

Site-Specific Fragmentation Caused by Si:1s Photoionization of Organosilicon Molecule Vapor

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1. Introduction

Although core electrons virtually do not participate in the chemical bonding, the energy of an atomic core-level in the molecule depends on the chemical environment around the atom. Monochromatized synchrotron radiation can selectively excite inner-shell electrons of an atom in a specific chemical environment, discriminating them from those of like atoms having different chemical environments in a molecule (site-specific excitation). The site-specific excitation results in fragmentation specific to that site (site-specific fragmentation), owing to the localized nature of the core electron.

In the present study, we have studied the ionic fragmentation caused by Si:1s core-level photoexcitation of 1-trifluorosilyl-2-trimethylsilylethane, $F_3SiCH_2CH_2Si(CH_3)_3$ (FSMSE). FSMSE has two Si atoms in fairly different chemical environments, the two Si sites (Si[Me] and Si[F]) are separated by two $-CH_2-$ groups, and FSMSE has the potential of showing

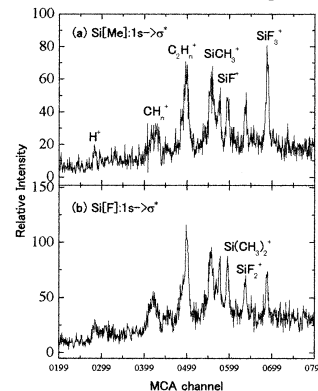
site-specific excitation and fragmentation.

2. Experimental

The experiments were performed using a time-of-flight spectrometer installed on the BL27SU beamline of SPring-8 synchrotron radiation facility. The setup and the experimental procedures were described in previous reports.

3. Results

The figure shown below represents the photoionization mass spectra of FSMSE taken in the pulse mode at the Si[Me] $\rightarrow\sigma^*$ and Si[F] $\rightarrow\sigma^*$ resonances. Site-specific fragmentation can be seen in the spectra.



Doppler-free Auger resonant Raman spectroscopy on photochemistry beamline at SPring-8

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Unlike in normal Auger spectroscopy, in resonant Auger electron spectroscopy the widths of observed electronic transitions are not limited by the natural lifetime of the initial state. High resolution soft X-ray monochromators and electron energy analyzers, allow one to perform resonant Auger spectroscopy with the resolution limited by experimental condition: photon- and electron energy width and Doppler width.

Auger decay of Ne1s⁻¹3p and H₂O O1s⁻¹2b₂ have been recently been studied in conditions where the resolution was limited by the Doppler effect [1,2]. Recently, we replaced the gas-cell with a gas-jet device on the high resolution electron spectrometer at the end of BL27SU. With this gas-jet we recorded Auger spectra from Ne1s⁻¹3p and H₂O O1s⁻¹2b₂ with the widths not Doppler-limited.

Fig. 1 shows Auger spectra from Ne1s⁻¹3p recorded with the gas-jet. The FWHM of 63 meV contains contributions from the analyzer and the monochromator bandwidths (~33 and ~54 meV). In previous measurements without the gas-jet the observed widths 100~105 meV contained contributions from instrumental widths 60~63 meV and the Doppler broadening of ~79 meV.

The Auger decay spectra of H₂O O1s⁻¹2b₂ in Fig. 2 were recorded with photon- and electron- energy bandwidths of ~33 and ~40 meV, with the gas-jet and gas-cell. All the bands in the figure contain clearer vibrational structure in the Doppler-free spectrum, especially for the bending vibration of the A band.

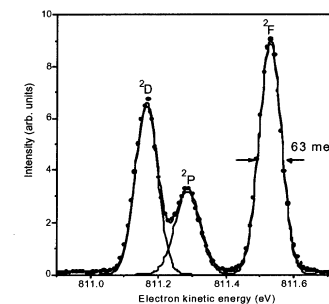


Fig 1. Ne1s⁻¹3p \rightarrow Ne⁺2p⁻²(D₂)3p Auger transition recorded with the gas-jet device.

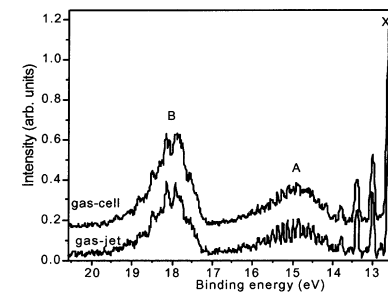


Fig 2. H₂O O1s⁻¹2b₂ Auger transition recorded with the gas-jet and gas-cell devices.

[1] Y. Shimizu et al. JPBL 33 L685 (2000)

[2] A. De Fanis et al. JPBL 35 L23 (2002)