

Production of neutral fragments of gaseous SiCl_4 following Si 2p core-level excitation studied by dispersed fluorescence spectroscopy

K.T. Lu^{a,*}, J.M. Chen^{a,*}, J.M. Lee^{a,b}, S.C. Ho^a, H.W. Chang^a

^aNational Synchrotron Radiation Research Center, Hsinchu, Taiwan, ROC

^bDepartment of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan, ROC

Abstract

State-specific dissociation dynamics for ionic fragments and excited fragments of gaseous SiCl_4 following Si 2p core-level excitation have been characterized by the dispersed UV/optical fluorescence spectroscopy and photionization mass spectroscopy. The Si 2p core-to-Rydberg excitation leads to a noteworthy production of excited atomic fragments, neutral and ionic (Si^* , Si^{+*}). In particular, the excited neutral atomic fragments Si^* are significantly reinforced. The Si 2p core-to-valence excitation generates an enhancement of excited molecular-ion SiCl_4^+ . The experimental results provide deeper insight into the dissociation dynamics for excited neutral fragments of molecules via core-level excitation.

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1. Introduction

The electronic relaxation processes and subsequent profound fragmentation processes of polyatomic molecules following core-level excitation have been a subject of extensive research over decades because of scientific importance and technological applications (Ueda et al., 2000; Armen et al., 2000; Ueda, 2003). Comprehensive understanding of site-selective X-ray generated molecular photolysis is important gateways for the development of evolving technology in the fabrication of microelectronic devices into the nanometer range (Levis et al., 2001).

Based on resonant photoemission studies, the decay processes of resonantly core-excited states of gaseous molecules and molecular adsorbates on surfaces have

been observed to decay predominantly by the spectator Auger transitions to form two-hole, one-electron ($2h1e$) states (Mase et al., 2003). The $2h1e$ states, in which two holes are produced in valence orbitals and one electron is excited to an antibonding valence orbital or a Rydberg orbital, have been shown to be important precursor in dissociation of gaseous molecules or molecular adsorbates on surfaces following inner-shell excitation (Baba, 2003). However, the fragmented ions reported in literatures were predominantly positive ions or negative ions (Mase et al., 2003; Baba, 2003; Nagaoka et al., 1997; Chen and Lu, 2001).

The photodesorption yield of neutral products for molecular adsorbates on surfaces via photoexcitation is much higher than that of ions due to ion reneutralization. However, the detection of neutral products or transient species is more difficult than for ions. For the gas phase, such measurements are very difficult because of the low density of gaseous molecules and the low efficiency of detectors for neutrals. The investigation of

*Corresponding authors. Tel.: +886 3578 0281;
fax: +886 3578 3892.

E-mail address: jmchen@nsrrc.org.tw (J.M. Chen).

neutral fragments produced by inner-shell photoexcitation in molecules is still in its infancy (Meyer et al., 2002; Romberg et al., 2000; Rosenberg et al., 1990; Chen et al., 2004). Until now, the dynamics for excited fragments, particularly for neutral products, generated from the 2h1e states are not fully understood. Dispersed fluorescence measurement in the visible and ultraviolet regions is a powerful method to detect excited neutral and ionic products produced by electronic excitation. Fluorescence excitation spectra provide the abundant information about the dissociation dynamics and electronic relaxation processes of core-excited molecules.

In this study, dissociation dynamics for ionic fragments and excited fragments of gaseous SiCl_4 following Si 2p core-level excitation to various resonances have been characterized by the dispersed UV/optical fluorescence and photoionization mass spectroscopy. The most striking observation is that the Si 2p core-to-Rydberg excitation leads to a noteworthy production of excited atomic fragments, neutral and ionic (Si^* , Si^{+*}). In particular, the excited neutral atomic fragments Si^* are significantly reinforced. The core-to-valence excitation at the Si 2p edge generates an enhancement of excited molecular-ion SiCl_4^+ . The experimental results have enabled us to gain intriguing insights into the mechanism of excited natural production following core-level excitation.

2. Experiments

The experimental measurements were carried out at the high-energy spherical grating monochromator (HSGM) beamline and the U5 undulator beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. Highly pure SiCl_4 (Merck) was degassed by several freeze–pump–thaw cycles before use. For dispersed fluorescence and photodissociation measurements, an effusive molecular beam produced by expanding the gas through an orifice (100 μm) into the experimental chamber was used. Fragmented ion yields were mass-selected through a quadrupole mass spectrometer (Hiden, IDP). Fluorescence was dispersed by a 0.39-m spectrometer using a f/1.5 fused silica extraction optic located normal to and in the plane of polarization of the synchrotron radiation. The fluorescence was then detected by a Hamamatsu R928 photomultiplier tube (PMT).

Due to the low signal levels for dispersed fluorescence measurements, the U5 undulator beamline was operated with a 100 μm entrance slit and a 300 μm exit slit (resolution $\approx 0.3\text{ eV}$ at 100 eV), while the spectral resolution of the spectrometer was set to $\sim 10\text{ nm}$. The pressure in the effusive beam chamber was kept at $\sim 9 \times 10^{-5}\text{ Torr}$. To obtain the high-resolution gaseous-phase X-ray absorption spectrum, the HSGM beamline

was operated with 50 μm slits corresponding to the photon resolution of $\sim 0.05\text{ eV}$ at 100 eV. All fragmented ion yield spectra, fluorescence excitation spectra, and X-ray absorption spectra were normalized to the incident photon flux in the Si 2p edge.

3. Result and discussion

In Fig. 1, the fragmented ion yields of Cl^+ , Si^+ , SiCl^+ , SiCl_2^+ , and SiCl_3^+ for gaseous SiCl_4 following the Si 2p core-level excitation to various resonances are reproduced along with the Si L-edge X-ray absorption spectrum for comparison. As noted from Fig. 1, the Si $L_{2,3}$ -edge X-ray absorption near edge structure (XANES) spectrum of gaseous SiCl_4 is rich in structure. The detailed assignments of Si $L_{2,3}$ -edge X-ray absorption spectrum of gaseous SiCl_4 have been discussed in Chen et al. (1995). The doublet structures at 104.10 and 104.71 eV labeled 1 and 1' were ascribed to transitions from the $\text{Si}(^2\text{P}_{3/2,1/2})$ initial states to the $8a_1^*$ state (Tse et al., 1989). The next doublet structures labeled 2 and 2' were assigned to excitations to the $9t_2^*$ state. The

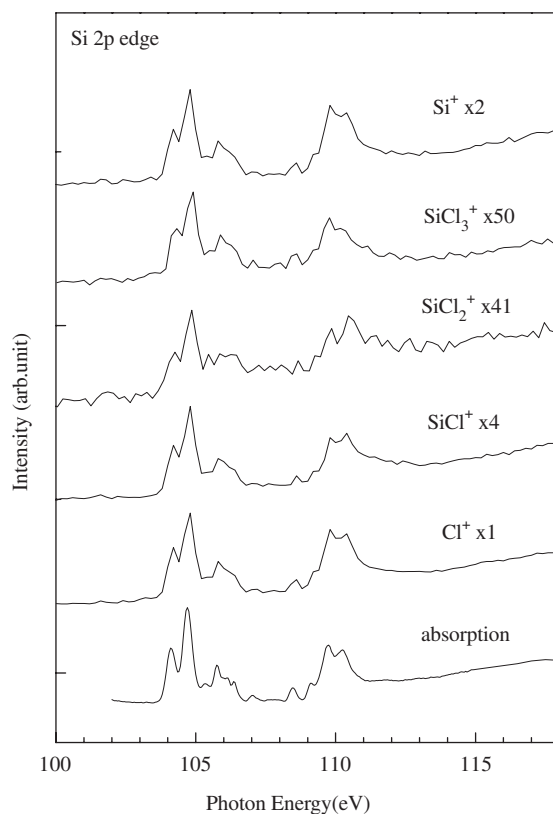


Fig. 1. Fragmented ion yields of Cl^+ , Si^+ , SiCl^+ , SiCl_2^+ , and SiCl_3^+ of gaseous SiCl_4 as a function of photon energy in the vicinity of Si 2p edge along with the Si L-edge X-ray absorption spectrum.

absorption features between 105 and 106.5 eV have mainly valence character. In contrast, the high-energy peaks between 108 and 110 eV possess strong Rydberg character (Chen et al., 1995). As shown in Fig. 1, the photon-energy dependence of various fragmented ion yields, Cl^+ , SiCl^+ , SiCl_2^+ , and SiCl_3^+ , of gaseous SiCl_4 resembles the Si L_{23} -edge photoabsorption spectrum. In contrast, a comparison between the Si^+ yield spectrum and the Si L_{23} -edge absorption spectrum in Fig. 1 shows that the Si $2p \rightarrow$ Rydberg excitation at ~ 110 eV produces enhancement of the Si^+ yield, as compared to the Si $2p \rightarrow 8a_1^*$ and Si $2p \rightarrow 9t_2^*$ excitations.

In Fig. 2, the dispersed fluorescence spectrum of gaseous SiCl_4 taken with the excitation photon of 230 eV is reproduced. The sharp structures between 200 and 320 nm are due to emission from excited Si atoms (Wiese et al., 1969). The broad features peaked at 413 and 568 nm have been assigned from $\text{SiCl}_4^+ \text{C} \rightarrow \text{X}$ and $\text{SiCl}_4^+ \text{C} \rightarrow \text{A}$ transitions, respectively (Lambert et al., 1988). The feature at ~ 390 nm is ascribed to overlapping emission of excited Si^+ and excited SiCl_4^+ (Wiese et al., 1969). Some emission features are due to a second-order light contribution from the 253 and 413 nm, as indicated in Fig. 2.

To understand how the various fluorescence channels vary as a result of excitations of Si 2p electrons to different empty orbitals, we monitored the relative yields of the excited fluorescing species observed in Fig. 2 as a function of photon energy in the vicinity of Si 2p edge. Fig. 3 shows the yields of the most intense excited fluorescing species observed in Fig. 2 following Si 2p core-level excitation. For comparison, the Si L-edge X-ray absorption spectrum of gaseous SiCl_4 is also plotted in Fig. 3.

As noted from Fig. 3, the excitation spectra of all light-emitting species show the same gross features as

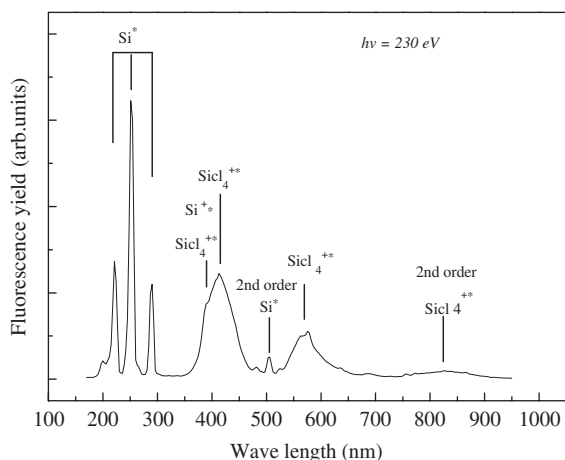


Fig. 2. Dispersed fluorescence spectrum of gaseous SiCl_4 following excitation with 230 eV photons.

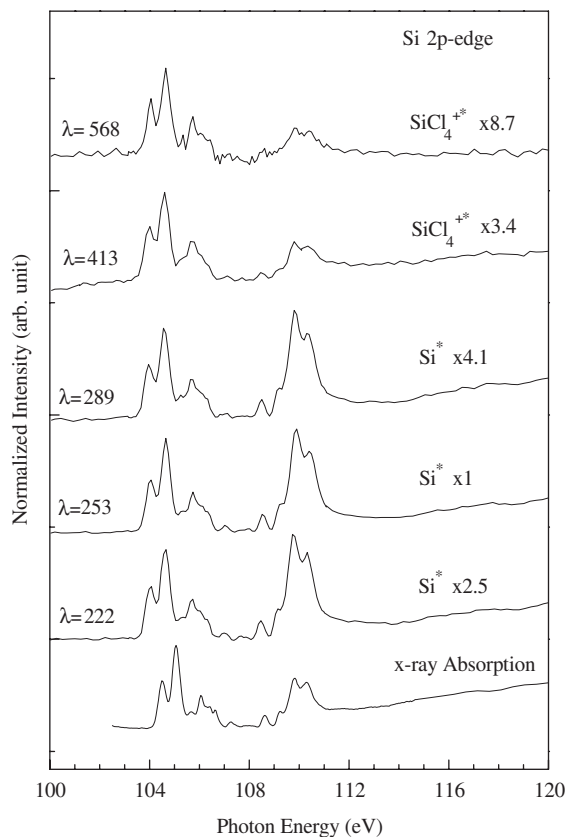


Fig. 3. Photon-energy dependence of various excited fluorescing species at the Si 2p edge along with the Si L-edge X-ray absorption spectrum of gaseous SiCl_4 .

the Si L-edge absorption spectrum. However, there are dramatic differences in the relative intensities of peaks due to excitation to valence levels and that due to excitation to Rydberg orbitals. As compared to the Si L-edge X-ray absorption spectrum, the relative intensity of core-to-Rydberg excitation is slightly lower in the excitation spectra of excited SiCl_4^+ and much higher in the excitation spectra of excited Si atoms. In other words, excitations of Si 2p electrons to the Rydberg orbitals lead to a significant enhancement of the excited neutral atomic fragments Si^* .

Based on resonant photoemission studies of gaseous SiCl_4 , it has been shown that, following Si 2p core-to-valence excitation, the excited SiCl_4 relaxes primarily by a spectator Auger transition resulting in a $2h1e$ state, but participant Auger decay makes a notable contribution (Aksela et al., 1988). On the contrary, the spectator Auger transition prevails completely at Si $2p \rightarrow$ Rydberg excitation. In other words, there is a large enhancement for the $\text{SiCl}_4(7t_2)^{-1}$ state upon excitations of Si 2p electrons to valence orbitals in gaseous SiCl_4 , but very little change as a result of Rydberg excitation. It has been demonstrated that the $\text{SiCl}_4^+ \text{C}$ states emission

results from ionization of an electron from the $7t_2$ orbital of SiCl_4 (Carlson et al., 1988). Accordingly, the excitation spectra of excited molecular-ion SiCl_4^+ will also have a higher relative yield following Si 2p \rightarrow valence excitation, as evidenced in Fig. 3.

As mentioned, the spectator Auger transitions are the dominant decay processes of gaseous SiCl_4 following Si 2p core-to-valence and Si 2p core-to-Rydberg excitations, which produce dominantly two-hole, one-electron ($2h1e$) states. Accordingly, a close resemblance of the photon-energy dependence of various fragmented ion yields and the Si L_{23} -edge absorption spectrum of gaseous and condensed SiCl_4 , as shown in Fig. 1, is attributed to the Auger decay of core-excited states and the subsequent Coulomb repulsion of multi-valence-hole final states.

As demonstrated, the Si 2p core-to-Rydberg excitation of gaseous SiCl_4 leads to a noteworthy production of excited atomic fragments. In other words, the $2h1e$ states with an excited Rydberg electron, as opposed to a spectator electron in the valence orbital, are more likely to produce the excited-state fragments. One possible explanation for this enhancement is that the wave function of a diffuse Rydberg electron has less overlap with the molecular-ion core and consequently the $2h1e$ states dissociate to produce the excited-state fragments before the excited Rydberg electron can relax. Similar phenomenon has been observed for SiCl_4 (Cl 2p edge), $\text{Si}(\text{CH}_3)_{4-n}\text{Cl}_n$ ($n = 1-3$, Si 2p and Cl 2p edges), $\text{CH}_{4-n}\text{Cl}_n$ ($n = 2-4$, Cl 2p edge), etc. (Chen et al., 2004). The enhanced production of excited neutrals following core-to-Rydberg excitation is thus not specific to SiCl_4 molecules. Thus, this finding is of general nature. As mentioned, the Si^+ yield spectrum has pronounced structure in the higher energy, Rydberg excitation. This infers that Si^+ may be formed by the same decay channel that produced the excited fragments.

4. Conclusion

We have investigated the dissociation dynamics for ionic fragments and excited fragments of gaseous SiCl_4 following Si 2p core-level excitation using monochromatized synchrotron radiation. The Si 2p core-to-Rydberg excitation leads to a significant production of excited atomic (Si^* , Si^{+*}) fragments, particularly for excited neutral atomic fragments Si^* . Accordingly, the Si 2p \rightarrow Rydberg excitation produces enhancement of the Si^+ yield, as compared to the Si 2p $\rightarrow 8a_1^*$ and Si $\rightarrow 9t_2^*$ excitations. In contrast, the Si 2p core-to-valence excitation generates an enhancement of excited molecular-ion SiCl_4^+ . The experimental results provide deeper insights into the state-selective dissociation dynamics for excited neutral fragments of molecules via core-level excitation.

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