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Dissociation dynamics of positive-ion and negative-ion fragments of gaseous and condensed Si(CH₃)₂Cl₂ via Si 2p, Cl 2p, and Cl 1s core-level excitations

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The state-selective positive-ion and negative-ion dissociation pathways of gaseous and condensed Si(CH₃)₂Cl₂ following Cl 2p, Cl 1s, and Si 2p core-level excitations have been characterized. The excitations to a specific antibonding state (15α₁ state) of gaseous Si(CH₃)₂Cl₂ at the Cl 2p, Cl 1s, and Si 2p edges produce significant enhancement of fragment ions. This ion enhancement at specific core-excited states correlates closely with the ion kinetic energy distribution. The results deduced from ion kinetic energy distribution are consistent with results of quantum-chemical calculations on Si(CH₃)₂Cl₂ using the ADF package. The Cl⁻ desorption yields for Si(CH₃)₂Cl₂/Si(100) at ~90 K are notably enhanced at the 15α₁ resonance at both Cl 2p and Si 2p edges. The resonant enhancement of Cl⁻ yield occurs through the formation of highly excited states of the adsorbed molecules. These results provide insight into the state-selective ionic fragmentation of molecules via core-level excitation. © 2006 American Institute of Physics. [DOI: 10.1063/1.2400229]

I. INTRODUCTION

The photodissociation of core-excited molecules induced by x-ray photons has received much attention because a comprehensive knowledge of such fragmentation is not only of scientific importance but also of interest in other fields, such as chemical reactions induced by high-energy particles on interstellar dust and radiation damage of biomolecules and x-ray optics. By means of synchrotron radiation with energy tunable in the x-ray region, the site-selective photoexcitation and subsequent cleavage of chemical bonds of molecules on tuning the x-ray energy to a particular absorption resonance have been a subject of extensive research. The site-specific fragmentation via core-level excitation was observed for several systems,¹⁻⁹ but not for some molecules.¹⁰,¹¹ A site-specific fragmentation via core-level excitation was observed for several systems;¹⁻⁹ but not for some molecules.¹⁰,¹¹ Such photofragmentation of molecules might arise from a rapid dissociation of ions;¹²,¹³ but no direct experimental evidence has been reported. The complicated reaction dynamics involved in site-selective fragmentation of core-excited molecules remains a topic of broad interest.¹⁴⁻¹⁷

Some highly excited states near or above the threshold energy for double ionization were observed for gaseous samples, such as SO₂ and CO,¹⁸⁻⁺ but little research has been devoted to these highly excited states and their role on ion desorption processes for adsorbates on surfaces. The detection of negative ions has proved to be a powerful method of exposing highly excited states above the threshold energy for single ionization. However, the investigation of negative-ion fragments produced by inner-shell excitation of molecules is still in its infancy.¹⁸⁻⁻²³ The desorption dynamics of negative-ion fragments of absorbates on surfaces following core-level excitation are not yet fully understood.

In this study, the dissociation dynamics for ionic (positive and negative ion) fragments from gaseous and condensed Si(CH₃)₂Cl₂ following excitations of Cl 2p, Cl 1s, and Si 2p electrons to various resonances have been characterized using synchrotron radiation. The most striking observation is a strong enhancement of fragment ions following excitation of a core electron to a specific unoccupied antibonding valence state (15α₁ state). We provide a clear demonstration that this ion enhancement of specific core-relaxed states correlates closely with the ion kinetic energy distribution. The Cl⁻ desorption yields for Si(CH₃)₂Cl₂/Si(100) at ~90 K are enhanced notably at the 15α₁ resonance at both Cl 2p and Si 2p edges. This resonant enhancement of Cl⁻ yield occurs through the formation of highly excited states of the adsorbed molecules. These results provide insight into the state-selective enhanced ionic fragments of gaseous and condensed molecules via core-level excitation.

II. EXPERIMENT

The experimental measurements were conducted at the high-energy spherical grating monochromator (HSGM)
beamline and the double-crystal monochromator (DCM) tender x-ray beamline in the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. For dissociation measurements in a condensed phase, an ultrahigh-vacuum (UHV) chamber with a base pressure of \( \sim 1 \times 10^{-10} \) Torr was used. The Si(100) surface was cleaned by repeated resistive heating to \( \sim 1100 \) °C under vacuum before the measurements. The high purity Si(CH\(_3\))\(_2\)Cl\(_2\) (Merck, 99.9\%) was degassed by several freeze-pump-thaw cycles before use. The vapor of Si(CH\(_3\))\(_2\)Cl\(_2\) was then condensed through a leak valve the Si(100) surface at \( \sim 90 \) K. X-ray absorption spectra were recorded by the total-electron yield (TEY) mode using a microchannel plate detector. Negative ions were mass selected with a quadrupole mass spectrometer (Balzers, QMA 410). The quadrupole detector was oriented perpendicular to the substrate surface, and photons were incident at an angle of 45° with respect to the substrate normal. The incident photon intensity \( (I_0) \) was monitored simultaneously by a Ni mesh located after the exit slit of the monochromator. To measure photodissociation in the gaseous phase, an effusive molecular beam produced by expanding the gas through an orifice (50 \( \mu \)m) into the experimental chamber was used. The pressure in this chamber was maintained at \( \sim 1 \times 10^{-5} \) Torr. Fragment ions were mass selected with a quadrupole mass spectrometer (Hidden, IDP). The ion kinetic energy (not calibrated) was measured by a quadrupole mass spectrometer with a 45° sector field analyzer (Hidden, EQS).

For ion kinetic energy distribution and photodissociation measurements, the HSGM beamline was operated with 100 \( \mu \)m slits corresponding to the energy resolution of \( \sim 0.2 \) eV at the Cl 2p edge and \( \sim 0.1 \) 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 \( \sim 0.05 \) eV at the Si 2p edge and \( \sim 0.1 \) eV at the Cl 2p edge. The energy resolution of the DCM tender x-ray beamline was set to \( \sim 0.6 \) eV at the Cl 1s edge. All yield spectra of fragment ions and x-ray absorption spectra were normalized to the incident photon flux at the Si 2p, Cl 2p, and Cl 1s edges.

The surface coverage was determined by thermal desorption spectroscopy (TDS). The Si(CH\(_3\))\(_2\)Cl\(_2\) TDS spectra show a single molecular desorption peak with an exposure of 4 L or less (1 L = \( 1 \times 10^{-6} \) Torr s). At a higher exposure, additional peak appears at a temperature of \( \sim 133 \) K and its intensity increases with Si(CH\(_3\))\(_2\)Cl\(_2\) exposures. 4 L exposure of Si(CH\(_3\))\(_2\)Cl\(_2\) on Si(100) at \( \sim 90 \) K thus corresponds to 1 ML.

**III. RESULTS AND DISCUSSION**

Figure 1(a) reproduces the yield spectra of fragment ions from gaseous Si(CH\(_3\))\(_2\)Cl\(_2\) following Cl 2p core-level excitation, with the Cl L\(_{2,3}\)-edge x-ray absorption spectrum at the Cl L\(_{2,3}\)-edge for comparison. The absorption features labeled as 1, 1′, and 2, 2′ in Fig. 1(a) are ascribed to the transitions to the Cl 2p → 15a\(_g\) (Si–Cl) antibonding orbital and Cl 2p → 10b\(_g\) (Si–Cl) antibonding orbital, respectively.\(^{24}\) Excitations to Rydberg orbitals are responsible for the absorption peaks labeled as 3, 3′. The broad band labeled as 4 is attributed to the shape resonance. As shown in Fig. 1(a), the photon-energy dependence of yields of various fragment ions, except Si(CH\(_3\))\(_2\)Cl\(_2\), ClCH\(_2\)Cl, and Si\(_2\), of gaseous Si(CH\(_3\))\(_2\)Cl\(_2\) resembles the Cl L\(_{2,3}\)-edge photoabsorption spectrum. Especially noteworthy is that excitations of Cl 2p to the 15a\(_g\) (Si–Cl) antibonding state of gaseous Si(CH\(_3\))\(_2\)Cl\(_2\) produce significant enhancement of Si(CH\(_3\))\(_2\) and ClCH\(_2\)Cl yields.

In Fig. 1(b), the ion yields of various ionic fragments for gaseous Si(CH\(_3\))\(_2\)Cl\(_2\) as a function of photon energy near the Si 2p edge are shown with the gaseous-phase Si L-edge x-ray absorption spectrum for comparison. The absorption peaks labeled as 1 and 1′ in Fig. 1(b) are assigned to transitions from Si2P\(_{3/2,1/2}\) initial states to the 15a\(_g\) (Si–Cl) antibonding orbital. The doublet structures labeled as 2 and 2′ are assigned to excitations to the 17a\(_g^*\) (Si–Cl) antibonding orbital.\(^{23}\) This result is consistent with the assignment in the Si K-edge absorption spectrum of gaseous-phase Si(CH\(_3\))\(_2\)Cl\(_2\) by Ferrer et al.\(^{26}\) The higher-energy peak labeled as 3 is due to excitation to Rydberg orbitals. As noted from Fig. 1(b), the photon-energy dependence of yields of various fragment ions, except Si(CH\(_3\))\(_2\)Cl\(_2\) and ClCH\(_2\)Cl, of gaseous Si(CH\(_3\))\(_2\)Cl\(_2\) exhibits a close resemblance to the Si L\(_{2,3}\)-edge x-ray absorption spectrum. In contrast, the Si 2p → 15a\(_g\) excitation of gaseous Si(CH\(_3\))\(_2\)Cl\(_2\) induces a substantially enhanced production of Si(CH\(_3\))\(_2\) and ClCH\(_2\)Cl yields, particularly of Si(CH\(_3\))\(_2\).

Figure 2 shows the ion yield spectra of various ionic fragments for gaseous Si(CH\(_3\))\(_2\)Cl\(_2\) via Cl 1s core-level excitation. The Cl K-edge x-ray absorption spectrum of gaseous Si(CH\(_3\))\(_2\)Cl\(_2\) is displayed also in Fig. 2 for comparison. The assignment of the Cl K-edge x-ray absorption spectrum of gaseous Si(CH\(_3\))\(_2\)Cl\(_2\) was discussed by Baba et al.\(^{27}\) In contrast to the Cl K-edge x-ray absorption spectrum of condensed phase, the double peaks labeled as 1 and 2 are clearly observed in the gaseous-phase Si(CH\(_3\))\(_2\)Cl\(_2\), as shown in Fig. 2. The absorption peaks labeled as 1 and 2 are virtually ascribed to excitations from Cl 1s to the 15a\(_g\) (Si–Cl) and 10b\(_g\) (Si–Cl) antibonding orbitals, respectively, similar to the Cl L-edge absorption spectrum. The higher-energy peak labeled as 3 is assigned to be a double excitation.\(^{27}\)

As noted from Fig. 2, the photon-energy dependence of yields of fragment ions H\(^+\), Cl\(_2\)\(^+\), and Si(CH\(_3\))\(_2\)Cl\(_2\) resembles the Cl K-edge x-ray absorption spectrum of gaseous Si(CH\(_3\))\(_2\)Cl\(_2\). In contrast, a significant dissimilarity of the several ion yield spectra, particularly for Cl\(_2^+\), and the Cl K-edge x-ray absorption spectrum of gaseous Si(CH\(_3\))\(_2\)Cl\(_2\) is observed. As noted, the Cl 1s → 15a\(_g\) excitation of gaseous Si(CH\(_3\))\(_2\)Cl\(_2\) leads to significant enhancement of Cl\(_2^+\) and SiCH\(_2\)Cl\(_2\) yields, particularly for Cl\(_2^+\). Besides, excitation of Cl 1s to a 15a\(_g^*\) state generates a moderate enhancement of Cl\(_2^+\) and Si\(_2^+\) yields, but a small enhancement of SiCl\(_2^+\) yield. Hence, yields of not only Cl\(_2^+\) and Cl\(_3^+\) but also Si\(_2^+\) and SiCH\(_2\)Cl\(_2^+\) were noticeably enhanced via the Cl 1s → 15a\(_g^*\) excitation of gaseous Si(CH\(_3\))\(_2\)Cl\(_2\).

Based on the resonant photoemission measurements of gaseous Si(CH\(_3\))\(_2\)Cl\(_2\), the spectator Auger transitions were the dominant decay channels for resonant excitations of Cl 2p (and Si 2p) to the antibonding valence orbitals (15a\(_g\) and 10b\(_g\)) and Rydberg orbitals of gaseous Si(CH\(_3\))\(_2\)Cl\(_2\).\(^{28}\) The
spectator Auger transition results in a two-hole, one-electron (2h1e) final state, in which two holes are produced in valence orbitals and one electron is excited into an antibonding valence orbital or a Rydberg orbital. The spectator electron is localized at the respective valence orbital during the Auger decay. In contrast, the higher-energy shape resonance excitation is followed by the normal Auger decay, which leads to a two-hole (2h) state. Accordingly, a close resemblance of the fragment ion yield spectra and the corresponding Cl L-edge or Si L-edge x-ray absorption spectra of gaseous SiCl₂•Cl₂ also lead to strong state-specific ion enhancement. As shown in Fig. 1(b), the yields of Si(CH₃)₂₁⁺ and SiCH₃⁺ via the Si 2p→15a₁⁺ excitation are clearly significantly enhanced, particularly for Si(CH₃)₂⁺, providing strong evidence to support this hypothesis.

As shown in Fig. 1(a), the Si(CH₃)₂⁻ and SiCH₃⁻ yields show significant enhancement following the Cl 2p→15a₁⁻ excitation when compared with the excitations of Cl 2p→10b₁⁺ and Cl 2p→shape resonance. This infers that the spectator Auger decay and succeeding 2h1e final states with a spectator electron localized in a strong antibonding orbital (15a₁⁻) produce significant enhancement of specific ion fragments. If this hypotheses is correct, it is reasonably expected that these specific 2h1e states populated by spectator Auger transitions of resonant Si(CH₃)₂Cl₂ also lead to strong state-specific ion enhancement. As shown in Fig. 1(b), the yields of Si(CH₃)₂⁺ and SiCH₃⁺ via the Si 2p→15a₁⁺ excitation are clearly significantly enhanced, particularly for Si(CH₃)₂⁺, providing strong evidence to support this hypothesis.
the spectator electron is localized in the antibonding orbital with a strong repulsive ionic potential, the breaking of the chemical bond can be enhanced.\textsuperscript{33} Hence, the ion yield correlates closely with the slope of repulsive ionic potential. A possible reason for the significant difference in the Si(CH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} yields following Cl 2p (or Si 2p) to 15a\textsubscript{i} \textsuperscript{*} and 10b\textsubscript{i} \textsuperscript{*} excitations might thus reflect the difference in the steepness of the repulsive potential between 15a\textsubscript{i} \textsuperscript{*} and 10b\textsubscript{i} \textsuperscript{*}. It is expected that the potential curve of 15a\textsubscript{i} \textsuperscript{*} is much steeper than that of 10b\textsubscript{i} \textsuperscript{*}. So, within the lifetime of 2h1e, Si(CH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} can gain more kinetic energy from 15a\textsubscript{i} \textsuperscript{*} state, increasing the Si(CH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} yield.

The kinetic energy distribution of ionic fragments produced by photoexcitation of molecules provides information about the dissociation dynamics such as the steepness of potential energy surfaces of electronically relaxed states and the energy partitioning among the internal degree of freedom of fragments.\textsuperscript{32} To elucidate the mechanism of state-specific enhancement of ionic fragments, we measure the kinetic energy distributions of various fragment ions from gaseous Si(CH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} following Cl 2p and Si 2p core-level excitations to various resonances. In Figs. 3(a)–3(e), the average kinetic energies of fragment ions [SiCl\textsuperscript{+}, Si\textsuperscript{+}, and Si(CH\textsubscript{3})\textsubscript{2}Cl\textsuperscript{+}, as representative examples] are shown as a function of the excitation energy near the Cl 2p edge. As noted, the average kinetic energies of fragment ions depend markedly on the excitation energy.

As shown in Figs. 3(a)–3(e), the average kinetic energies of various fragment ions, such as SiCl\textsuperscript{+}, at the shape resonance are much higher than those at Cl 2p core-to-valence and Cl 2p core-to-Rydberg excitations. This is due to the fact that the Coulomb repulsion of electronically relaxed two-hole (2h) states at the shape resonance is much larger than that of 2h1e final states at resonant Cl 2p core-to-valence and Cl 2p core-to-Rydberg excitations. In Fig. 3(d), the kinetic energy distributions of Si(CH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} following Cl 2p core-level excitation are reproduced. The resultant average kinetic energy of Si(CH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} is shown in Fig. 3(e) as a function of the excitation energy near the Cl 2p edge. As noted from Figs. 3(d) and 3(e), the ion kinetic energy distribution of Si(CH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} via the Cl 2p→15a\textsubscript{i} \textsuperscript{*} excitation is shifted to an energy of ∼0.2–0.3 eV greater than those via excitations of Cl 2p to 10b\textsubscript{i} \textsuperscript{*}, state, Rydberg orbital, and shape resonance. As mentioned, the kinetic-energy distribution of ionic fragments from molecules via core-level excitation is related to the steepness of the potential energy curves of the electronically relaxed states.\textsuperscript{32} Accordingly, the electronically relaxed 2h(15a\textsubscript{i})\textsubscript{1} states with a spectator electron localized at the 15a\textsubscript{i} \textsuperscript{*} states would have steeper repulsive-potential curves along the Si–Cl coordinates than for 2h(10b\textsubscript{i})\textsubscript{1} and 2h states.

After the Auger decay of resonant core-excited molecules, the kinetic energy released to the dissociation processes is given the difference between the Coulomb repulsive energy of two holes and the dissociation energy of a specific bonding. We assumed that the Coulomb repulsive energy of two holes produced by the Cl(2p)→15a\textsubscript{i} \textsuperscript{*} resonance is approximately the same as that generated by the Cl(2p)→10b\textsubscript{i} \textsuperscript{*} resonance. As presented in Fig. 3, the kinetic energy for ionic fragment Si(CH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} via the Cl 2p→15a\textsubscript{i} \textsuperscript{*} excitation of gaseous Si(CH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} is ∼0.2–0.3 eV greater than that via the Cl 2p→10b\textsubscript{i} \textsuperscript{*} excitation. Hence the dissociation energy of Si–Cl bonding of Si(CH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} at the 2h1e states with a spectator electron in the 15a\textsubscript{i} \textsuperscript{*} orbital is smaller than that at the 2h1e states with a spectator electron in the 10b\textsubscript{i} \textsuperscript{*} orbital.

Based on the molecular-orbital calculations in Si(CH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} performed with the ADF package, the atomic populations of the Si–Cl orbital, such as 11a\textsubscript{i} state, are composed mainly of Si 3s orbital and Cl 3p orbital. It is therefore expected that the spectator electron in the Si 3s* orbital or Cl 3p* orbital assists in breaking the Si–Cl bond. The 15a\textsubscript{i} \textsuperscript{*} orbital is composed of Si 3s (22%), Si 3p (34%), Cl 3p (26%), and other minor components. The 10b\textsubscript{i} \textsuperscript{*} orbital consists mainly of Si 3s (<1%), Si 3p (61%), and Cl 3p (10%). The contents of the Si 3s* and Cl 3p* orbital components in the 15a\textsubscript{i} \textsuperscript{*} orbital are much greater than those in the 10b\textsubscript{i} \textsuperscript{*} orbital. As a result, a spectator electron in the 15a\textsubscript{i} \textsuperscript{*} orbital is more effective in the cleavage of the Si–Cl bond than that in the 10b\textsubscript{i} \textsuperscript{*} orbital. This theoretical prediction is consistent with the present ion kinetic energy distribution measurements.

FIG. 2. Photon-energy dependence of fragment ion yields of gaseous Si(CH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} near the Cl 1s edge with the Cl K-edge x-ray absorption spectrum.
ionization threshold) exceed those at Si 2p core-to-valence excitations. In Fig. 4(c), the ion kinetic energy distributions of Si(CH<sub>3</sub>)<sub>2</sub>Cl<sup>+</sup> of gaseous Si(CH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> following Si 2p core-level excitation are reproduced. The resultant average kinetic energy of Si(CH<sub>3</sub>)<sub>2</sub>Cl<sup>+</sup> is shown Fig. 4(d) as a function of the excitation energy in the vicinity of the Si 2p edge. As noted from Figs. 4(c) and 4(d), the average kinetic energy for fragment Si(CH<sub>3</sub>)<sub>2</sub>Cl<sup>+</sup> at the Si(2p)<sup>-1</sup>(15a<sub>1</sub>)<sup>1</sup> resonance is greater than those at the Si(2p)<sup>-1</sup>(17a<sub>1</sub>)<sup>1</sup> resonance and above the Si 2p ionization threshold. Hence the slope of the potential en-

FIG. 3. Average kinetic energies of (a) SiCl<sup>+</sup>, (b) Si<sup>+</sup>, and (b) Si(CH<sub>3</sub>)<sub>2</sub>Cl<sup>+</sup> as a function of excitation energy near the Cl 2p edge. (d) Kinetic energy distributions of Si(CH<sub>3</sub>)<sub>2</sub>Cl<sup>+</sup> of gaseous Si(CH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> following Cl 2p core-level excitation. The photon energy used for excitation is indicated in each spectrum. The number indicated in each spectrum corresponds to an absorption peak marked in the absorption spectrum in Fig. 1(a). (e) Average kinetic energy of Si(CH<sub>3</sub>)<sub>2</sub>Cl<sup>-</sup> as a function of the photon energy in the vicinity of the Cl 2p edge.
ergy curves along the Si–Cl coordinates of the electronically
relaxed 2h
/ H20849
15
a
1
* / H20850
17
a
1
states is steeper than those of the 2h
/ H20849
17
a
1
* / H20850
1 and 2h states, as confirmed by Cl 2
p
excitation in
Figs. 3
d
/ H20849
102
and 3
e
/ H20849
103.

The enhancement of the Si
/ H20849
CH3
2
+ yield
at the specific resonance therefore correlates strongly with
the ion kinetic energy distribution which is related to the
steepness of potential surface of core-relaxed states. Accord-
ingly, after spectator Auger decay of resonant Si 2
p
, Cl 2
p
, and Cl 1s core-excited states of gaseous Si(CH3)2Cl2, the
subsequent electronically relaxed 2h1e or multihole, one-
electron (mh1e) final states with a steeper potential energy
surface along the dissociation coordinates lead to significant
enhancement of specific ion fragments. The present results
clearly demonstrate that the bond breaking is assisted by a
specific antibonding state, not just any antibonding state. Per-
haps for this reason site selectivity was not found in some
molecules.11

Unlike positive-ion desorption, Cl− and H− were the ions
predominantly observed in the negative-ion desorption of
Si(CH3)2Cl2/Si(100) following Cl 2p and Si 2p core-level excita-
tions. Figures 5(a) and 5(b) show the Cl− yield and H−
yield spectra from Si(CH3)2Cl2/Si(100) following Cl 2p and
Si 2p core-level excitations, respectively, with the corre-
sponding Cl L-edge and Si L-edge TEY spectra of condensed
Si(CH3)2Cl2 for comparison. As noted from Figs. 5(a) and
5(b), the H− yield curves nearly follow the corresponding Cl
L-edge and Si L-edge total electron yield curves. The pos-
sible desorption mechanism of H − from
Si
/ H20849
CH3
2
Cl2 /Si
/ H20849
100
was likely due to dissociative attach-
ment on molecules of secondary electrons produced by pho-
toabsorption of molecular adsorbates. This desorption
mechanism was called dissociative electron attachment
(DEA). Also, the H− and Cl− yields at ~101 eV, indicated by
arrows in Fig. 5(b), are induced by the secondary electrons
produced by the Si 2p core-level excitation of the Si(100)
substrate, likewise providing evidence of the existence of
DEA processes.22,33

Especially noteworthy is that the Cl 2p → 15a
1
excitation

FIG. 4. Average kinetic energies of (a) SiCl+ and (b) Cl+ as a function of excitation energy near the Si 2p edge. (d) Kinetic energy distributions of Si(CH3)2+
of gaseous Si(CH3)2Cl2 following Si 2p core-level excitation. The photon energy used for excitation is indicated in each spectrum. The number indicated in
each spectrum corresponds to an absorption peak marked in the absorption spectrum in Fig. 1b. (e) Average kinetic energy of Si(CH3)2+ as a function of the
photon energy in the vicinity of the Si 2p edge.
significantly enhanced the Cl⁻ desorption yield. To elucidate the origin of the Cl⁻ enhancement at the 15σ₁ resonance, we measured the Cl⁻ yield spectra from Si(CH₃)₂Cl₂/Si(100) with variable coverage following Cl 2p core-level excitation, as presented in Fig. 5(a). As noted, the Cl⁻ yield at shape resonance increases with Si(CH₃)₂Cl₂ exposures and thus show a linear behavior with electron yield. Hence the desorption mechanism of Cl⁻ at shape resonance excitation for Si(CH₃)₂Cl₂/Si(100) is likely due to DEA. If the enhancement of Cl⁻ yield at the 15σ₁ resonance is due to a DEA process, the Cl⁻ yield at the 15σ₁ resonance should show a trend like that at the shape resonance, because the energy distribution of the secondary electrons becomes indistinguishable for photoexcitation at shape resonance and at other photon energies. Hence, the Cl⁻ yield at the 15σ₁ resonance should monotonically increase with Si(CH₃)₂Cl₂ exposure. However, as noted from Fig. 5(a), the Cl⁻ yield at the 15σ₁ resonance increased up to 10 L exposure and then slowly decreased after 10 L exposure of Si(CH₃)₂Cl₂ on Si(100). Moreover the observed 15σ₁ resonances have the same energies and widths between Cl⁻ yield and TEY spectra. It allows us to give a reasonable explanation that the enhancement of Cl⁻ yield at the 15σ₁ resonance is due not to DEA processes but to unimolecular processes.

It is speculated that the enhancement of Cl⁻ yield at the Cl(2p)⁻15σ₁ resonance might originate from some highly excited states of the parent ions that are predissociated by an ion-pair or direct dissociation.18–20 It was proposed that the core-excited states of Si(CH₃)₂Cl₂ molecules via the Cl 2p core-level excitation can decay by an Auger transition to these highly excited states. If such highly excited states exist, it is thus expected that these states can also be populated by an Auger transition of Si 2p core-excited states of Si(CH₃)₂Cl₂. As shown in Fig. 5(b), the Cl⁻ yield at ~103.8 eV via the Si 2p→15σ₁ excitation shows a notable enhancement relative to that at ~105.5 eV on excitation to Si–C antibonding states. This gives evidence in support of the existence of some highly excited states. A similar phenomenon has been found for OPCl₃ (P 2p and Cl 2p edges), Si(CH₃)ₓClₙ (x=1–4) (Si 2p and Cl 2p edges), etc.21 The formation of negative ions through highly excited states is thus not specific to Si(CH₃)₂Cl₂ molecules. It is therefore believed that the present experimental finding is of a general nature.

IV. CONCLUSION

In conclusion, the state-selective positive-ion and negative-ion dissociation pathways of gaseous and condensed Si(CH₃)₂Cl₂ following Cl 2p, Cl 1s, and Si 2p core-level excitations have been characterized using photon-induced dissociation, x-ray absorption spectroscopy, and ion kinetic energy distribution. The excitations to a specific antibonding state (15σ₁ state) of gaseous Si(CH₃)₂Cl₂ at the Cl 2p, Cl 1s, and Si 2p edges lead to significant enhancement of fragment ions. This ion enhancement at specific core-excited states correlates strongly with the ion kinetic energy which is related to the steepness of a potential surface along the dissociation coordinates of core-relaxed states. The results deduced from ion kinetic energy distribution are consistent with results of molecular orbital calculations on Si(CH₃)₂Cl₂ using the ADF package. The Cl⁻ desorption yields from Si(CH₃)₂Cl₂/Si(100) at ~90 K are notably enhanced at the 15σ₁ resonance at both Cl 2p and Si 2p edges. The resonant enhancement of Cl⁻ yield occurs through the formation of highly excited states of the adsorbed molecules. These highly excited states hence play an important role in ion desorption of adsorbed molecules via core-level excitation. Our experimental results provide important insight into the roles and relative importance of dissociative electron attachment, highly excited states, and Auger initiated desorption. These results contribute to a comprehensive understanding of the state-selective ionic (positive ions and negative ions) fragmentation of gaseous and condensed molecules via core-level excitation.

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18 Y. Baba, Low Temp. Phys. 29, 228 (2003), and references therein.