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Dissociation dynamics of anionic and excited neutral fragments of gaseous SiCl_4 following Cl 2p and Si 2p core-level excitations

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Abstract. The state-selective dissociation dynamics for anionic and excited neutral fragments of gaseous SiCl_4 following Cl 2p and Si 2p core-level excitations were characterized by combining measurements of the photon-induced anionic dissociation, x-ray absorption and UV/visible dispersed fluorescence. The transitions of core electrons to high Rydberg states/doubly excited states in the vicinity of both Si 2p and Cl 2p ionization thresholds of gaseous SiCl_4 lead to a remarkably enhanced production of anionic, Si^- and Cl^- , fragments and excited neutral atomic, Si^* , fragments. This enhancement via core-level excitation near the ionization threshold of gaseous SiCl_4 is explained in terms of the contributions from the Auger decay of doubly excited states, shake-modified resonant Auger decay, or/and post-collision interaction. These complementary results provide insight into the state-selective anionic and excited neutral fragmentation of gaseous molecules via core-level excitation.

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1. Introduction

Benefiting from the advancement of high resolution and high photon flux soft x-ray beamlines at third-generation synchrotron radiation facilities, core-level spectroscopies of gaseous molecules and molecular adsorbates on surfaces have been subjects of extensive research. On tuning the photon energy in the soft x-ray region, one can excite selectively a specific atom or a specific site in a molecule. Inner-shell electrons of a particular element in a molecule can be promoted selectively to a specific valence state or a Rydberg orbital below the core ionization threshold, or ejected into a shape resonance or a continuum above the ionization threshold. Relaxation of these core-excited or core-ionized molecules typically involves resonant or normal Auger processes, producing multiply charged molecular ions that are unstable and subsequently undergo dissociation. Excitations of highly localized core electrons conduct the site-selective fragmentation of molecules in several systems [1]–[7]. The dynamics of the photodissociation of core-excited molecules are not only of scientific significance but also of interest in other fields, such as chemical reactions induced by highly energetic particles on interstellar dust and radiation damage of biomolecules [8]–[10]. The complexity of the dissociation and the dynamics of relaxation of gaseous molecules and molecular adsorbates on surfaces via inner-shell excitation is hence a topic of broad interest ([11]–[15] and references therein).

The dynamics of photoionization of an atom or molecule near the threshold of an inner shell and the subsequent relaxation are known to involve many-electron correlations. When an inner-shell electron of an atom or a molecule is ionized near an ionization threshold, a slowly moving photoelectron is ejected into the continuum. For light or medium mass atoms in a molecule, the resulting core-ionized state relaxes predominantly via a radiationless decay, with emission of a rapid Auger electron. The Coulomb interaction between a slow photoelectron and a rapid Auger electron, a so-called post-collision interaction (PCI), causes the slow photoelectron to lose energy and the Auger electron correspondingly to gain energy. This PCI manifests itself through a modified Auger line shape and energy shifts in the photoemission spectra, and through trends in ion-yield spectra. Although this effect has been investigated extensively and is well understood for free atoms [16]–[23], little research has been conducted on molecules [24]–[27]. Little is known about the formation of anions of core-excited molecules mediated by the PCI effect [28]–[38].

The investigation of the dissociation dynamics of neutral fragments of molecules via inner-shell photoexcitation is still novel [6], [39]–[46]. Measurement of neutral fragments in the gaseous phase is difficult because detectors of neutral species are inefficient. The measurement of dispersed fluorescence in the visible and ultraviolet regions is a powerful method to detect neutral and ionic products produced by electronic excitation. There are few reports of

coordinated investigation of anionic and excited neutral fragments produced on excitation of inner shells of gaseous molecules.

In this study, the dissociation dynamics of anionic and excited neutral fragments of gaseous SiCl_4 following photoexcitations of Si 2p and Cl 2p electrons to various resonances were investigated by combining measurements of the photon-induced anionic dissociation, x-ray absorption and UV/visible dispersed fluorescence. The most striking observation is that the transitions of core electrons to high Rydberg states/doubly excited states in the vicinity of both Si 2p and Cl 2p edges of gaseous SiCl_4 lead to significantly enhanced production of anionic, Si^- and Cl^- , fragments and excited neutral atomic, Si^* , fragments.

2. Experiments

Experiments were carried out at the 6 m high-energy spherical grating monochromator (HSGM) beamline and the U5 undulator beamline coupled with a spherical grating monochromator of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. To measure anionic photofragments in the gaseous phase, an effusive molecular beam on expanding the gas through an orifice (diameter $50 \mu\text{m}$) into the experimental chamber was used. The pressure in this chamber was maintained at $\sim 2 \times 10^{-5}$ Torr. Negative fragment ions were selected by mass with a quadrupole mass filter and detected with an off-axis channel electron multiplier (Hiden, EQS). To obtain satisfactory statistics, spectra for the anion yield were the sum of ~ 10 recordings, each of which was separately normalized. To ensure that detected negative ions were produced in unimolecular processes, absorption spectra of anion yield were tested at varied pressures of gas. UV/visible 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 detected with a photomultiplier tube (PMT, Hamamatsu R928). During the measurement of dispersed fluorescence, the pressure in the effusive-beam chamber was kept at $\sim 9 \times 10^{-5}$ Torr. Gas-phase absorption spectra were measured with an ion chamber at pressure $\sim 1 \times 10^{-4}$ Torr.

For photodissociation measurements, the HSGM beamline was operated with $100 \mu\text{m}$ slits corresponding to an energy resolution of ~ 0.2 eV at the Cl 2p edge and of ~ 0.1 eV at the Si 2p edge. To obtain the high-resolution x-ray absorption spectrum, the HSGM beamline was set to a photon resolution of ~ 0.1 eV at the Cl 2p edge and of ~ 0.05 eV at the Si 2p edge. Due to the low signal levels for dispersed fluorescence measurements, the U5 undulator beamline was operated with a $100 \mu\text{m}$ entrance slit and a $300 \mu\text{m}$ exit slit attaining resolution ~ 0.3 eV at the Cl 2p edge, whereas the spectral resolution of the spectrometer was set to ~ 10 nm. The incident photon intensity (I_0) was monitored simultaneously by a Ni mesh located after the exit slit of the monochromator. All yield spectra of anion fragments, x-ray absorption spectra, and fluorescence excitation spectra were normalized to the incident photon flux at the Cl 2p and Si 2p edges. The photon energies were calibrated within an accuracy of 0.1 eV using the Si 2p absorption peak at 104.1 eV and Cl 2p absorption peak at 201.7 eV in gaseous SiCl_4 [47, 48].

3. Results and discussion

The negative photo-ion fragments dominantly produced from gaseous SiCl_4 via Cl 2p core-level excitation were Cl^- and Si^- . We monitored the dispersed UV/optical fluorescence of gaseous SiCl_4 also via Cl 2p core-level excitation. The main features in the dispersed fluorescence

spectrum for photoionization of a Cl 2p electron in gaseous SiCl₄ were identified as emission from the SiCl₄⁺ C state, at 413 and 518 nm, and from excited Si*, at 222, 253 and 289 nm [49]. In figure 1, the yields of anion fragments Cl⁻ and Si⁻ following Cl 2p core-level excitation of gaseous SiCl₄ are reproduced with the Cl L-edge x-ray absorption spectrum. The emission recorded at 253 nm from the excited neutral Si* fragment as a function of photon energy at the Cl 2p edge of gaseous SiCl₄ is depicted in figure 1 for comparison. The absorption features labeled 1 and 1' are assigned to transition Cl 2p → 8a₁^{*}. The features labeled 2 and 2' correspond to excitations Cl 2p → 9t₂^{*} [48]. Broad absorption features labeled 3 and 4 in gaseous absorption spectrum are clearly persisted with reduced intensities, but sharper profiles, in the solid-phase Cl 2p-edge x-ray absorption spectrum of SiCl₄, indicating that these final states have a noteworthy valence character with some contributions from Rydberg states [14]. According to the theoretical calculation, the valence-electron excitation energy for the highest occupied molecular orbital (HOMO, 8t₂) to the lowest unoccupied molecular orbital (LUMO, 8a₁) of SiCl₄, is = ~7 eV [50]. These absorption features may include some contributions from doubly excited states. Accordingly, the broad absorption features labeled 3 and 4 in figure 1 are explained by a mixing of the Rydberg states with the double excitations, similar to the assignment of absorption profiles near 110 eV in the Si L₂₃-edge x-ray absorption spectrum of gaseous SiCl₄, as discussed below [47]. The broad band at ~216 eV labeled 5 is ascribed to a shape resonance.

Discernible in figure 1, the relative intensities of various features in anion-yield spectra and excitation spectra of excited neutral Si* fragments differ significantly from those of the Cl L₂₃-edge absorption spectrum. As shown, excitations of Cl 2p electrons to Rydberg orbitals/doubly excited states (absorptions labeled 3 and 4) near the Cl 2p ionization threshold of gaseous SiCl₄ enhance greatly the yields of anions Cl⁻ and Si⁻ and excited neutral Si* fragments, compared with the ratio of the intensity of the corresponding transition to the core-to-valence excitation (absorption labeled 1) at ~201.7 eV in the Cl L₂₃-edge x-ray absorption spectrum. In particular, the Cl⁻ anion is considerably reinforced. These anions might hence be formed in the same decay that produced the excited neutral fragments. As noted, the peak position for the anion enhancement about 207.0 eV is just above the threshold, 206.9 eV [51], for Cl 2p_{3/2} ionization of gaseous SiCl₄.

Resonant core-excited states with an excited electron in the unoccupied states generally decay primarily by a spectator or participant Auger transition. This spectator Auger decay produces a two-hole, one-electron (2h1e) final state in which the two holes are in valence orbitals, and one electron is excited into an antibonding valence orbital or a Rydberg orbital. Also demonstrated, in the excitation of a specific core electron of an atom or molecule into the lowest unoccupied Rydberg states, the resonant Auger processes are dominated by the spectator Auger decay, i.e. the excited electron remains in the same Rydberg orbital during the decay. For excitations to higher Rydberg states, the shake-modified resonant Auger decay with a transition of an outer electron to a valence shell or a Rydberg orbital, a so-called shake-up, plays a crucial role in resonant Auger processes [52]–[58]. This shake-modified resonant Auger decay produces multiple-hole, multiple-electron (mhme) final states, such as three-hole, two-electron states. In contrast, when the molecule is photoionized just above the threshold for specific core-shell ionization, the slowly moving photoelectron is still near the molecular ion when Auger decay occurs. Through a PCI, the slow photoelectron becomes retarded and might be recaptured by the molecular ion into the valence state or a Rydberg orbital, a so-called shake-down. The gradual evolution of a transition from the regime of resonant Auger decay

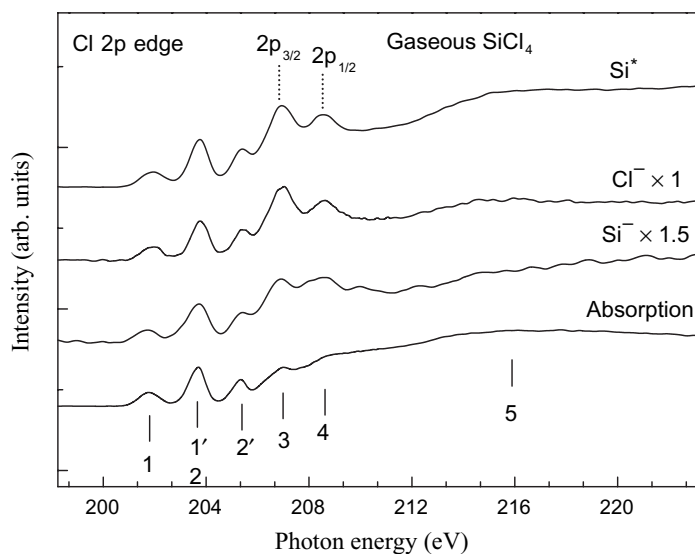


Figure 1. Yields of anion fragments Cl^- and Si^- and excited neutral fragment Si^* from gaseous SiCl_4 following Cl 2p core-level excitation, with the Cl *L*-edge x-ray absorption spectrum. The Cl 2p_{3/2} and Cl 2p_{1/2} ionization thresholds are marked by vertical dashed lines [51].

induced by photoexcitation below the threshold to the regime of PCI just above the threshold has been investigated both theoretically and experimentally for several systems [59]–[64]. Besides, doubly excited states generally converge to the shake-up states, as one of the excited electrons is lifted to an increasingly higher Rydberg orbital and finally to the ionization continuum. The Auger decay of doubly excited states is very similar to shake-up resonant Auger decay, leading to the mhme final states [65].

Based on resonant photoemission studies, the shape of spectator Auger peaks via high Rydberg excitations or/and double excitations (full width at half maximum (FWHM) ~ 10 eV) near the Cl 2p ionization threshold is much broader than that of the spectator Auger peak via Cl 2p core-to-valence excitation, at ~ 201.7 eV, (FWHM ~ 4 eV) and that of the normal Auger peak (FWHM ~ 6 eV) [66]. The broad spectator Auger peak is likely due to the contributions of shake-up or shake-down processes of spectator Auger electrons at more highly excited Rydberg states or Auger decay of doubly excited states. Originating from the shake-modified resonant Auger decay or Auger decay of doubly excited states, the mhme, such as three-hole, two-electron, highly excited states, particularly for one or two electrons remaining in higher Rydberg states, efficiently produce excited atomic neutral fragments. This is due to the fact that the wave function of a diffuse Rydberg electron has small overlap with that of the molecular-ion core and consequently the 2h1e or mhme states dissociate to produce the excited-state fragments before the excited Rydberg electron can relax. The detection of excited neutral particles and anion fragments has been demonstrated to be a sensitive probe for the investigation of the shake-modified resonant Auger decay and PCI dynamics [27, 28, 43, 46, 67, 68]. Fluorescence emission was also observed to be a sensitive probe of the doubly excited states and core-ionized/core-excited shake-up states [45, 69].

The enhanced atomic anionic— Cl^- and Si^- —and excited neutral atomic— Si^* —fragments via excitations from core level to Rydberg states/doubly excited states near the Cl 2p ionization

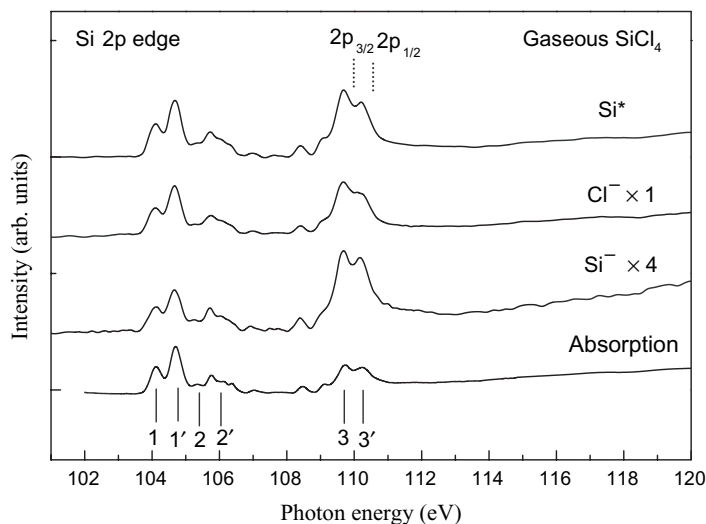


Figure 2. Yields of anion fragments Cl^- and Si^- and excited neutral fragment Si^* from gaseous SiCl_4 following Si 2p core-level excitation, with the Si L -edge x-ray absorption spectrum. The Si $2p_{3/2}$ and Si $2p_{1/2}$ ionization thresholds are marked by vertical dashed lines [51].

threshold of gaseous SiCl_4 , as shown in figure 1, is accordingly explained in terms of the contribution from highly excited states resulting from the shake-modified resonant Auger decay, Auger decay of doubly excited states, or/and PCI. Similar observations have been reported for several small molecules following core-level excitation [26, 27, 40, 44, 67, 68]. Especially noteworthy from figure 1 is that prominently produced anion yields of Cl^- and Si^- are observed in the shape-resonance region of the Cl 2p edge of gaseous SiCl_4 , analogous to other large molecules (e.g. SF_6 , SiF_4), and at variance with many smaller molecules (e.g. CO, CO_2 , NO, N_2O) for which the shape resonance is almost completely suppressed [24, 29, 30, 32], [70]–[72]. Many studies showed that multiple scattering of photoelectrons by neighboring atoms is essential for the interpretation of shape resonance features in x-ray absorption spectra, particularly for large molecules and the solid phase [73]–[76]. The shape resonance for the Cl 2p edge of gaseous SiCl_4 shows accordingly a less localized character, and the resonant intensity of anions is increased in the shape-resonance regime.

If this model is valid, we expect that the excitations of core electrons to high Rydberg states/doubly excited states near the Si 2p ionization threshold of gaseous SiCl_4 might also enhance the production of Cl^- , Si^- and Si^* . We therefore measured the yields of anionic and excited neutral fragments as a function of energy at the Si 2p edge of gaseous SiCl_4 . In figure 2, the yields of anions Cl^- and Si^- and excited neutral Si^* fragments from gaseous SiCl_4 following Si 2p core-level excitation are reproduced with the Si L -edge x-ray absorption spectrum for comparison. This Si L_{23} -edge x-ray absorption near-edge spectrum of gaseous SiCl_4 has abundant structure. The doublet structures labeled 1 and 1' are ascribed to transitions from initial states $\text{Si}(^2P_{3/2,1/2})$ to the $8a_1^*$ state. The doublet features labeled 2 and 2' are assigned to excitations to the $9t_2^*$ state. The absorption features between 105 and 106.5 eV have a mainly valence character, whereas the energetic lines between 108 and 111 eV possess a strong Rydberg character [47]. The absorption features labeled 3 and 3' in figure 2 have diminished intensity, but

Table 1. Ratio of the areas under peaks via core-to-Rydberg excitations or double excitations near the Si 2p and Cl 2p ionization thresholds to peaks via a core-to-valence excitation (peak 1 in figures 1 and 2) for the anionic fragments and excited neutral fragment Si*.

Fragment	Si 2p edge		Cl 2p edge
	Peak 3 (109.7 eV) ^a	Peak 3'(110.2 eV) ^b	Peak 3 (207 eV) ^c
Cl ⁻	1.7	1.5	5.9
Si ⁻	3.1	2.9	4.5
Si*	2.1	1.8	4.9
XAS	1.1	1.0	1.9

^aRatio of peak 3 (109.7 eV) to peak 1 (104.1 eV).

^bRatio of peak 3 (110.2 eV) to peak 1 (104.1 eV).

^cRatio of peak 3 (207 eV) to peak 1 (201.7 eV).

have not vanished, in the solid-phase x-ray absorption spectrum [47]. We accordingly propose to attribute the features labeled 3 and 3' to the superimposition of Rydberg states and doubly excited states [47, 77].

Based on resonant photoemission studies, the shape of the spectator Auger spectrum following excitations of Si 2p electrons to Rydberg states/doubly excited states, at ~ 110 eV, of gaseous SiCl₄ is much broader than that of the spectator Auger spectrum via Si 2p core-to-valence excitation, at ~ 104 eV, and is nearly the same as that of the normal Auger spectrum [65]. As noted from figure 2, excitations of the Si 2p electrons to Rydberg orbitals/double excited states, at ~ 110 eV, near the Si 2p ionization threshold of gaseous SiCl₄ enhance significantly the yields of atomic anionic—Cl⁻ and Si⁻—and the excited neutral atomic—Si*—fragments, consistent with the results via Cl 2p excitation. In particular, Si⁻ anion and the excited neutral Si* fragments are significantly reinforced. Table 1 lists the ratio of the areas under peaks via core-to-Rydberg excitations or double excitations near the Si 2p and Cl 2p ionization thresholds to peaks via a core-to-valence excitation for the anionic fragments and excited neutral Si* fragments. Based on the results in figures 1 and 2, we conclude that the shake-modified resonant Auger decay, Auger decay of doubly excited states, or/and PCI contribute to enhanced formation of atomic anionic and excited atomic neutral fragments in the regime of core-ionization continua. If the shake-modified resonant Auger decay or/and the PCI is dominant, the peak positions for anionic enhancement coincide with the core-ionization thresholds of molecules, as shown in figure 1. Because the contribution of the doubly excited states to the absorption cross section near the Si 2p edges is large, as evidenced in figure 2, the peak position (~ 109 eV) for the enhancement of anionic and excited neutral fragments is different from the Si 2p_{3/2} ionization threshold (~ 110 eV) of gaseous SiCl₄.

Revelation of a detailed mechanism for the production of anionic and excited neutral fragments requires detailed calculations of both potential-energy curves for highly excited molecular SiCl₄⁺ states and further analysis of the resonant Auger decay channels of SiCl₄ at high Rydberg resonances and doubly excited states. A sophisticated method such as threshold electron fluorescence coincidence or electron anion coincidence spectroscopy is crucial to gain detailed information about the dissociation dynamics [33].

4. Conclusion

Combining measurements of photochemical anionic dissociation, x-ray absorption and UV/visible dispersed fluorescence has enabled characterization of the state-selective dissociation dynamics of anionic and excited neutral fragments of gaseous SiCl_4 following excitations of Cl 2p and Si 2p core levels. The transitions of core electrons to high Rydberg states/doubly excited states near both Si 2p and Cl 2p ionization thresholds of gaseous SiCl_4 lead to remarkably enhanced production of anionic, Si^- and Cl^- , and excited atomic neutral, Si^* , fragments. This enhancement is attributed to the contributions from the shake-modified resonant Auger decay, Auger decay of doubly excited states, or/and PCI. These complementary results provide insight into the state-selective anionic and excited neutral fragmentations of gaseous molecules via core-level excitation. Negative photo-ion spectra and excited-fragment emission are powerful tools for the investigation of the dissociation dynamics of core-excited molecules.

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