X-ray absorption spectra of SiF₄ and Si(CH₃)₄ in the Si K-shell excitation region

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Abstract. X-ray photo-absorption (XA) spectra of SiF₄ and Si(CH₃)₄ have been measured in the Si K-shell transition region using monochromatized undulator radiation and theoretical calculations have been performed within the framework of density functional theory. For SiF₄, main peak structures of the XA spectrum have been reproduced well with the calculation. Further we theoretically simulated a small peak of Si:1s→6a₁ excitation, by sampling distorted geometries using classical trajectory calculations at the ground state, which is a forbidden transition under the dipole selection rule. For Si(CH₃)₄ only one peak was observed and reproduced well with the calculation, which was ascribed to the characteristic of broad Rydberg orbitals coupled with valence orbitals.

1. Introduction
Electronic structure and reactivity of compounds including silicon atoms at the molecular level are of great interests due to its importance in the semiconductor industry. During recent development of synchrotron radiation facility, core-level electron spectroscopy has been extensively studied, and
understanding on electronic structures and chemical reactions at the atomic level has been advanced. As one of typical examples, site-specific chemical reactions of SiF₃C₂H₄Si(CH₃)₃ (FSMSE) in the gas phase have been observed near the Si L-edge [1] and especially site-selectivity in an yield of a certain fragment ion was almost 100 %. Furthermore, similar experiments were investigated near the Si K-edge [2]. The fragmentation caused through the Si:1s ionization is more violent than that caused through the Si:2p ionization. Using a variety of techniques such as multi-coincidence spectroscopies, investigations of FSMSE are continuing for deep understanding on the reaction mechanism of ion fragmentation following core-excitation [3, 4]. Although many spectroscopic studies of molecules including silicon atoms have been performed near the Si L-edge, studies near the Si K-edge were limited so far [3, 5, 6]. Investigations using similar techniques for related molecules are useful in order to understand the reactivity and the electronic structure of FSMSE efficiently. In the present study, X-ray absorption (XA) spectra of SiF₄ and Si(CH₃)₄ as model molecules of FSMSE are investigated experimentally and theoretically, because these molecules correspond to terminal chemical constituents of FSMSE.

SiF₄ and Si(CH₃)₄ are simple compounds including a silicon atom with T₄ symmetry, and chemical environment around an Si atom is different: An Si atom in SiF₄ is surrounded by four electron-withdrawing groups, on the other hand, that in Si(CH₃)₄ is surrounded by four electron-repelling groups. Various spectroscopic data of these simple molecules have been accumulated experimentally [5, 7-10] and theoretically [5, 11, 12]. XA spectra of SiF₄ and Si(CH₃)₄ near the Si K-edge were reported by several authors [5, 6] and in particular Bodeur et al. performed theoretical calculations using ab initio configuration interaction (CI) method in the same paper [5]. They discussed valence and Rydberg mixing for double peaks observed in the XA spectra of SiF₄, which were not observed in that of Si(CH₃)₄. However, the first small peak observed in that of SiF₄, which is assigned as Si:1s → 6a₁ transition, was not given a sufficient explanation. We are attempting to describe this transition theoretically by taking into consideration geometries distorted from the equilibrium geometry.

A treatment based on the density functional theory (DFT) is now available to inner-shell excitations for analyses of XA spectra and is widely applied to relatively small molecules in the gas phase [13, 14], molecular clusters [15], polymers [16], surface-adsorbed molecules [17], and liquid phase [18, 19]. In the present study, XA spectra of SiF₄ and Si(CH₃)₄ near the Si K-edge have been measured, and theoretical XA spectra have been produced within the framework of DFT.

2. Methods

2.1. Experimental setup

The experiments were performed on the c branch of the soft X-ray photochemistry beamline BL27SU at the SPring-8 facility [20-22]. The beamline provides linearly polarized monochromatic light ranging from 0.2 to 2.8 keV. The photon energy resolving power during the measurements was set at 3500. The energy calibration of the monochromator was performed with respect to the binding energies of the Ne:1s photoelectrons [23]. The intensity of the monochromatized incident photon-beam during the measurement was monitored by collecting the drain current of the post-focusing mirror on the beamline. The experimental XA spectra were measured using a total-ion-yield (TIY) method. The monochromatized photon beam in the Si K-edge region was crossed with an effusive beam of sample gases, SiF₄ and Si(CH₃)₄, and produced ions were extracted downward with an applied electric field. Ion yields were detected without mass selection using a simple combination of a set of electrodes and micro-channel plates of tandem configuration.

2.2. Theoretical Methods
Firstly, computational methods for the equilibrium geometry are described. Geometry optimizations of SiF$_4$ and Si(CH$_3$)$_4$ were carried out using the GAUSSIAN 03 program [24] at the MP2/cc-pVTZ level of approximation. Vibrational frequencies were calculated using the analytical second derivatives at the same level of the geometry optimization.

The XA spectra calculations were performed using the StoBe-deMon program [25]; the detailed computational method was described in previous reports [13, 14, 16]. In brief, the theoretical XA spectra were generated by the transition potential (DFT-TP) method [13]. The gradient-corrected exchange (PD86) [26] and correlation functional (PD91) [27] established by Perdew and Wang were applied. The orbitals for the molecules were determined with a half-occupied core orbital at the ionization site using the IGLO-III basis of Kutzelnigg et al. [28] for Si atoms, the (311/211/1) basis set for C atoms, and the (311/1) basis set for H atoms. The augment basis sets on Si atoms were used for Rydberg orbitals: $\zeta_s = 0.017$ and 0.0056667, $\zeta_p = 0.014$ and 0.0046667, $\zeta_d = 0.015$ and 0.003. The auxiliary basis sets were the (5,4;5,4) for Si atoms, the (5,2;5,2) for C and F atoms, and the (3,1;3,1) for H atoms, where the nomenclature ($N_c(s)$, $N_c(spd)$; $N_{xc}(s)$, $N_{xc}(spd)$) indicates the number of $s$ and $spd$-type functions to fit the Coulomb and exchange correlation potentials, respectively. The orbitals for the excited electron were then obtained by diagonalizing the Kohn–Sham matrix built from the density with the basis set extended by a large set of diffuse basis functions centered on the excited atom. The obtained orbital energies and computed transition moments provided the excitation energy and associated intensities in the theoretical spectrum. The DFT-TP calculation of the spectrum corresponded to the static exchange approach, and the relaxation effect of the created ion core was neglected by adding the excited electron. This effect is the largest for valence-like excitations, and these states were computed with fully-relaxed Kohn–Sham calculations [14]. For a more accurate estimate of the absolute excitation energy, relativistic and functional corrections were added to the excitation energy [29]. The relativistic corrections added to the ionization potential were 2.0 eV for the Si $K$-edge, whose value was estimated by extrapolating the linear relation between the nuclear charge and the relativistic correction of the second row elements [29]. Functional corrections of 3.6 eV for SiF$_4$ and 3.8 eV for Si(CH$_3$)$_4$ were added for the whole spectra. These values were estimated from the difference between the computational and experimental Si:1$s$ ionization energies. Finally, the spectra were generated by a Gaussian convolution of the discrete lines by varying the broadenings. The computed spectra of SiF$_4$ were broadened using Gaussian functions with a constant full width at half maximum (FWHM) of 1.0 eV below 1846 eV, then linearly increasing up to 7.0 eV at 1852 eV. The computed spectra of Si(CH$_3$)$_4$ were broadened using Gaussian functions with a constant FWHM of 1.0 eV below 1840 eV, then linearly increasing up to 7.0 eV at 1846 eV.

As described below, a symmetry-forbidden transition Si:1$s$ $\rightarrow$ 6$a_1$ of SiF$_4$ was observed as the lowest resonant excitation peak in the TIY spectrum. To simulate this transition theoretically, distorted geometries from the equilibrium geometry at the ground state are needed, which are considered to originate from the vibrational motions. To sample them systematically, classical trajectory calculations at the ground state were performed with zero-point vibrational energies without any symmetry constraints. Time step set to 0.5 fs and the calculation was propagated by 10,000 times. Two hundred points in the obtained snapshots were sampled randomly and XA spectra calculations were performed for these selected geometries. Final XA spectra were obtained by a summation of these spectra weighted by the distribution on the ground state because sampled geometries were generally deviated from the equilibrium geometry. The quantum mechanical distribution for the $i$-th vibrational mode $w(i)$ can be calculated using deviations from the equilibrium geometry and the vibrational frequencies,

$$w(i) = \exp(-\sqrt{\omega_i \Delta_i^2}),$$

where $\omega_i$ is the $i$-th vibrational frequency and $\Delta_i$ is deviation along the normal mode of the $i$-th vibrational frequency. Note that equation (1) corresponds to the square of the wavefunction of the $i$-th
vibrational mode with the vibrational quantum number of zero. Total weight \( W \) is defined by the products of \( w(i) \),

\[
W = \prod_{i=1}^{m} w(i),
\]

where \( m \) is the number of vibrational modes. For \( \text{SiF}_4 \), all vibrational modes contribute in equation (2). For \( \text{Si(CH}_3)_4 \), a few \( w(i) \)'s become almost zero due to large deviations from the equilibrium geometry for some degrees of freedom. To avoid that the total weight \( W \) becomes extremely small, \( w(i) \)'s larger than a threshold value of \( 1.0 \times 10^{-3} \) were only used in this analysis.

3. Results and discussion

\( \text{SiF}_4 \) and \( \text{Si(CH}_3)_4 \) are of \( T_d \) symmetry in the ground state, and electron configuration and unoccupied valence orbitals may be written as follows [8, 10].

\[
\begin{align*}
\text{SiF}_4 & \quad (1a_1)^2(1t_2)^6(2a_1)^2(3a_1)^2(2t_2)^6(4a_1)^2(3t_2)^6(5a_1)^2(4t_2)^6(1e)^4(1t_1)^6(5t_2)^6(6a_1)^0(6t_2)^0 \\
\text{Si}(\text{CH}_3)_4 & \quad (1a_1)^2(2a_1)^2(1t_2)^6(3a_1)^2(2t_2)^6(4a_1)^2(3t_2)^6(5a_1)^2(4t_2)^6(1e)^4(1t_1)^6(5t_2)^6(6a_1)^0(6t_2)^0 \\
\end{align*}
\]

\( \text{Si} \ 1s \quad \text{F} \ 1s \quad \text{Si} \ 2s \quad \text{Si} \ 2p \quad \text{inner valence} \quad \text{outer valence} \quad \text{unoccupied} \)

\( \text{Si}(\text{CH}_3)_4 \)

\( \text{Si} \ 1s \quad \text{C} \ 1s \quad \text{Si} \ 2s \quad \text{Si} \ 2p \quad \text{inner valence} \quad \text{outer valence} \quad \text{unoccupied} \)

\( \text{TIY} \) spectrum usually approximates a photoabsorption spectrum in the inner-shell excitation of molecules because this excitation generally produces ions with some masses and charges. Figure 1 shows experimental TIY spectra and calculated XA spectra of \( \text{SiF}_4 \) and \( \text{Si}(\text{CH}_3)_4 \) near the \( \text{Si} \) K-edge. Contrary to the case of the \( L \)-shell excitation spectra [8], structures of XA spectra near the Si K-edge become simple due to the absence of the spin-orbit splitting.

\( \text{XA} \) spectra of \( \text{SiF}_4 \) and \( \text{Si}(\text{CH}_3)_4 \) near the \( \text{Si} \) K-edge were observed by several research groups [5, 6], and we follow the peak assignments proposed by Bodeur et al. and summarized in Table 1. Our experimental peak positions are consistent with Bodeur et al. within their experimental error. They discussed assignments around main peaks below the ionization threshold and broad continuum bands

**Table 1.** Peak positions \( E \) (in eV), term values \( T \) (in eV), and assignments of XA spectra of \( \text{SiF}_4 \) and \( \text{Si}(\text{CH}_3)_4 \).

| SiF\(_4\) | Peak No. | \( E_{\text{exp}} \) | \( T_{\text{exp}} \) | Assignment | \( E_{\text{exp}} \) | \( T_{\text{exp}} \) | \( E_{\text{cal}} \) | \( T_{\text{cal}} \) | Assignment |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 1 | 1846.5 | 6.0 | \( a_1 \) | 1846.1 | 6.2 | 1845.6 | 6.7 | 6\( a_1 \) |
| 2 | 1849.0 | 3.5 | \( t_2 \) | 1848.5 | 3.8 | 1848.2 | 4.1 | 6\( t_2 \) |
| 3 | 1850.2 | 2.3 | \( 4p \) | 1850.3 | 2.0 | 1850.2 | 2.1 | 7\( t_2, 4p \) |
| IP | 1852.5 | | | 1852.3\(^b\) | | 1852.3 |

| \( \text{Si}(\text{CH}_3)_4 \) | Peak No. | \( E_{\text{exp}} \) | \( T_{\text{exp}} \) | \( E_{\text{exp}} \) | \( T_{\text{exp}} \) | \( E_{\text{cal}} \) | \( T_{\text{cal}} \) | Assignment |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 1 | 1843.6 | 2.5 | \( t_2 \) | 1843.6 | 2.7 | 1843.6 | 2.7 | 6\( t_2 \) |
| IP | 1846.1 | | | 1846.3\(^b\) | | 1846.3 |

\(^a\) This work. \(^b\) Nagaoka et al. (to be published)
above the threshold. However, the first small peak observed in that of SiF₄, which is assigned as Si:1s → 6a₁ transition, was not given a sufficient explanation. Our experimental spectral shapes of both molecules are similar to the previous ones due to wide natural broadening even if the high-resolution measurements were performed. For SiF₄, three peaks were observed below the ionization threshold, and theoretical spectrum shown in figure 1(b) is consistent with this result. In the same figure, a line spectrum corresponding to oscillator strength is shown. Note that the origin of a vertical axis of the band spectra is shifted to show an existence of the a₁ symmetry transition clearly. The lowest excited state has no intensity due to the forbidden transition under the dipole selection rule, but this transition seems to occur to some extent (see below). The second peak having the highest intensity can be assigned to Si:1s → 7t₂ transition. Although the third peak should be assigned to Si:1s → 6t₂ state, Bodeur et al. proposed this peak to be assigned as Si:1s → 4p Rydberg state.

Let us focus ourselves to the lowest excitation here. Under T₄d symmetry the transition from the 1a₁ orbital to the lowest unoccupied 6a₁ orbital should not appear in the XA spectra due to the forbidden transition under the dipole selection rule. However, transition to the 6a₁ orbital in SiF₄ F:1s excitation [9, 30] and that to the 4a₁ orbital in CH₄ C:1s excitation [31] were observed, which originate from symmetry breaking through vibrational motions. The symmetry breaking for either a core orbital or an excited orbital is necessary for activation of this a₁ into a₁ transition. We have attempted to reproduce this transition as follows. Distorted geometries from the equilibrium through classical trajectory calculations were sampled randomly. An unoccupied orbital which was 6a₁ orbital at the equilibrium does not belong to the a₁ symmetry in instances of distorted geometries. XA spectra calculations were

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**Figure 1.** XA spectra of SiF₄ and Si(CH₃)₄. (a) and (d) Experimental TIY spectra. Peak numbers and ionization potentials (IP) of an Si:1s electron are shown. (b) and (e) Calculated XA spectra for the equilibrium geometry. Some peak assignments are also shown. Line spectrum corresponding to oscillator strength is shown as red lines. (c) and (f) Calculated XA spectra for distorted geometries.
Table 2. Orbital sizes ($<r^2>^{1/2}$) (in Å) for some lower-lying unoccupied orbitals at the core-hole state for SiF₄ and Si(CH₃)₄. Those for Si atom are also shown. Corresponding atomic orbitals are shown in parentheses.

|        | SiF₄  | Si(CH₃)₄ | Si atom       |
|--------|-------|----------|---------------|
| 6$a_1$ | 3.56  | 7.13     | 6.32 (4$s$), 8.37 (4$p$), 5.87 (4$d$) |
| 6$t_2$ | 3.72  | 7.42     |               |
| 7$t_2$ | 9.16  | 7.34     | 18.16 (5$s$), 23.57 (5$p$) |

performed for more than hundreds geometries and summed spectra with the distribution function $w(i)$ were produced. The obtained spectrum was shown in figure 1(c), of which the correspondence with the experimental result is much better than the spectrum for the equilibrium geometry of figure 1(b).

On the other hands, only one peak, which is supposed to originate from many excited states, was observed in the TIY spectrum of Si(CH₃)₄. Theoretical spectra of figure 1(e) and (f) have reproduced the experimental spectra well. The lowest $6a_1$ state which was clearly observed as a separate peak for SiF₄, was not observed, because the splitting between $a_1$ and $t_2$ orbitals in Si(CH₃)₄ is smaller than that of SiF₄; that is, the $6a_1$ and $7t_2$ peaks are buried in the large $6t_2$ peak because of a peak broadening by the geometry relaxation. The present splitting corresponds to 4$s$ and 4$p$ splitting of Si valence orbitals, and the orbital picture is expected to be asymptotic to that of hydrogen like atom by increasing the principal quantum number. In the case of hydrogen like atom of $K_h$ symmetry, the degeneracy of these two orbitals is due to the characteristic of the coulomb field [32]. Enlargement of the orbital size is often derived from the atomic like character of the orbital, and thus the energy splitting between related orbitals is expected to be small. Table 2 shows spatial sizes of relevant orbitals ($<r^2>^{1/2}$) at the core-hole state for SiF₄ and Si(CH₃)₄, and related values for Si atom. $<r^2>^{1/2}$ values for $6a_1$ and $6t_2$ orbitals of SiF₄ are smaller than those of Si(CH₃)₄ and Si atom, suggesting that the energy splitting of SiF₄ is larger than that of Si(CH₃)₄.

4. Summary

XA spectra of SiF₄ and Si(CH₃)₄ in the region of the Si $K$-edge have been studied using synchrotron radiation and theoretical calculations within the framework of the DFT. The calculated spectra are in agreement with the experimental results. In particular the measured Si:$1s \rightarrow 6a_1$ transition for SiF₄ have been reproduced well theoretically. As successive studies, we are measuring resonant Auger spectra of SiF₄ and Si(CH₃)₄ near the Si $K$-edge for evaluation of excited orbitals. In near future, the electric structures and dissociation processes following the core-excitation of these molecules are being clarified more precisely and being understood more deeply.

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