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Electron-ion-ion triple-coincidence spectroscopic study of site-specific fragmentation caused by Si:2*p* core-level photoionization of $F_3SiCH_2CH_2Si(CH_3)_3$ vapor

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Site-specific fragmentation caused by Si:2*p* core-level photoionization of $F_3SiCH_2CH_2Si(CH_3)_3$ vapor was studied by means of high-resolution energy-selected-electron photoion-photoion triple-coincidence spectroscopy. The *ab initio* molecular orbital method was used for the theoretical description. $F_3SiCH_2CH_2{}^+$-$Si(CH_3)_3{}^+$ ion pairs were produced by the 2*p* photoionization of the Si atoms bonded to the three methyl groups, and SiF^+-containing ion pairs were produced by the 2*p* photoionization of the Si atoms bonded to the three F atoms.

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The core-level chemical shift shown by atoms in a molecule depends on their chemical environments, so atoms that have the same atomic number but are in different chemical environments will show different chemical shifts. Furthermore, the core hole created by the photoionization in an atom is localized very close to the nucleus of that atom. These properties have been used to study site-specific fragmentation [1–4], in which bonds around the site of core-ionized atoms are dissociated selectively. Site-specific fragmentation is potentially useful for controlling chemical reactions and also offers possibilities for analyzing the structures and properties of molecules, molecular assemblies, and nanoscale devices by controlling matter at the level of individual atoms. To realize these exciting possibilities, we need to understand what controls fragmentation at the atomic level.

A molecule M including several atoms with the same atomic number in different chemical environments is expected to show core-photoelectron peaks reflecting chemical shifts differing site by site. In a normal Auger transition, the core-electron emission makes a valence electron fall into the core orbital and creates a valence hole that spatially overlaps the core-ionized atomic site in the molecule (M^+). The electron falling into the core orbital usually gives its energy to another valence electron, which is emitted as a normal Auger electron, creating a second valence hole in the molecule (M^{2+}). Since these valence holes weaken chemical bonds around the initially core-ionized atom, site-specific fragmentation ($M^{2+} \rightarrow F_1{}^+ + F_2{}^+$) often occurs around it. To observe such a fragmentation process selectively, we have to detect ion pairs ($F_1{}^+$-$F_2{}^+$) in coincidence with energy-selected photoelectrons that originate from each of several nonequivalent atomic sites in the different chemical environments. That is, we have to use energy-selected-photoelectron/Auger-electron photoion-photoion triple-coincidence (PEPIPICO/AEPIPICO) spectroscopy.

In this work we used the PEPIPICO and AEPIPICO methods and the *ab initio* molecular orbital (MO) method to study site-specific fragmentation caused by Si:2*p* core-level photoionizations of 1-trifluorosilyl-2-trimethylsilylethane [$F_3SiCH_2CH_2Si(CH_3)_3$, FSMSE] in the vapor phase. FSMSE is useful for such a study because the chemical environment of a Si atom bonded to three F atoms (here denoted Si[F]) is very different from that of one bonded to three methyl groups (Si[Me]). The dimethylene group ($-CH_2CH_2-$) between the two Si atoms maintains the site-specificity of the fragmentation by inhibiting intersite electron migration [5]. This study has provided clear evidence for almost 100% site-selectivity of the ion/ion-pair production in Si:2*p* photoionization.

The electron-ion coincidence measurements were performed using a hemispherical electron energy analyzer (Gammadata-Scienta SES-2002) and a time-of-flight (TOF) ion spectrometer, both of which were equipped with position-sensitive delay-line detectors [6]. FSMSE vapor was introduced to the photoionization region through a needle as an effusive beam. The coincidence apparatus was mounted behind the high-resolution plane-grating monochromator installed on the *c* branch of the soft x-ray figure-8 undulator beamline 27SU at the SPring-8 facility [7]. The data analysis method was modified from the original one [6] to extract PEPIPICO and AEPIPICO counts [8]. The experimental and computational methods and procedures used in the present work have been described in detail in previous papers [6,9] and an EPAPS document [10].

The photoelectron spectrum (PES) of FSMSE vapor shown in Fig. 1(a) has two peaks in the region of Si:2*p* photoemission. The peaks at lower and higher binding energies (106.4 and 109.8 eV) are, respectively, assigned to Si[Me]:2*p* and Si[F]:2*p* photoelectron emissions [11]. Thus, the chemical shift difference originating from the two Si sites of FSMSE vapor is clearly evident in the photoelectron spectrum. Computational results [10] show that the molecular motion immediately after emission of the Si:2*p* photoelectrons of FSMSE is negligible.

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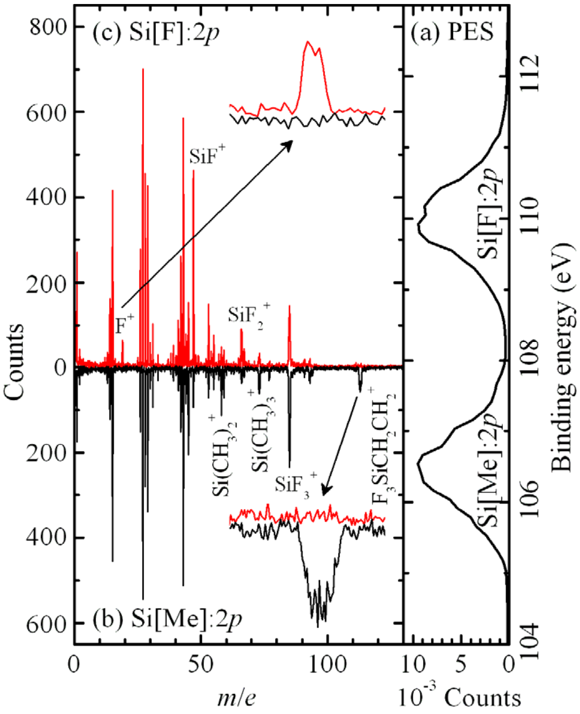

FIG. 1. (Color online) (a) Si:2p PES of FSMSE vapor obtained during the PEPICO measurement. (b) and (c) Ion mass spectra measured in coincidence with the Si[Me]:2p and Si[F]:2p photoelectrons. The insets show the regions of F^+ and $F_3SiCH_2CH_2^+$ with enlarged scales.

The ion mass spectra measured in coincidence with the Si[Me]:2p and Si[F]:2p photoelectrons (PEPICO spectra) are shown in Figs. 1(b) and 1(c). The peaks corresponding to $C_nH_m^+$ groups ($m/e<40$) are larger than those corresponding to ions containing F atoms because C_nH_m is easily ionized than F [12]. As seen in Fig. 1 and described below, site-specific fragmentation is clearly evident in the ion mass spectra. The Si[Me]:2p photoionization increased the production of $Si(CH_3)_2^+$, $Si(CH_3)_3^+$, SiF_3^+, and $F_3SiCH_2CH_2^+$, whereas the Si[F]:2p photoionization increased the production of F^+, SiF^+, and SiF_2^+ [10]. The fragments most sensitive to the site of the initial energy deposition were $F_3SiCH_2CH_2^+$ and F^+, and the site-selectivity for the production of these ions was almost 100%. Except in the case of SiF_3^+, the above site-specific bond dissociation occurs at the Si site where the photoionization has taken place. The Si[Me]:2p photoionization may have produced SiF_3^+ in the following two-step dissociation mechanism:

$$\begin{aligned}&\mathrm{FSMSE} + h\nu\\&\quad\rightarrow \mathrm{FSMSE}^{2+} + 2e^- \ (\mathrm{Si[Me]}{:}2p\ \mathrm{INAT})\\&\qquad\hookrightarrow \mathrm{F_3Si^+CH_2CH_2}\ (\text{large excess energy})\\&\qquad\qquad\hookrightarrow \mathrm{SiF_3^+}\end{aligned}\tag{1}$$

where INAT denotes ionization and normal Auger transition. Similar two-step dissociation mechanisms could also account for the production of $Si(CH_3)_2^+$ from $Si(CH_3)_3^+$ in the Si[Me]:2p photoionization and the production of F^+ and/or SiF^+ from SiF_2^+ in the Si[F]:2p photoionization.

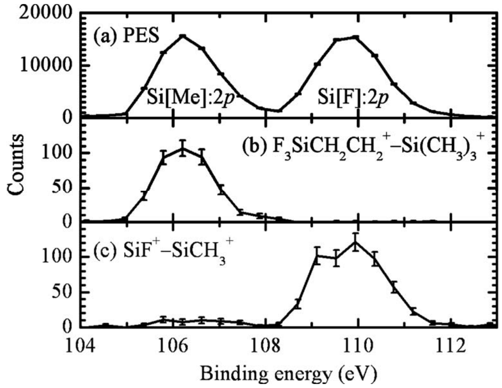

FIG. 2. (a) Si:2p PES of FSMSE vapor obtained during the PEPIPICO measurement. (b) and (c) Plots of the PEPIPICO counts of $F_3SiCH_2CH_2^+$-$Si(CH_3)_3^+$ and SiF^+-$SiCH_3^+$ versus the photoelectron binding energy.

Figure 2 shows plots of the PEPIPICO counts of $F_3SiCH_2CH_2^+$-$Si(CH_3)_3^+$ and SiF^+-$SiCH_3^+$ versus the photoelectron binding energy, together with the PES of FSMSE. The plots for $F_3SiCH_2CH_2^+$-$Si(CH_3)H_2^+$ and SiF_3^+-$Si(CH_3)_2^+$ are similar to that for $F_3SiCH_2CH_2^+$-$Si(CH_3)_3^+$, and the plots for SiF^+-$SiCH_2^+$, SiF^+-SiC_2H^+, and SiF^+-SiH^+ (and/or -$C_2H_5^+$) are similar to that for SiF^+-$SiCH_3^+$ [10]. The ion pair most sensitive to the site of the initial energy deposition is $F_3SiCH_2CH_2^+$-$Si(CH_3)_3^+$, and the site-selectivity for its production is almost 100%. In similar plots, the PEPIPICO counts of F^+- and SiF_2^+-containing ion pairs are concealed by the background. Possible ion pairs with the same m/e, like F^+-F^+, were not detected because of the dead time of the ion detector.

Since the plot of the PEPIPICO count of $F_3SiCH_2CH_2^+$-$Si(CH_3)_3^+$ shows a peak at the binding energy of the Si[Me]:2p photoelectron, the Si[Me]-C_2H_4 bond dissociation and subsequent formation of $F_3SiCH_2CH_2^+$-$Si(CH_3)_3^+$ are thought to result from the Si[Me]:2p photoionization. The production of $F_3SiCH_2CH_2^+$-$Si(CH_3)H_2^+$ and SiF_3^+-$Si(CH_3)_2^+$ by the Si[Me]:2p photoionization seems to be possible in two-step dissociation (and rearrangement) mechanisms similar to (1). Since the plots of the PEPIPICO counts of the SiF^+-containing ion pairs show a peak at the binding energy of the Si[F]:2p photoelectron, we know that the Si[F]-F and Si[F]-C_2H_4 bond dissociations and subsequent formation of the ion pairs result from the Si[F]:2p photoionization.

In Fig. 2 and EPAPS document [10], the Si[F]:2p photoionization always breaks both of the Si[F]-C_2H_4-Si[Me] bonds and the $Si(CH_3)_3$ group falls apart, while the Si[Me]:2p photoionization leaves the Si[F]-C_2H_4 bond intact except in mechanism (1). So in general the Si[F]:2p photoionization seems to lead to more violent fragmentation than the Si[Me]:2p photoionization. This may be due to the different degrees of freedom at the Si[Me] and Si[F] sites. Although the dissociation in the SiF_3 moiety takes place only

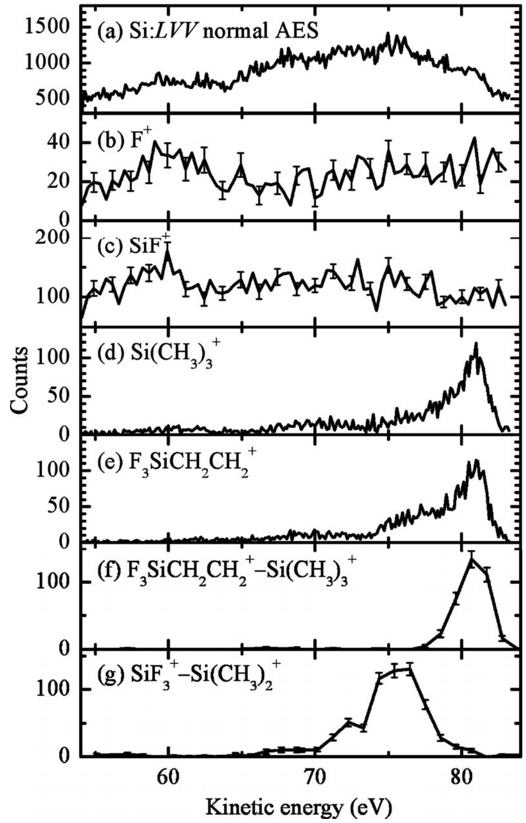

FIG. 3. (a) Si:*LVV* normal AES of FSMSE vapor obtained during the AEPICO measurement. (b)–(e) Plots of the AEPICO counts of F$^+$, SiF$^+$, Si(CH$_3$)$_3^+$, and F$_3$SiCH$_2$CH$_2^+$ versus the Auger-electron kinetic energy. (f) and (g) Plots of the AEPIPICO counts of F$_3$SiCH$_2$CH$_2^+$-Si(CH$_3$)$_3^+$ and SiF$_3^+$-Si(CH$_3$)$_2^+$.

at three Si-F bonds, the Si(CH$_3$)$_3$ moiety has a lot of bonds that can be broken: three Si-C bonds and nine C-H bonds. In other words, the Si[Me] site has a larger energy reservoir of the vibrational mode. As a result, in the Si [Me]:2*p* photoionization, dissociation takes place mainly around the Si[Me] atom. In the Si[F]:2*p* photoionization, however, it takes place not only around the Si[F] atom but also at various other bonds because of the fast energy transfer to the whole molecule.

Figure 3(a) shows the Si:*LVV* normal Auger-electron spectrum (AES) of FSMSE vapor, and Figs. 3(b), 3(c), 3(d), and 3(e), respectively, show plots of the Auger-electron photoion coincidence (AEPICO) counts of F$^+$, SiF$^+$, Si(CH$_3$)$_3^+$, and F$_3$SiCH$_2$CH$_2^+$ versus the Auger-electron kinetic energy. The plots of the AEPICO counts of Si(CH$_3$)$_2^+$ and SiF$_3^+$ show peaks at lower kinetic energies than those of F$_3$SiCH$_2$CH$_2^+$ and Si(CH$_3$)$_3^+$ [10]. Figures 3(f) and 3(g) show plots of the AEPIPICO counts of F$_3$SiCH$_2$CH$_2^+$-Si(CH$_3$)$_3^+$ and SiF$_3^+$-Si(CH$_3$)$_2^+$. In similar plots, the AEPIPICO counts of F$^+$-, SiF$^+$-, and SiF$_2^+$-containing ion pairs are concealed by the background.

The plot of the AEPIPICO count of F$_3$SiCH$_2$CH$_2^+$-Si(CH$_3$)$_3^+$ [Fig. 3(f)], which is a site-specific ion pair formed by the Si[Me]:2*p* photoionization (Fig. 2), shows a peak at the high-kinetic-energy edge of the Auger band (82 eV), as do the plots of the AEPICO counts of Si(CH$_3$)$_3^+$ and F$_3$SiCH$_2$CH$_2^+$ shown in Figs. 3(d) and 3(e). Therefore the Si[Me]-C$_2$H$_4$ bond dissociation and subsequent formation of F$_3$SiCH$_2$CH$_2^+$-Si(CH$_3$)$_3^+$ are results of an Auger decay with a kinetic energy of 82 eV. The emission of the Auger electron leads to various Si[Me]:*LVV* normal Auger final states, each of which has two holes in the valence MOs. We have used *ab initio* calculations to estimate the probabilities leading to the Auger final states, have selected some states with high probability, and in Fig. 4(a) have illustrated their valence MOs with one or two holes in the Si[Me]:*LVV* normal Auger final states at about 82 eV. The present finding that the Si[Me]-C$_2$H$_4$ bond dissociation and subsequent formation of F$_3$SiCH$_2$CH$_2^+$-Si(CH$_3$)$_3^+$ occur is consistent with the computational result that two MOs with a character of Si[Me]-C$_2$H$_4$ bonding ($\sigma_{\text{Si[Me]-C2H4}}$) have, with high probability, one or two holes in those Si[Me]:*LVV* normal Auger final states (MO Nos. 14 and 17). The hole creation in $\sigma_{\text{Si[Me]-C2H4}}$ is thought to result in the Si[Me]-C$_2$H$_4$ bond dissociation and the formation of F$_3$SiCH$_2$CH$_2^+$-Si(CH$_3$)$_3^+$:

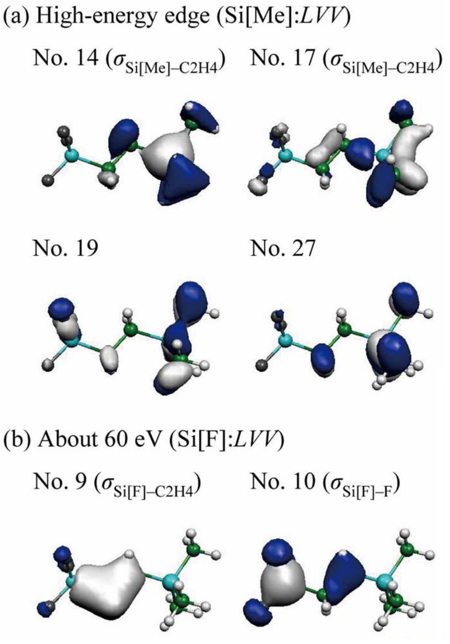

FIG. 4. (Color online) (a) Main MOs with one or two holes in the Si[Me]:*LVV* normal Auger final states corresponding to the high-kinetic-energy edge of the Auger band of FSMSE. The MOs are numbered in ascending order of orbital energy, and the highest occupied MO is No. 36. (b) Main MOs with one or two holes in the Si[F]:*LVV* normal Auger final states corresponding to an Auger-electron kinetic energy of about 60 eV.

$$
\begin{aligned}
&\text{FSMSE} + h\nu \\
&\qquad \rightarrow \; 2e^- \,(\text{Si[Me]}{:}2p\ \text{INAT}) \\
&\qquad + \text{FSMSE}^{2+}\,(\text{1-2 holes in } \sigma_{\text{Si[Me]-C2H4}}) \\
&\qquad\qquad \Rightarrow \text{F}_3\text{SiCH}_2\text{CH}_2^+ + \text{Si(CH}_3)_3^+ \qquad (2)
\end{aligned}
$$

The SiF_3^+-$Si(CH_3)_2^+$ ion pair, which like the $F_3SiCH_2CH_2^+$-$Si(CH_3)_3^+$ ion pair is site-specifically produced by the Si[Me]:2*p* photoionization [10], seems to be formed from upper Auger final states with two holes in deeper-lying MOs because the AEPIPICO count of SiF_3^+-$Si(CH_3)_2^+$ shows a peak at a lower kinetic energy [Fig. 3(g)]. The plot for SiF_3^+-$Si(CH_3)H_2^+$ is similar to that for SiF_3^+-$Si(CH_3)_2^+$ [10]. The AEPIPICO counts of $F_3SiCH_2CH_2^+$-$Si(CH_3)H_2^+$ and some other ion pairs show peaks at other low kinetic energies [10].

The plots of the AEPICO counts of F^+ and SiF^+, which are site-specific fragments formed by the Si[F]:2*p* photoionization (Fig. 1 and [10]), show a hump at about 60 eV [Figs. 3(b) and 3(c)] as does the plot of the AEPICO count of F^+ in the condensed phase [13]. One can also see a hump at about 60 eV in the Si:*LVV* normal AES [Fig. 3(a)]. By means of the PEPIPICO method, it is seen that some SiF^+-containing ion pairs are efficiently produced by the Si[F]:2*p* photoionization [Fig. 2(c) and [10]]. Therefore the Si[F]-F and Si[F]-C_2H_4 bond dissociations and subsequent formation of the SiF^+-containing ion pairs are thought to result from the Si[F]:*LVV* normal Auger final states corresponding to an Auger-electron kinetic energy of about 60 eV. This interpretation is consistent with the computational result that a MO with a character of Si[F]-F bonding ($\sigma_{\mathrm{Si[F]\text{-}F}}$) and another MO with a character of Si[F]-C_2H_4 bonding ($\sigma_{\mathrm{Si[F]\text{-}C2H4}}$) have, with high probability, one or two holes in the Auger final states at about 60 eV [Fig. 4(b)]. The hole creation in $\sigma_{\mathrm{Si[F]\text{-}F}}$ and $\sigma_{\mathrm{Si[F]\text{-}C2H4}}$ is thought to result in the dissociation of the Si[F]-F and Si[F]-C_2H_4 bonds and the formation of the SiF^+-containing ion pairs:

$$
\begin{aligned}
&\mathrm{FSMSE} + h\nu \\
&\qquad \to 2e^- \ (\mathrm{Si[F]{:}2}p\ \mathrm{INAT}) \\
&\qquad + \mathrm{FSMSE}^{2+}\ (\text{1-2 holes in } \sigma_{\mathrm{Si[F]\text{–}F}} \text{ and } \sigma_{\mathrm{Si[F]\text{–}C2H4}}) \\
&\qquad\qquad \Lsh\ \mathrm{SiF}^+\text{-containing ion pair}
\end{aligned}
\tag{3}
$$

In conclusion, site-specific fragmentation caused by the Si:2*p* core-level photoionization of FSMSE vapor was measured by means of high-resolution PEPIPICO/AEPIPICO spectroscopy and was interpreted by means of the *ab initio* MO method. $F_3SiCH_2CH_2^+$-$Si(CH_3)_3^+$ and some SiF^+-containing ion pairs were formed according to mechanisms (2) and (3). Site-specific fragmentation thus offers an approach to controlling chemical reactions [14] by controlling the sites at which holes are created (e.g., by a resonant excitation). This elucidation of the details of the fragment production mechanism brings the goal of chemical synthesis and some other applications one step closer to realization, but further investigations are needed.

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[10] See EPAPS Document No. E-PLRAAN-75-R10702 for the experimental and computational details, the description of the comparison with the condensed phase, the computational animations of the molecular dynamics immediately after emission of the Si[Me]:2*p* and Si[F]:2*p* photoelectrons, and the detailed results of the coincidence measurements. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).

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