominant CH3+ and CHO+ fragments. The branching ratios from MTFA showed that site-selective dissociation takes place via the excitation from the different atomic sites to the same π*CO resonance state, (O1sCO→π*CO) and (O1sOMe→π*CO). A pronounced O1sOMe site-selectivity was identified by a significant increment of CHO+ formation at the (O1sOMe→π*CO) band. The site-selectivity was also justified by an equivalent core approximation using the density functional theory calculation. State-selective dissociation was identified among the (O1sOMe→π*CO), (O1sOMe→σ*O-Me) and (O1sOMe→σ*C-OMe) transitions originated from the same OMe core. State-selective production of CH3+ could be found at the (O1sOMe→σ*O-Me) band, whereas state-selective formation of CHO+ was observed at the (O1sOMe→π*CO) and (O1sOMe→σ*C-OMe) bands.

1. Introduction

Using tunable soft X-rays from synchrotron radiation sources, excitation site-specific and/or state-selective reactions following inner-shell excitation have been fundamental subjects for condensed molecules on the surface and isolated molecules in the gas phase [1,2]. Tinone et al. [3] observed photon stimulated ion desorption of poly-methylmethacrylate (PMMA: -(CH2ClCH2ClO)OCH3)n thin film in the oxygen K-edge region and found efficient desorption of specific cations (CH3+ and CHO+) that strongly depend on the anti-bonding character of the excited state. In order to elucidate the changes in the fragmentation mechanisms between macromolecules on the surface and isolated molecules in the gas phase, state-selective fragmentation of methy-isobutylate (MIB: (CH3)2CHC(O)OCH3), i.e. a monomer unit of PMMA, has been examined in the isolated condition [4]. In the latter case, state-selective CHO+ production was observed at the O1sOMe→π*OMe transition whereas state-selective CH3+ enhancement could not be identified at the O1sOMe→σ*OMe, as opposed to the efficient production of CH3+ found in PMMA. Kawasaki et al. [5] used deuterium labelled methyl-ester in the distinction of important functional group to avoid possible interfering production of CH3+ from the side branch of MIB, via excess energy delocalization within the isolated molecule. Deuterium labelled...
experiment of methyl-d$_3$ acetate (Md$_3$A: CH$_3$C(O)OCD$_3$) also showed that the state-selective excitation to the O1s$_{\text{OMe}}$$^-$ $^1\sigma^*_{\text{O-Me}}$ does not lead to prominent CD$_3^+$ yield. The absence of the state-selectivity found for these simple esters has been attributed to the small cross-section of the O1s$_{\text{OMe}}$$^-$ $^1\sigma^*_{\text{O-Me}}$ transition which is buried into the congestion of Rydberg transitions.

Here, we studied inner-shell excitation and fragmentation of methy-trifluoroacetate (MTFA: CF$_3$C(O)OCH$_3$), i.e. an analogue of MIB and Md$_3$A, and examined the site-specific and state-selective reactions. Most of the O1s core-to-valence bands for MTFA, including the O1s$_{\text{OMe}}$$^-$ $^1\sigma^*_{\text{O-Me}}$, were clearly resolved and properly assigned. Characteristic site-selectivity of the C=O/OMe cores and distinct excited-state-selectivity were identified from the CH$_3^+$/CHO$^+$ fragment analysis.

2. Experimental

The experiments were performed using a photoreactive scattering apparatus [6] connected to a plane-grating monochromator on the beamline BL-6 of the HiSOR facility. An effusive beam was prepared by direct introduction of pure MTFA under the stagnation pressure of $P_0=7.5$ kPa through a φ200 μm nozzle. The beam was skimmed and crossed with a monochromatized beam of soft X-ray at the ionization region of a Wiley-McLaren type time-of-flight (TOF) mass-spectrometer [7]. The photon energy was calibrated using the O1s $\rightarrow$ 4p/5s Rydberg transition of CO$_2$ at 540.01 eV. The resolution of the monochromator was $E/\Delta E=2000$ at the energy corresponding to the oxygen K-edge. The space resolution [7] of the present TOF-mass detector was $M_s=39.9$ amu.

MTFA sample was supplied by Aldrich at a purity of $\geq99\%$.

3. Results and discussion

3.1. Total-ion-yield (TIY) spectrum and TOF mass-spectra of MTFA at the oxygen K-edge

Figure 1(a) shows a typical TIY spectrum of MTFA in the effusive beam. The oxygen K-edge excitation involves electron transitions from C=O/OMe oxygen sites. Their ionization energies have been determined as $\text{IP}_{\text{CO}}=539.03$ and $\text{IP}_{\text{OMe}}=540.48$ eV in the X-ray photoelectron spectroscopy [8]. We assigned the O1s core-to-valence bands of MTFA as follows. The $\pi^*_{\text{CO}}$ transitions (1:O1s$_{\text{CO}}$$^-$ $^1\pi^*_{\text{CO}}$) and (2:O1s$_{\text{OMe}}$$^-$ $^1\pi^*_{\text{CO}}$) from the two oxygen sites occur at 531.76 and 534.79 eV; the (3:O1s$_{\text{OMe}}$$^-$ $^1\sigma^*_{\text{C-OMe}}$) band is clearly resolved at 537.17 eV, unlike the MIB and Md$_3$A; the two broad maxima for (4:O1s$_{\text{OMe}}$$^-$ $^1\sigma^*_{\text{C-OMe}}$) and (5:O1s$_{\text{CO}}$$^-$ $^1\sigma^*_{\text{CO}}$) appear at 541.34 and 547.56 eV, respectively.

TOF spectrum was derived by subtraction of TOF intensities of the background at the off-resonance region from those recorded at each core-to-valence band. In order to determine correct mass-intensities, a Gaussian curve-fitting analysis [5] has been made for the CH$_3^+$/CHO$^+$ mass-peaks (figure 1(b)). As was the case for core-excitation of other esters [3,5], significant production of CHO$^+$ must arise from the dissociation of parent cation at the C-OCH$_3$ bond as CF$_3$C(O)OCH$_3$$^+$ $\rightarrow$ CF$_3$CO + CH$_3$O$^+$, because the CH$_3$O$^+$ precursor is known to be a transient species that spontaneously
decomposes into CHO$^+$ and H$_2$. Similarly, CH$_m^+$ are generated via the direct scission at the RCO-CH$_3$ bond, CF$_3$C(O)OCH$_3$ $\rightarrow$ CF$_3$CO$_2$ + CH$_m^+$ + (3-$m$)H. The production of CH$_m^+$ from parent cation also comes to be important when delocalization rate of excess-energy is significant after the Auger relaxation. Summarizing the origin of the predominant products, CHO$^+$ and CH$_3^+$ (CH$_m^+$) are the ones that reflect the dissociation-site specificity following the core excitation. Here, we chose the intense CH$_3^+$ cation with mass of a single component as the representative of CH$_m^+$ species.

3.2. Site- and state-selective dissociation of MTFA at the oxygen K-edge
3.2.1. Site-selective dissociation of MTFA

The site-selective dissociation can be examined by comparing the product intensities between the (1:$\text{O}1\text{sCO} \rightarrow \pi^*\text{CO}$) and (2:$\text{O}1\text{sOMe} \rightarrow \pi^*\text{CO}$) bands, since only the atomic site to be core-excited is different in these excitations. The intense CHO$^+$ ratio at the band 2, relative to the band 1, can be interpreted as being due to the site-selective enhancement of the C-CH$_3$ dissociation. In contrast, core-excitation at the C=O site does not lead to direct dissociation, rather induces excess-energy transfer to give fragment cations via the scission at weak bonds. Core-excited fragmentation is expected to take place after the fast electronic relaxation involving the Auger decays. It has been suggested in a simple ester [9] that the spectator Auger decay to two-holes/one-electron states was important for the resonant Auger processes. Since the $\pi\text{CO}/\pi^*\text{CO}$ orbitals of MTFA are localized both on the carbonyl C=O atoms and methoxy-oxygen atom based on our DFT calculation [10], $\pi^*\text{CO}$ character that remains at the Auger final-states may provide a repulsive nature for the subsequent C-OMe dissociation process.

![Figure 3. (a) Potential energy curve of the O1sCO$^{-1}\pi^*\text{CO}$ state against $r_{\text{C=O}}$, calculated using the ECA by substitution of F atom for the equivalent core oxygen (C=O). (b) Molecular configuration at the ECA potential minimum along $r_{\text{C=O}}$ coordinate.](image)

In order to justify the dynamic behaviour on the core-excited states and spectator Auger states, we employed the equivalent-core approximation (ECA) for the early stages of excited molecules, where excitation of O1s electron to the lowest unoccupied molecular orbital $\pi^*\text{CO}$ is described by substitution of F atom for the equivalent core of O atom. Initial geometry was chosen as that of MTFA in the electronic ground state. The excitation of O1sCO to $\pi^*\text{CO}$ state produces equivalent core molecule shown in figure 3, where the potential energy surface was calculated [10] using the B3LYP/cc-PVDZ level of DFT. The results indicate that the excited state of carbonyl oxygen site is definitely bound against the $r_{\text{C=O}}$ coordinate. This is less likely to produce immediate dissociation.

When core-excitation of methoxy oxygen site is made to $\pi^*\text{CO}$ state, in contrast, one may find that potential surface is strongly repulsive along the $r_{\text{C=OMe}}$ coordinate (figure 4). The present ECA calculation clearly supports our view that the O1sOMe$^{-1}\pi^*\text{CO}$ state is strongly dissociative to lead effective CHO$^+$ formation, whereas that of the O1sCO$^{-1}\pi^*\text{CO}$ is characterized as being definitely bound around C=O bond distance. Early stage of the core-excited state induces such a swift dynamics that the kinematic motion gained during the stage may well affect the final dissociation. The lack of site selective dissociation at the O1sCO$^{-1}\pi^*\text{CO}$ in the esters could be thus convincible from the ECA approximation.
3.2.2. State-selective dissociation of MTFA
The excited-state-selective dissociation can also be examined by comparison of the product intensities at the (3:O1s\textsubscript{OMe}→σ\textsuperscript{*}O-Me) and (4:O1s\textsubscript{OMe}→π\textsuperscript{*}C-OMe) bands, including those at the (2:O1s\textsubscript{OMe}→π\textsuperscript{*}CO) as described above, since electron transitions from the same core to different excited states are involved. Excitation at the (3:O1s\textsubscript{OMe}→σ\textsuperscript{*}O-Me) shows clear enhancement of CH\textsubscript{3}⁺ ratio that indicates the state-selectivity arising from the antibonding σ\textsuperscript{*}(O-Me) character in the core-excited and/or Auger final states. At the (4:O1s\textsubscript{OMe}→σ\textsuperscript{*}C-OMe) band preferential production of CHO⁺ over the CH\textsubscript{3}⁺ can be seen in figure 1. The relative enhancement of CHO⁺ is not so significant due to the transition in the ionization continua but it is the very evidence of state-selective fragmentation that occurs originating from the σ\textsuperscript{*}(C-OMe) orbital. Significant production of CHO⁺ at the (2:O1s\textsubscript{OMe}→π\textsuperscript{*}CO) is discussed in the previous section and regarded as being strongly due to π\textsuperscript{*}(C=O) orbital extending to the C-OMe bond.

4. Summary
The site- and state-selective dissociation of methyl-trifluoroacetate following the O1s core-excitation has been studied in the effusive beam. Characteristic site-selectivity of the C=O/OMe core excitation and distinct excited-state-selectivity for the dissociation were identified from the CH\textsubscript{3}⁺/CHO⁺ fragment analysis. The site-selectivity was also justified by an equivalent core approximation using the density functional theory calculation.

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