

# Photoabsorption and fluorescence cross sections of $\text{SiCl}_4$ in the region of 6.2–31 eV

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Absolute photoabsorption and fluorescence cross sections of gaseous  $\text{SiCl}_4$  have been measured in the energy region 6.2–31 eV using synchrotron radiation as the light source. Higher order light from the 1-m Seya monochromator was suppressed by use of an Ar gas filter in the energy range 11.3–15.5 eV (110–80 nm) and a LiF window at  $h\nu < 11.8$  eV (105 nm). Emissions have been observed for the  $\tilde{C}^2T_2 \rightarrow \tilde{A}^2T_2$  and  $\tilde{C}^2T_2 \rightarrow \tilde{X}^2T_1$  processes of the  $\text{SiCl}_4^+$  molecular ion and the  $\tilde{A}^1B_1 \rightarrow \tilde{X}^1A_1$  and  $^3B_1 \rightarrow \tilde{X}^1A_1$  of the  $\text{SiCl}_2$  radical. The total fluorescence cross section has been determined to be  $22.4 \pm 1.0$  Mb at 21.22 eV. By comparing with the partial cross section for formation of the  $\tilde{C}^2T_2$  ionic state [Carlson *et al.*, *J. Chem. Phys.* **84**, 641 (1986)], it has been concluded that the  $\text{SiCl}_4^+(\tilde{C}^2T_2)$  formed decays via radiative processes with quantum yield  $\phi \approx 1$ . The experimental results provide information on the breakdown pathways of the  $\text{SiCl}_4^+(\tilde{C}^2T_2)$  ion state. The bands observed in photoabsorption and fluorescence excitation spectra have been assigned as the  $(4s, np, \text{ and } np') \leftarrow 3t_2$ ,  $(4s \text{ and } np) \leftarrow 1e$ ,  $(4s \text{ and } np) \leftarrow 1e$ ,  $(4s \text{ and } 4p) \leftarrow 2t_2$ , and  $(np \text{ and } nd) \leftarrow 2a_1$  Rydberg series. The ionization energies for the  $(2t_2)^{-1}$  and  $(2a_1)^{-1}$  processes have been found to be  $15.04 \pm 0.03$  and  $18.17 \pm 0.03$  eV, respectively. © 1997 American Institute of Physics. [S0021-9606(97)02512-9]

## I. INTRODUCTION

Vacuum ultraviolet photolysis of silanes is of considerable interest because of its importance in material processing. Some chlorinated silanes have been used as the materials for silicon epitaxial growth.<sup>1,2</sup> Photoexcitation of silicon tetrachloride has recently been reported in the energy region 12.8–35.4 eV (97–35 nm).<sup>3–5</sup> Fluorescence from the  $\text{SiCl}_4^+(\tilde{C}^2T_2)$  molecular ion has been observed<sup>3</sup> and its decay channels have been examined by employing coincidence techniques such as threshold photoelectron-photoion coincidence (TPEPICO), photoion-fluorescence coincidence (PIFCO), and threshold photoelectron-fluorescence coincidence (TPEFCO) spectroscopies.<sup>5</sup>

The determination of total photoabsorption cross sections for a material over a wide energy range is a fundamental step involved in its physical and chemical investigation. Absolute cross sections obtained using synchrotron radiation can be subject to serious errors unless higher order light is eliminated. In order to suppress contamination by higher order light some thin metal films have been developed.<sup>6</sup> However, the transmittance of these films in their bandpass is not high, hence valuable photons are wasted. On the contrary, the rare gases have a high transmittance at the energies lower than their ionization potentials (IP).<sup>7</sup> Neon has been used

successfully as a suppressor of the higher order harmonics in an undulator beamline.<sup>8</sup> However, a high concentration of the rare gas has to be introduced between the gas cell and the exit slit of the monochromator because of its small photoabsorption cross section. Therefore, a powerful differential pumping system must be installed.

The total photoabsorption cross section of  $\text{SiCl}_4$  has been reported in the energy region 6.2–11.3 eV (200–110 nm)<sup>9</sup> in which a LiF window was used to suppress higher order radiation, and 12.4–16.5 eV (100–75 nm) and 16.8–24.8 eV (74–50 nm)<sup>10</sup> where thin metal films of Te, Sn, and In were inserted in front of the entrance to the gas cell. In the 11.3–12.4 eV region where photoabsorption data do not exist, large photoabsorption oscillator strengths have been predicted by an *ab initio* calculation.<sup>11</sup>

In the present work we have developed an argon gas filter in order to quantitatively measure the absolute total photoabsorption and fluorescence cross sections of  $\text{SiCl}_4$  in the primary photon energy region 6.2–31 eV (200–40 nm). Emissions were dispersed to identify the emitting species. The Rydberg series observed are discussed below.

## II. EXPERIMENT

The experimental setup and procedure used for the photoabsorption and fluorescence excitation spectra have been

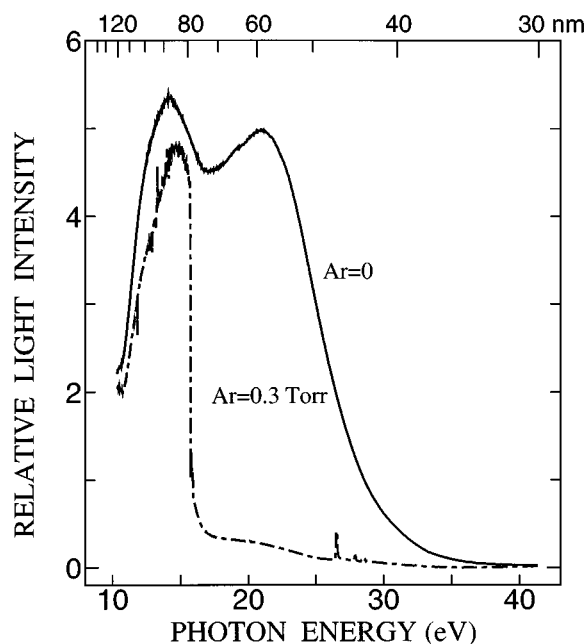


FIG. 1. Transmitted  $I_0$  intensities with Ar and without Ar gas.

described previously.<sup>12,13</sup> In brief, the light source was synchrotron radiation (SR) from the 750 MeV electron storage ring of the Ultraviolet Synchrotron Orbital Radiation (UVSOR) facility at the Institute for Molecular Science (IMS). A 1-m Seya monochromator, which was installed with a grating blazed at 96 nm, was used to disperse the SR. We employed a gas filter using argon gas in a long channel which had a cross section of 2.5 mm $\times$ 5.0 mm $\times$ 170 mm long, since without it a considerable intensity of the higher order light from the Seya monochromator prevented us from obtaining reliable photoabsorption and fluorescence excitation cross sections. The long channel filter was placed before the monochromated SR entered a windowless gas cell. The gas filter and vacuum cell were placed in the main vacuum chamber which was evacuated by a 5000 l/s diffusion pump (Varian, Model VHS10). The base pressure was  $1.8 \times 10^{-6}$  Torr. The pressure in the Seya monochromator was kept better than  $3 \times 10^{-9}$  Torr by differential pumping with three 300 l/s turbomolecular pumps between the monochromator and the main chamber. The argon gas in the filter was kept at a constant pressure  $\approx 0.3$  Torr. The argon effusing out from the filter was evacuated by the diffusion pump. Figure 1 shows the transmitted light intensities ( $I_0$ ) with and without argon gas, both of which are normalized to the ring current. The exciting photons at wavelengths longer than 40 nm or  $h\nu < 31$  eV are practically usable. Obviously the argon gas works as a sharp cutoff filter to transmit light longer than 80 nm (or 15.5 eV). The photon flux dispersed by the grating is extremely weak at  $h\nu > 35$  eV, hence we think contamination by higher order light should be negligible when the monochromator is tuned to 17.5–35 eV. In the region of 15–17.5 eV the contribution of the higher order light may not be neglected since it is estimated to be about 8% of the total photons at 15 eV. The nonzero intensity in the region of

16–30 eV when the argon is present may be due to the stray light, the contribution of which is estimated to be 6% at 20 eV. In the actual measurements no filter was used down to 15.5 eV (80 nm), the argon gas filter was for 15.5–11.3 eV (80–110 nm), and a LiF window was used at primary photon energies lower than 11.8 eV (105 nm).

Fluorescence excitation spectra were measured by a combination of the appropriate cutoff filter and photomultiplier tube (PMT) installed at right angles to the primary SR beam: A Hamamatsu R585 PMT and an Asahi-500 bandpass filter were used to detect the 350–500 nm emission, and a cooled Hamamatsu R955 PMT and a Toshiba Y-50 filter were used for 500–910 nm radiation. Dispersed fluorescence spectra were measured by excitation with the He I (21.22 eV), Ne I (16.85 eV), Ar I (11.83 eV), and hydrogen Lyman- $\alpha$  (10.20 eV) resonance lines. These atomic resonance lines were generated by a 2.54 GHz microwave discharge. The response of the fluorescence detecting system was calibrated by using a standardized bromine lamp with a known spectral irradiance.<sup>13</sup> For the time-dependent measurements of the electronically excited SiC<sub>2</sub> radical, light pulses of about 10 ns FWHM duration were produced by a dc discharge in H<sub>2</sub> gas at  $\approx 1$  Torr.<sup>14</sup>

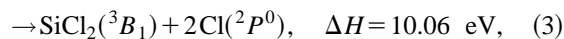
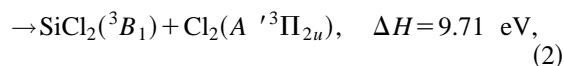
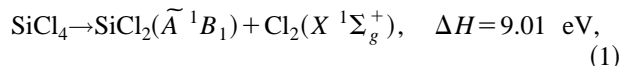
Silicon tetrachloride with stated purity of 99.999% was purchased from Asahi Denka Kogyo Co. and was used without further purification.

### III. RESULTS AND DISCUSSION

#### A. Dispersed fluorescence

The dispersed fluorescence spectra observed in the photodissociative excitation of SiCl<sub>4</sub> using Ar I and He I lines are depicted in Fig. 2. Excitation by H Lyman- $\alpha$  and Ne I lines showed similar spectra to those excited by Ar I and He I radiation, respectively. A low spectral resolution of  $\approx 5$  nm was employed because of the weakness of the emission intensities. The emission peaked at  $\approx 320$  nm in Fig. 2(a) has been assigned as the SiCl<sub>2</sub>( $\tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1$ ) dipole allowed transition.<sup>15</sup> The broadband around 560 nm should be due to the electronically excited SiCl<sub>3</sub> or SiCl<sub>2</sub> radical because the exciting photon energy is lower than the first IP of SiCl<sub>4</sub>.<sup>5</sup> A few papers have been published on the electronic states of the SiCl<sub>3</sub> radical: Even the IP of SiCl<sub>3</sub> seems to be an open question since values of 6.9–10.2 eV have been reported.<sup>16,17</sup> Theoretical considerations of the SiCl<sub>3</sub> radical do not explicitly predict any radiative processes.<sup>18</sup>

In the collision of SiCl<sub>4</sub> with metastable Ar( $^3P_{2,0}$ ) atoms, emission in the 500–620 nm region has been observed and assigned as the SiCl<sub>2</sub>( $^3B_1 \rightarrow ^1A_1$ ) forbidden transition.<sup>19</sup> The thermochemical thresholds to produce the radiative singlet and triplet SiCl<sub>2</sub> radicals are estimated to be:



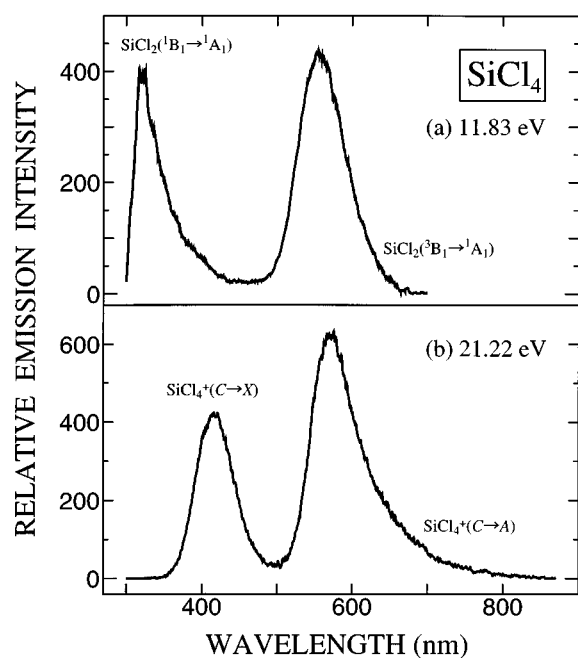


FIG. 2. Dispersed fluorescence of  $\text{SiCl}_4$  excited at (a) 11.83 and (b) 21.22 eV.

where the heats of formation for  $\text{SiCl}_4$ ,  $\text{SiCl}_2$ , and  $\text{Cl}$  are  $\Delta H_f^0 = -6.93$ ,  $-1.64$ , and  $1.24$  eV, respectively.<sup>20</sup> The energy levels of the first electronically excited singlet and triplet  $\text{SiCl}_2$  radicals lie above the ground state by 3.72 and 2.29 eV, respectively.<sup>19,21</sup> The energy gap between the lowest triplet state and the ground state of the  $\text{Cl}_2$  molecule is 2.13 eV.<sup>22</sup> If the observed emission peaked at  $\approx 560$  nm originates from the triplet  $\text{SiCl}_2$  radical, it is expected that the radiative lifetime would be longer than the allowed  $\text{SiCl}_2(\tilde{A}^1B_1 \rightarrow \tilde{X}^1A_1)$  transition. The radiative lifetimes obtained from the spectra are  $\tau_0 = 73.3 \pm 2.2$  and  $355 \pm 8$  ns from the  $\lambda = 300\text{--}420$  and  $500\text{--}650$  nm radiation, respectively. The lifetime for the  $\tilde{A}^1B_1$  state is in good agreement with the reported  $77 \pm 3$  ns.<sup>21</sup> The deduced  $\tau_0 = 355 \pm 8$  ns is much longer than that for the  $\text{SiCl}_2(\tilde{A} \rightarrow \tilde{X})$  transition. Judging from the dispersed spectra and the radiative lifetimes measured, we assign the emission with a local maximum around 560 nm to be the  $\text{SiCl}_2(^3B_1 \rightarrow \tilde{X}^1A_1)$  transition. This is the first observation to detect the triplet  $\text{SiCl}_2(^3B_1)$  radical in the photodissociative excitation of the  $\text{SiCl}_4$  molecule.

In Fig. 2(b) the broadbands with maxima at 410 and 570 nm have been assigned by Lambert *et al.* to be the  $\tilde{C}^2T_2 \rightarrow \tilde{X}^2T_1$  and  $\tilde{C}^2T_2 \rightarrow \tilde{T}^2T_1$  transitions of the molecular  $\text{SiCl}_4^+$  ion, respectively, with a radiative lifetime of 38.4 ns.<sup>3</sup> In their experiment, electron impact was used to ionize a molecular  $\text{SiCl}_4$  beam seeded in He, and many atomic impurity lines were observed in the dispersed spectra.<sup>3</sup>

The total fluorescence cross section of  $\text{SiCl}_4$  at 21.22 eV has been determined to be  $22.4 \pm 1.0$  Mb by normalizing the fluorescence intensity to the cross section for  $\text{N}_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$ .<sup>23</sup> The partial formation cross section for the  $\text{SiCl}_4^+(\tilde{C}^2T_2)$  state has been independently obtained by photoelectron spectroscopy (PES) and reported to be 21.2

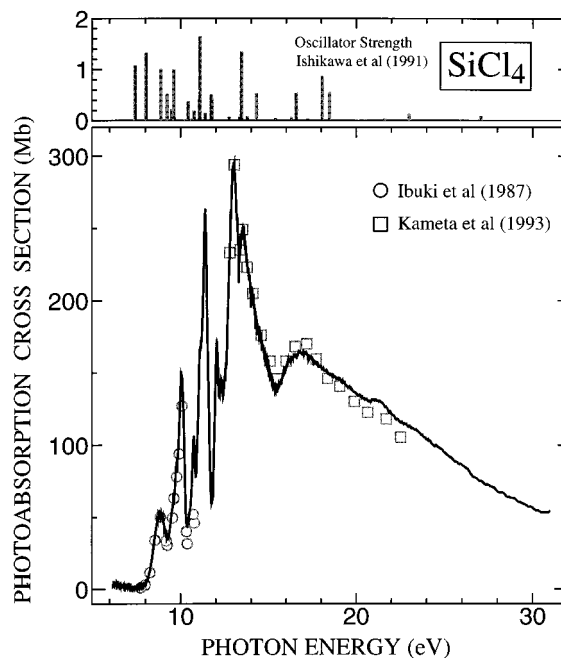


FIG. 3. Total photoabsorption cross section of  $\text{SiCl}_4$  in the 6.2–31 eV region. Open circles and squares are taken from Refs. 9 and 10, respectively. Calculated oscillator strengths are taken from Ref. 11.

$\pm 2.1$  Mb at 21.2 eV.<sup>24</sup> Taking into consideration the experimental errors in both cross sections, we can say that the  $\text{SiCl}_4^+(\tilde{C}^2T_2)$  state formed at 21.2 eV completely decays through radiative processes.

## B. Photoabsorption cross section

Figure 3 shows the total photoabsorption cross section of  $\text{SiCl}_4$  in the region 6.2–31 eV. The open circles are the previous values obtained by using a LiF window<sup>9</sup> and the squares are the data measured by means of thin metal films.<sup>10</sup> SR was employed as a the light source in both experiments. Agreement between these independent studies is satisfactory. The bars at the top of the figure are the *ab initio* oscillator strengths and have been assigned as the valence excitations.<sup>11</sup> Agreement between the theoretical oscillator strengths and the experimental ones is not satisfactory. Fine structures observed in the photoabsorption spectrum will be discussed along with the results of the emission spectra in the next section.

## C. Emission excitation spectra and the Rydberg assignments

Emission cross sections are shown in Fig. 4 as a function of the primary photon energy. The strong emissions at  $h\nu \geq 15$  eV are attributed to the  $\tilde{C}^2T_2 \rightarrow \tilde{X}^2T_1$  and  $\tilde{C}^2T_2 \rightarrow \tilde{A}^2T_2$  transitions of the  $\text{SiCl}_4^+$  molecular ion,<sup>3</sup> the cross sections of which are deduced to be 6.9 and 15.5 Mb at 21.22 eV, respectively, from the integrated intensities in Fig. 2(b). The breakdown pathways of the  $\tilde{C}^2T_2$  ionic state will be given later and hence the fine structures observed in the spectra are discussed in this section. The weak emissions in

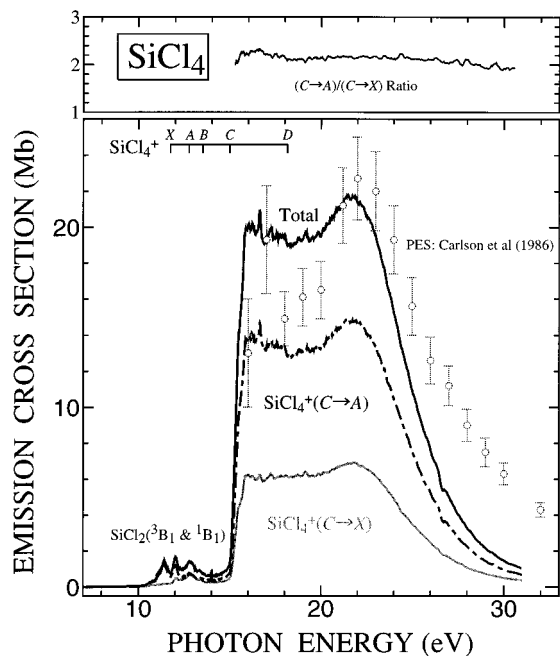


FIG. 4. Emission cross sections of  $\text{SiCl}_4$  in the 7–31 eV region. The total and partial emission cross sections are shown for the  $\text{SiCl}_2(^3B_1$  and  $^1B_1)$  radical at  $h\nu < 15$  eV and for the  $\text{SiCl}_4^+(\tilde{C}^2T_2)$  molecular ion at  $h\nu > 15$  eV. The emission intensity of the  $\tilde{C}^2T_2 \rightarrow \tilde{A}^2T_2$  transition relative to that of the  $\tilde{C}^2T_2 \rightarrow \tilde{X}^2T_1$  transition is given in the top panel. Partial formation cross sections of the  $\text{SiCl}_4^+(\tilde{C})$  state reported in Ref. 24 are also depicted. See text for details.

the 10–15 eV range originate from the  $^3B_1 \rightarrow \tilde{X}^1A_1$  and  $\tilde{A}^1B_1 \rightarrow \tilde{X}^1A_1$  transitions of the  $\text{SiCl}_2$  radical, as discussed in the previous section.

The valence shell electron configuration of the  $\text{SiCl}_4$  molecule is  $(2a_1)^2(2t_2)^6(1e)^4(3t_2)^6(1t_1)^6$  in  $T_d$  symmetry. The three outermost molecular orbitals (MOs) are mostly occupied by the Cl lone-pair electrons. The electrons of the fourth and fifth MOs,  $2t_2$  and  $2a_1$ , have their origins in the  $3s$  and  $3p$  atomic orbitals of the Si and Cl atoms, and form the Si–Cl chemical bonds.<sup>11</sup> The adiabatic IPs of the outermost  $1t_1$  and  $3t_2$  MOs have been obtained by TPEPICO spectroscopy to be 12.7 and 13.5 eV, respectively.<sup>25</sup> Figure 5 shows the expanded photoabsorption and fluorescence cross sections of  $\text{SiCl}_4$  in the 7–15.5 eV region. The peak positions are given in Table I. The first photoabsorption band at 8.84 eV was originally assigned as the valence excitation of the  $3t_2$  MO,<sup>26</sup> while Robin has claimed that this band is the  $4s \leftarrow 3t_2$  Rydberg transition by comparing the photoabsorption bands of the group IV tetrachlorides.<sup>27</sup> He has also assigned the peaks at 9.77 and 10.07 eV to the  $4p$ - and  $4p'$ -terminating Rydberg transitions since the  $3t_2$  MO is split in the Rydberg excited state by the Jahn–Teller effect. These assignments by Robin have been re-examined by Ishikawa *et al.*<sup>11</sup> who have performed an *ab initio* calculation of  $\text{SiCl}_4$ . They re-assigned the 8.84 eV band as two overlapped transitions composed of the  $3a_1 \leftarrow 3t_2$  and  $4t_2 \leftarrow 1t_1$  valence transitions.<sup>11</sup> However, the transition energies calculated are lower than the observed ones by 1–2 eV. For example, the strongest pole calculated lies at 11.1 eV, while the experi-

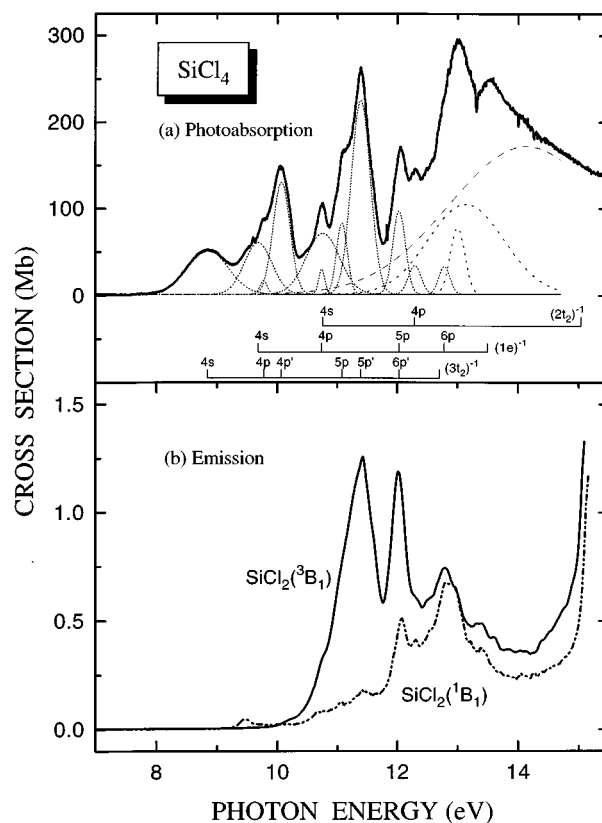


FIG. 5. Expanded photoabsorption and emission spectra at 7.5–14 eV.

mental one is at 13.0 eV. In addition, peak assignments in the previous papers<sup>9,11,26,27</sup> were based on the photoabsorption data obtained in the photon energy region below 11.27 eV (110 nm).<sup>9,26</sup>

TABLE I. The Rydberg assignments for  $\text{SiCl}_4$  in the 7.5–15 eV region.

Peak (eV) <sup>a</sup>	Term value (eV)	Quantum defect ( $\delta$ )	Assignment
8.84 <sub>4</sub>	3.86	2.12	$4s \leftarrow 3t_2$
9.68 <sub>2</sub>	3.82	2.11	$4s \leftarrow 1e$
9.77 <sub>4</sub>	2.93	1.84	$4p \leftarrow 3t_2$
10.07 <sub>1</sub>	2.63	1.73	$4p' \leftarrow 3t_2$
10.74 <sub>2</sub>	2.76	1.78	$4p \leftarrow 1e$
10.75 <sub>9</sub>	4.28	2.22	$4s \leftarrow 2t_2$
11.07 <sub>8</sub>	1.62	2.16	$5p \leftarrow 3t_2$
11.39 <sub>2</sub>	1.31	1.78	$5p' \leftarrow 3t_2$
12.03 <sub>0</sub>	0.67	1.49	$6p \leftarrow 3t_2$
	1.47	1.96	$5p \leftarrow 1e$
12.29	2.75	1.78	$4p \leftarrow 2t_2$
(12.7) <sup>b</sup>			$(3t_2)^{-1}$
12.85 <sub>1</sub>	0.72	1.65	$6p \leftarrow 1e$
13.00			?
13.14			?
(13.5) <sup>b</sup>			$(1e)^{-1}$
(15.04)			$(2t_2)^{-1}$

<sup>a</sup>Peak positions were determined by deconvoluting the photoabsorption spectrum (see Fig. 5).

<sup>b</sup>Ionization potentials from Ref. 25.  $\delta(4s) = 2.15 \pm 0.06$ ,  $\delta(np) = 1.78 \pm 0.22$ , and  $\delta(np') = 1.76 \pm 0.04$ .

Since the  $s \leftarrow t_1$  transition is forbidden in a  $T_d$  symmetry,<sup>28</sup> we assign the first broadband at 8.84 eV as the  $4s \leftarrow 3t_2$  Rydberg transition as did Robin.<sup>27</sup> The second broad photoabsorption band at 9.68 eV, which seems to correspond to the weak band at 9.5 eV in the  $\text{SiCl}_2(\tilde{A}^1B_1 \rightarrow \tilde{X}^1A_1)$  fluorescence excitation spectrum, is attributed to the  $4s$  Rydberg level originating from the  $1e$  MO. We assign the broad band at 10.76 eV as the  $4s \leftarrow 2t_2$  Rydberg transition. The quantum defects for these  $4s$  excitations lie at  $\delta = 2.15 \pm 0.06$ . This  $\delta$  value can be compared with the quantum defects for the Rydberg transitions of the  $\text{Cl}(3p)$  atom. That is,  $\delta = 2.14 \pm 0.04$ ,  $1.68 \pm 0.07$ , and  $0.63 \pm 0.14$  for the  $4s$ ,  $np(n=4-6)$ , and  $4d$  levels, respectively.<sup>29</sup> The other photoabsorption and emission peaks observed are mostly assigned as the  $p$ - or  $p'$ -terminating Rydberg bands of the  $3t_2$  and  $1e$  MOs. The band at 12.29 eV is assigned as the  $4p \leftarrow 2t_2$  Rydberg transition. The  $\delta$  values for the  $np$ - and  $np'$ -bands are deduced to be  $1.88 \pm 0.19$  and  $1.67 \pm 0.16$ , respectively, which show good consistency with those of the  $\text{Cl}$  atom.<sup>29</sup> The assignment of the two photoabsorption peaks at 13.00 and 13.14 eV remains as an open question. The very wide dotted curve should be a background feature.

When the fluorescence excitation spectra of  $\text{SiCl}_2$  radicals in Fig. 5 are compared with the photoabsorption peaks, it can be seen that the  $5p$ ,  $5p'$  and  $6p' \leftarrow 3t_2$  Rydberg transitions are strongly correlated to a potential curve releasing the triplet  $\text{SiCl}_2(^3B_1)$  radical. Since the thermochemical onset of  $\text{SiCl}_2(^3B_1)$  is 9.71 or 10.06 eV as given in reactions (2) and (3), the emission of  $\text{SiCl}_2(^3B_1 \rightarrow \tilde{X}^1A_1)$  is energetically insufficient at the  $4s \leftarrow 3t_2$  Rydberg excitation at 8.84 eV. The  $1e$  Rydberg series seems to be correlated to singlet  $\text{SiCl}_2(\tilde{A}^1B_1)$  radical generation. The onsets of emissions from the  $\text{SiCl}_4^+$  molecular ion give a vertical IP of  $15.04 \pm 0.03$  eV for  $\text{SiCl}_4^+(\tilde{C}^2T_2)$ , which agrees with the recently reported IP of 15.0 eV.<sup>5</sup>

The features of the photoabsorption spectrum between 16 and 18.5 eV in Fig. 6 are in striking contrast to the emission excitation spectra: The emission shows normal peaks while the photoabsorption bands observed give a Fano type structure though the intensity is weak. This observation suggests that autoionization of the Rydberg state occurs in preference to dissociation into neutral fragments. The Rydberg series in emission has been first observed by Lambert *et al.*<sup>3</sup> who have assigned it as the  $np \leftarrow 2a_1$  transition with  $\delta \approx 1.0$ . Kameta *et al.*<sup>10</sup> have observed the Rydberg series as windowlike Fano profiles in their photoabsorption experiments. However, the peak at 16.6 eV has not been observed in their total photoabsorption and photoion efficiency curves, hence they have assigned the 17.3 eV band to be the first member of the  $nd \leftarrow 2a_1$  Rydberg series ( $\delta = 0.12 \pm 0.09$ ) with  $n = 4$ .<sup>10</sup>

In the present simultaneous measurements of photoabsorption and emission spectra, it is clear that the 16.6 eV peak does exist as member of the Rydberg series. This strongest emission band gives a single peak whereas the bands at 17.3 and 17.6 eV are split into doublets both in emission and photoabsorption. Electronic transitions to the  $np$  and  $nd$  Rydberg levels are candidates for the  $2a_1$  orbital electrons.

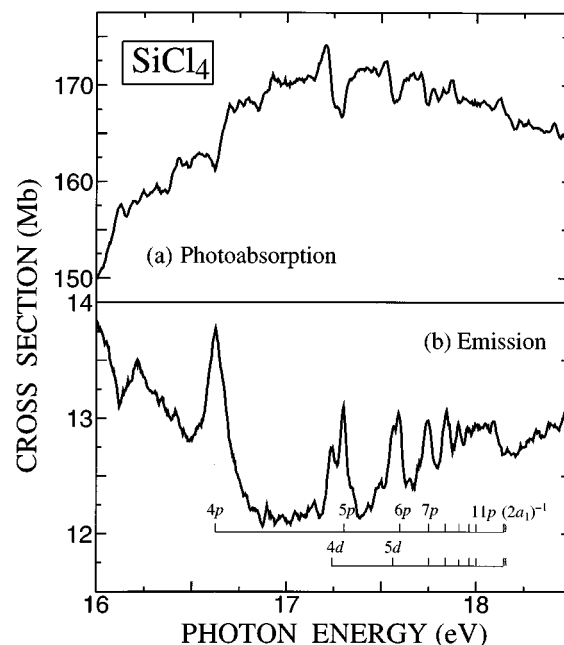


FIG. 6. Expanded photoabsorption and emission spectra at 16–18.5 eV.

Judging from the changing features of the peak intensities and the term values deduced in Table II, we assign the band at 16.6 eV as the first member of the  $np(n \geq 4) \leftarrow 1a_1$  Rydberg series and the emission peaks at 17.24 and 17.56 eV (and also in photoabsorption) as the  $4d$  and  $5d$  Rydberg levels, respectively, since transitions from the  $\text{Si}(3p)$  to the  $3d$  levels seem unlikely. At high principal quantum number the transitions from these two series may be overlapped which give rise to a single structure ( $\Delta\lambda \approx 0.1$  nm in the present primary photon beam). The deduced  $\delta$ 's for these  $np$  and  $nd$  Rydberg series are  $1.10 \pm 0.10$  and  $0.22 \pm 0.16$ , respectively. These term values are little smaller than those expected from  $\text{Cl}$  and/or  $\text{Si}$  atoms. Expected values are  $\delta = 1.43 \pm 0.04$  and  $0.45 \pm 0.06$  for the  $np(n=4,5)$  and  $nd(n=4-7)$  transitions, respectively.<sup>29</sup> However, we think the present assignments are reasonable. The converging limit of these Rydberg series was found to be  $18.17 \pm 0.03$  eV. This is

TABLE II. The Rydberg assignments for  $\text{SiCl}_4$  in the 16–18.5 eV region. The  $np(n \geq 6)$  bands may be overlapped by the  $nd(n \geq 6)$  Rydberg bands.  $\delta(nd) = 0.22 \pm 0.16$ ;  $\delta(np) = 1.10 \pm 0.10$ .

Peak (eV)	Term value	Quantum defect ( $\delta$ )	Assignment
16.62 <sub>1</sub>	1.55	1.01	$4p \leftarrow 2a_1$
17.23 <sub>5</sub>	0.94	0.12	$4d \leftarrow 2a_1$
17.29 <sub>6</sub>	0.87	0.99	$5p \leftarrow 2a_1$
17.55 <sub>6</sub>	0.61	0.17	$5d \leftarrow 2a_1$
17.59 <sub>5</sub>	0.58	1.01	$6p \leftarrow 2a_1$
17.73 <sub>6</sub>	0.43	1.20	$7p \leftarrow 2a_1$
17.84 <sub>2</sub>	0.33	1.24	$8p \leftarrow 2a_1$
17.92	0.25	1.14	$9p \leftarrow 2a_1$
17.97	0.20	1.06	$10p \leftarrow 2a_1$
18.00	0.17	1.14	$11p \leftarrow 2a_1$
(18.17 ± 0.03)			$(2a_1)^{-1}$

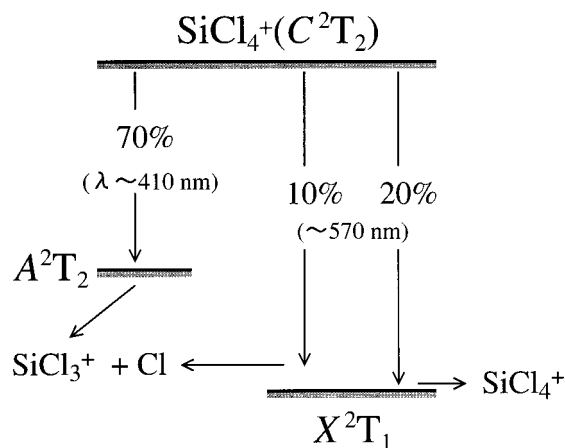


FIG. 7. Diagram of the breakdown pathways of the  $\text{SiCl}_4^+(\tilde{C}^2T_2)$  molecular ion.

the adiabatic IP for the  $(1a_1)^{-1}$  or  $\text{SiCl}_4^+(\tilde{D})$  state. This agrees well with the previously reported 18.1 eV.<sup>3</sup>

#### D. Breakdown pathways of the $\text{SiCl}_4^+(\tilde{C}^2T_2)$ state

The  $\text{SiCl}_4^+(\tilde{C})$  molecular ion formed by direct photoionization decays completely through radiative processes into the ground  $\tilde{X}^2T_1$  and  $\tilde{A}^2T_2$  ionic states. The probability of the transition from the  $\tilde{C}$  state into the lower  $\tilde{A}$  state relative to the transition to the  $\tilde{X}$  state is constant as shown at the top of Fig. 4: The ratio is  $2.2 \pm 0.2$  over the wide energy range 15–31 eV. The relative fluorescence intensity of the  $\tilde{C}$  ionic state is not affected even in the region where the  $\text{SiCl}_4^+(\tilde{D}^2A_1)$  state is formed at  $h\nu \geq 18.17$  eV. The open circles with error bars in Fig. 4 are the partial formation cross sections of the  $\text{SiCl}_4^+(\tilde{C})$  state determined by PES.<sup>24</sup> These partial formation cross sections of  $\text{SiCl}_4^+(\tilde{C})$  agree with the total fluorescence cross sections obtained in the present work up to  $h\nu \approx 22$  eV.

From the PIFCO experiment it has been concluded that the  $\text{SiCl}_4^+(\tilde{A})$  molecular ion exclusively decomposes into  $\text{SiCl}_3^+ + \text{Cl}$ .<sup>5</sup> TPEPICO spectra<sup>5</sup> have shown that the signal intensity for the  $\text{SiCl}_4^+$  molecular ion relative to that for the  $\text{SiCl}_3^+$  fragment is  $1 \approx 4$ . By combining these results in Ref. 5 with the present results, the breakdown pathways of the  $\text{SiCl}_4^+(\tilde{C}^2T_2)$  molecular ion are deduced as shown in Fig. 7. That is, about 70% of the  $\text{SiCl}_4^+(\tilde{C})$  ions decompose into  $\text{SiCl}_3^+ + \text{Cl}$  via the  $\tilde{A}^2T_2$  state after radiating  $\approx 570$  nm light. The residual  $\approx 30\%$  of the  $\tilde{C}$  state relaxes into the ground state fluorescing  $\approx 410$  nm light. In this diagram the ground state molecular ion which decomposes into  $\text{SiCl}_3^+ + \text{Cl}$  may be vibrationally excited.

#### IV. CONCLUDING REMARKS

Absolute total photoabsorption and emission cross sections of the  $\text{SiCl}_4$  molecule have been measured over a wide energy range from 6.2 to 31 eV. The emitting species are identified to be the singlet  $\tilde{A}^1B_1$  and triplet  $\tilde{B}^3B_1$  states of the  $\text{SiCl}_2$  radical and the  $\text{SiCl}_4^+(\tilde{C}^2T_2)$  molecular ion. Forma-

tion of the triplet  $\text{SiCl}_2$  radical by photoexcitation of  $\text{SiCl}_4$  has been first observed in the present work. The radiative lifetime of  $\text{SiCl}_2(\tilde{B}^3B_1)$  was obtained to be  $\tau_0 = 355 \pm 8$  ns. From the total emission cross section measured at  $h\nu = 21.2$  eV and the partial formation cross section previously reported for the  $\tilde{C}$  ionic state,<sup>24</sup> it has been concluded that the  $\text{SiCl}_4^+(\tilde{C})$  ions radiatively decay with quantum yield  $\phi \approx 1$ . The relative emission intensity of the  $\text{SiCl}_4^+(\tilde{C})$  ions decaying into the ground and  $\tilde{A}$  ionic states has been determined to be 1.0:2.2. From this ratio it has been estimated that one third of the ground state molecular ions formed through the radiative  $\tilde{C}$  state decompose into  $\text{SiCl}_3^+ + \text{Cl}$ .

The peaks observed in the photoabsorption and fluorescence excitation spectra can be assigned as Rydberg transitions: The Rydberg transitions converging to  $18.17 \pm 0.03$  eV are assigned as the  $np$ - and  $nd$ -terminating series. The Rydberg excitations  $(4s, np, \text{ and } np') \leftarrow 3t_2$ ,  $(4s \text{ and } np) \leftarrow 1e$ , and  $(4s \text{ and } 4p) \leftarrow 2t_2$  have also been observed.

It has been shown that an argon gas filter 17 cm long at a pressure  $\approx 0.3$  Torr is useful to cut off the higher order light in the region of 80–120 nm.

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