Dissociation dynamics of excited neutral fragments of gaseous SiCl₄ following Si 2*p* and Cl 2*p* core-level excitations

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State-specific dissociation dynamics for excited fragments of gaseous SiCl₄ following Cl 2*p* and Si 2*p* core-level excitations were characterized by the dispersed UV/optical fluorescence spectroscopy. The core-to-Rydberg excitations at both Si 2*p* and Cl 2*p* edges lead 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 2*p* edge generates an enhancement of excited molecular-ion SiCl₄⁺. The experimental results provide deeper insight into the dissociation dynamics for excited neutral fragments of molecules via core-level excitation.

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I. INTRODUCTION

The relaxation processes and subsequent profound dissociation channels of polyatomic molecules following inner-shell excitation have been a subject of extensive research over decades because of scientific importance and technological applications [1–3]. Understanding of site-selective x-ray initiated molecular photolysis is important gateway for the development of evolving technology in the fabrication of microelectronic devices into the nanometer range [4].

Resonant photoemission spectroscopic techniques have been widely applied to monitor the decay channels of resonantly core-excited states which have been observed to decay predominantly by the spectator Auger transitions to form two-hole, one-electron (*2h1e*) states [5]. 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 molecules or molecular adsorbates on surfaces following core-level excitation [6]. However, the fragmented ions reported in literature were predominantly positive ions or negative ions [5–8].

It is known that the photodesorption yield of neutral products for molecular adsorbates on surfaces via photoexcitation is much higher than that of ions, because reneutralization process plays a very important role in photon stimulated ion desorption. 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 neutral fragments produced by inner-shell photoexcitation in molecules is still in its infancy [9–12]. Until now, the dynamics for excited fragments, particularly for neutral products, generated from the *2h1e* states are not fully understood. The investigation of dissociation dynamics of neutral fragments of gaseous-phase molecules and molecular adsorbates on surfaces following core-level excitation is a promising field due to the complexity of the physical processes involved in molecular dissociation. 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 excited fragments of gaseous SiCl₄ following Cl 2*p* and Si 2*p* core-level excitations to various resonances were characterized by the dispersed UV/optical fluorescence spectroscopy. The most striking observation is that the core-to-Rydberg excitations at both Si 2*p* and Cl 2*p* edges lead 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 2*p* edge generates an enhancement of excited molecular-ion SiCl₄⁺. The experimental results have enabled us to gain intriguing insights into the mechanism of excited natural production following core-level excitation.

II. 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 SiCl₄ (Merck) was degassed by several freeze-pump-thaw cycles before use. For dispersed fluorescence measurements, an effusive molecular beam produced by expanding the gas through an orifice (100 μm) into the experimental chamber was used. 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). The relative fluorescence signal was not corrected for the efficiency of the PMT.
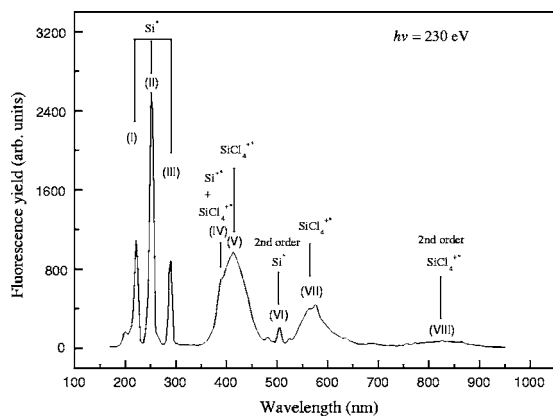
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FIG. 1. Dispersed fluorescence spectrum of gaseous $SiCl_4$ following excitation with 230 eV photons.

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 $= \sim 0.3$ eV at 100 eV), while the spectral resolution of the spectrometer was set to ~ 10 nm. The pressure in the effusive beam chamber was kept at $\sim 9 \times 10^{-5}$ 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 ~ 0.05 eV at 100 eV. All fluorescence excitation spectra and x-ray absorption spectra were normalized to the incident photon flux in the Si $2p$ edge and Cl $2p$ edge.

III. RESULT AND DISCUSSION

In Fig. 1, 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 labeled I, II, and III are due to emission from excited Si atoms [13]. The broad features peaked at 413 nm (labeled V) and 568 nm (labeled VII) have been assigned from $SiCl_4^+$ $C \rightarrow X$ and $SiCl_4^+$ $C \rightarrow A$ transitions, respectively [14]. The feature at ~ 390 nm labeled IV is ascribed to overlapping emission of excited Si$^+$ and excited $SiCl_4^+$ [13]. Some emission features labeled VI and VIII are due to a second-order light contribution from the 253 and 413 nm, as indicated in Fig. 1.

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. 1 as a function of photon energy in the vicinity of Si $2p$ edge. Figure 2 shows the yields of the most intense excited fluorescing species observed in Fig. 1 following Si $2p$ core-level excitation. For comparison, the Si L-edge x-ray absorption spectrum and total fluorescence yield spectrum of gaseous $SiCl_4$ are also plotted in Fig. 2. As seen from Fig. 2, the Si L_{23}-edge x-ray absorption near edge structure (XANES) spectrum of $SiCl_4$ is rich in structure. The doublet structures at 104.10 and 104.71 eV were ascribed to transitions from the $Si(^2P_{3/2,1/2})$ initial states to the $8a_1^*$ state [15]. The absorption features between 105 and 106.5 eV have mainly valence character, In
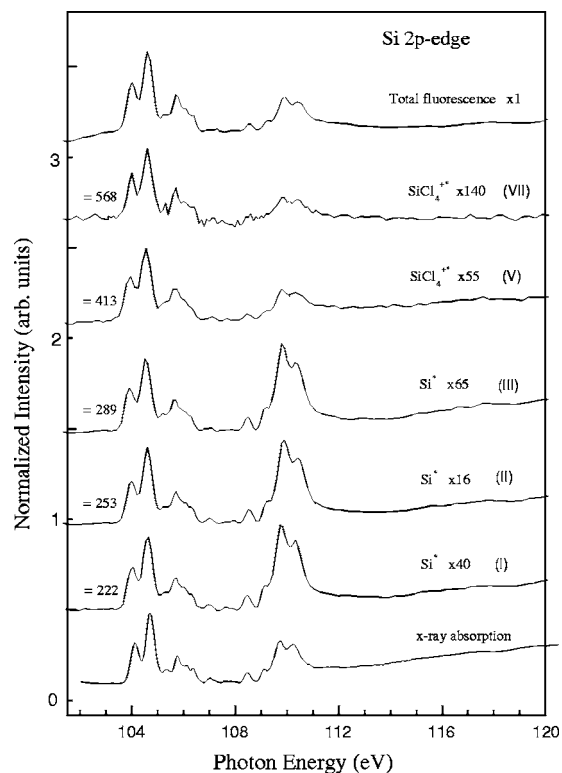

FIG. 2. Photon-energy dependence of various excited fluorescing species at the Si $2p$ edge along with the Si L-edge x-ray absorption spectrum and total fluorescence yield spectrum of gaseous $SiCl_4$. The Roman letter indicated in each spectrum corresponds to an emission peak marked in the dispersed fluorescence spectrum in Fig. 1.

contrast, the high-energy peaks between 108 and 110 eV possess strong Rydberg character [16].

As noted from Fig. 2, the excitation spectra of all light-emitting species show the same gross features as 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 core-to-valence excitations in the Si $2p$ edge, the excited $SiCl_4$ relaxes primarily by a spectator Auger transition resulting in a $2h1e$ state, but participant Auger decay makes a notable contribution [17]. 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 $SiCl_4(7t_2)^{-1}$ 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 $SiCl_4^+$ C states emission results from ionization of an electron from the $7t_2$ orbital of $SiCl_4$ [18]. Accordingly, the excitation spectra of excited
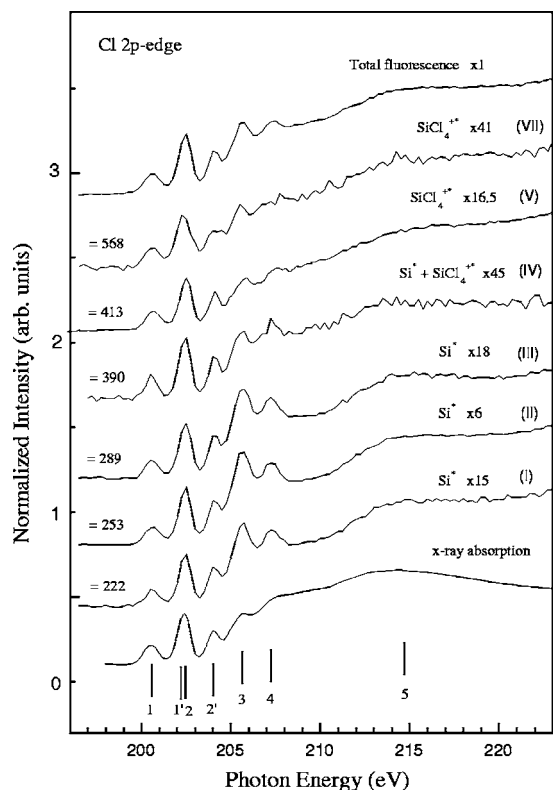
FIG. 3. Excitation spectra of various excited fluorescing species and total fluorescence yield spectrum in the vicinity of Cl $2p$ edge with the Cl L-edge x-ray absorption spectrum of gaseous $SiCl_4$. The Roman letter indicated in each spectrum corresponds to an emission feature marked in the dispersed fluorescence spectrum in Fig. 1.

molecular-ion $SiCl_4^+$ will also have a higher relative yield following Si $2p \rightarrow$ valence excitation, as evidenced in Fig. 2. The total fluorescence yield spectrum is a weighted average of the individual fluorescence channels observed in Fig. 1. In the Si $2p$ edge, most of the fluorescence intensity is due to transitions from the excited $SiCl_4^+$ state, which has a lower relative intensity upon Si $2p \rightarrow$ Rydberg excitation [11]. Therefore, the total fluorescence yield spectrum will also have a smaller relative yield following Si $2p \rightarrow$ Rydberg excitation.

In Fig. 3, photon-energy dependence of the various excited fluorescing species observed in Fig. 1 in the vicinity of Cl $2p$ edge is depicted along with the Cl L-edge x-ray absorption spectrum and total fluorescence yield spectrum of gaseous $SiCl_4$ for comparison. The absorption peaks labeled 1 and 1′ are assigned to the transition, Cl $2p \rightarrow 8a_1^*$ [15]. The features labeled 2 and 2′ correspond to the Cl $2p \rightarrow 9t_2^*$ excitations. Excitations of Cl $2p$ electrons to the Rydberg states are responsible for the absorption peaks labeled 3 and 4. The broadband at ~216 eV labeled 5 is ascribed to the shape resonance. As noted from Fig. 3, the excitation spectra of excited $SiCl_4^+$ resemble the Cl L_{23}-edge photoabsorption spectrum of gaseous $SiCl_4$. In contrast, the relative intensities of various features in excitation spectra of excited atomic fragments (Si* and Si$^+$) and total fluorescence yield spectrum differ significantly from those of Cl L-edge absorption spec-

trum. As noted, excitations of the Cl $2p$ electrons to Rydberg orbitals lead to a dramatic enhancement in the yield of the excited atomic fragments (Si* and Si^{+*}). In particular, the excited neutral atomic fragments Si* are significantly enhanced.

The resonant photoemission studies of gaseous $SiCl_4$ revealed that the spectator Auger transitions are the dominant decay channels following Cl $2p \rightarrow$ valence and Cl $2p \rightarrow$ Rydberg excitations, which produce dominantly $2h1e$ states [17]. The contribution from the participant Auger decay to the resonant Auger processes of gaseous $SiCl_4$ following Cl $2p$ excitation is almost negligible. The shape resonance excitation is followed by the normal Auger decay, which leads to a $2h$ state.

As demonstrated, the core-to-Rydberg excitations at both Si $2p$ and Cl $2p$ edges of gaseous $SiCl_4$ lead 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 $Si(CH_3)_{4-n}Cl_n$ ($n=1–3$, Si $2p$ and Cl $2p$ edges), $CH_{4-n}Cl_n$ ($n=2–4$, Cl $2p$ edge), etc. [12,19]. 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. The Rydberg states indeed play a notable role on the production of excited atomic neutral fragments of molecules via core-level excitation.

IV. CONCLUSION

Using monochromatized synchrotron radiation, we have investigated the dissociation dynamics for excited fragments of gaseous $SiCl_4$ following Cl $2p$ and Si $2p$ core-level excitations. The core-to-Rydberg excitations at both Si $2p$ and Cl $2p$ edges lead to a significant production of excited atomic (Si*, Si^{+*}) fragments, particularly for excited neutral atomic fragments Si*. In contrast, the core-to-valence excitation at the Si $2p$ edge generates an enhancement of excited molecular-ion $SiCl_4^+$. The present findings may be used to help determine the identity of an emitting species and assign the character of absorption features, by using the excitation spectrum of excited fragments as a fingerprint. The experimental results provide deeper insights into the state-selective dissociation dynamics for excited neutral fragments of molecules via core-level excitation.

ACKNOWLEDGMENTS

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