Photoabsorption and fluorescence cross sections of SiCl₄ in the region of 6.2–31 eV

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Absolute photoabsorption and fluorescence cross sections of gaseous SiCl₄ 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 $C^2T_2 \rightarrow A^2T_2$ and $C^2T_2 \rightarrow X^2T_1$ processes of the SiCl₄⁺ molecular ion and the $A^1B_1 \rightarrow X^1A_1$ and $3B_1 \rightarrow X^1A_1$ of the SiCl₂ radical. The total fluorescence cross section has been determined to be 22.4±1.0 Mb at 21.22 eV. By comparing with the partial cross section for formation of the $C^2T_2$ ionic state [Carlson et al., J. Chem. Phys. 84, 641 (1986)], it has been concluded that the SiCl₄⁺($C^2T_2$) formed decays via radiative processes with quantum yield $\phi$=1. The experimental results provide information on the breakdown pathways of the SiCl₄⁺($C^2T_2$) ionic state. The bands observed in photoabsorption and fluorescence excitation spectra have been assigned as the (4s, np, and np')−→3t₂, (4s and np)−→1e, (4s and np)−→1e, (4s and 4p)−→2t₂, and (np and nd)−→2a¹ Rydberg series. The ionization energies for the (2t₂)−¹ and (2a¹)−¹ processes have been found to be 15.04±0.03 and 18.17±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.¹,² Photoexcitation of silicon tetrachloride has recently been reported in the energy region 12.8–35.4 eV (97–35 nm)³–⁵ Fluorescence from the SiCl₄⁺($C^2T_2$) molecular ion has been observed³ 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 (TPEFICO) spectroscopies.⁵

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.⁶ 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).⁷ Neon has been used successfully as a suppressor of the higher order harmonics in an undulator beamline.⁸ 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 SiCl₂ has been reported in the energy region 6.2–11.3 eV (200–110 nm)⁹ 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)¹⁰ 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.¹¹

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 SiCl₄ 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
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 photomulti-
plier 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-α (10.20 eV) resonance lines. These atomic reso-
nance lines were generated by a 2.54 GHz microwave dis-
charge. The response of the fluorescence detecting system
was calibrated by using a standardized bromine lamp with a
known spectral irradiance. For the time-dependent mea-
surements of the electronically excited SiC₂ radical, light
pulses of about 10 ns FWHM duration were produced by a
dc discharge in H₂ gas at ≈1 Torr.

Silicon tetrachloride with stated purity of 99.999% was
purchased from Asahi Denka Kogyo Co. and was used with-
out further purification.

III. RESULTS AND DISCUSSION

A. Dispersed fluorescence

The dispersed fluorescence spectra observed in the pho-
dotodissociative excitation of SiCl₄ using Ar I and He I lines
are depicted in Fig. 2. Excitation by H Lyman-α and Ne I
lines showed similar spectra to those excited by Ar I and He I
radiation, respectively. A low spectral resolution of ≈5 nm
was employed because of the weakness of the emission in-
stensities. The emission peaked at ≈320 nm in Fig. 2(a) has
been assigned as the SiCl₂(3P₂,0) atoms, emission in the 500–620 nm region should be due to the
electronically excited SiC₂ or SiCl₂ radical because the
exciting photon energy is lower than the first IP of SiCl₃. A
few papers have been published on the electronic states of
the SiCl₂ radical: Even the IP of SiCl₃ seems to be an open
question since values of 6.9–10.2 eV have been reported. The
theoretical considerations of the SiCl₂ radical do not explic-
itly predict any radiative processes.

In the collision of SiCl₄ with metastable Ar(3P₂,0) atoms,
in emission in the 500–620 nm region has been observed and
assigned as the SiCl₂(3P₂,0) forbidden transition. The
thermochemical thresholds to produce the radiative singlet
and triplet SiCl₂ radicals are estimated to be:

\[ \text{SiCl}_4 \rightarrow \text{SiCl}_2(A^1B_1) + \text{Cl}_2(X^1Σ_g^-), \quad ΔH = 9.01 \text{ eV}, \quad (1) \]

\[ \rightarrow \text{SiCl}_3(3B_1) + \text{Cl}_2(A^1Π_2u), \quad ΔH = 9.71 \text{ eV}, \quad (2) \]

\[ \rightarrow \text{SiCl}_2(3B_1) + 2\text{Cl}(^3P^0), \quad ΔH = 10.06 \text{ eV}, \quad (3) \]
where the heats of formation for SiCl₄, SiCl₂, and Cl are \( \Delta H_f^0 = -6.93 \), \(-1.64 \), and \(1.24\) eV, respectively.\(^{20}\) The energy levels of the first electronically excited singlet and triplet SiCl₂ radicals lie above the ground state by 3.72 and 2.29 eV, respectively.\(^{19,21}\) The energy gap between the lowest triplet state and the ground state of the Cl₂ molecule is 2.13 eV.\(^{22}\) If the observed emission peaked at \( \lambda \approx 560 \) nm originates from the triplet SiCl₂ radical, it is expected that the radiative lifetime would be longer than the allowed SiCl₂ \( (A^1B_1 \rightarrow X^1A_1) \) transition. The radiative lifetimes obtained from the spectra are \( \tau = 73.3 \pm 2.2 \) and \(355 \pm 8\) ns for the \( \lambda = 300-420 \) and \( 500-650 \) nm radiation, respectively.\(^{21}\) The lifetime for the \(A^1B_1\) state is in good agreement with the reported 77 \(\pm 3\) ns.\(^{21}\) The deduced \( \tau \approx 355 \pm 8\) ns is much longer than that for the SiCl₂ \( (A \rightarrow X) \) 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 triplet SiCl₂ \( (B_1 \rightarrow A_1) \) radical in the photodissociative excitation of the SiCl₄ molecule.

In Fig. 2(b) the broadbands with maxima at 410 and 570 nm have been assigned by Lambert \textit{et al.} to be the \(C^2T_2 \rightarrow X^2T_1\) and \(C^2T_2 \rightarrow T^2T_1\) transitions of the molecular SiCl₄ ion, respectively, with a radiative lifetime of 38.4 ns.\(^{3}\) In their experiment, electron impact was used to ionize a molecular SiCl₄ beam seeded in He, and many atomic impurity lines were observed in the dispersed spectra.\(^{3}\)

The total fluorescence cross section of SiCl₄ 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 N₂\(^1\) \( (B^2Σ_u^+ \rightarrow X^2Σ_g^-) \).\(^{23}\) The partial formation cross section for the SiCl₄\(^1\) \( (C^2T_2) \) state has been independently obtained by photoelectron spectroscopy (PES) and reported to be 21.2 \(\pm 2.1\) Mb at 21.2 eV.\(^{24}\) Taking into consideration the experimental errors in both cross sections, we can say that the SiCl₄\(^1\) \( (C^2T_2) \) state formed at 21.2 eV completely decays through radiative processes.

**B. Photoabsorption cross section**

Figure 3 shows the total photoabsorption cross section of SiCl₄ in the region 6.2–31 eV. The open circles are the previous values obtained by using a LiF window\(^9\) and the squares are the data measured by means of thin metal films.\(^{10}\) SR was employed as the light source in both experiments. Agreement between these independent studies is satisfactory. The bars at the top of the figure are the \(ab\) \textit{initio} oscillator strengths and have been assigned as the valence excitations.\(^{11}\) 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 \( h\nu \approx 15 \) eV are attributed to the \(C^2T_2 \rightarrow X^2T_1\) and \(C^2T_2 \rightarrow A^2T_2\) transitions of the SiCl₄\(^1\) molecular ion,\(^3\) 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 \(C^2T_2\) ionic state will be given later and hence the fine structures observed in the spectra are discussed in this section. The weak emissions in

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**References:**

1. Ibuki et al. (1987), Kameta et al. (1989)

2. SiCl₄ \( (B_1 \rightarrow A_1) \)

3. SiCl₄ \( (C \rightarrow B) \)

4. SiCl₄ \( (D \rightarrow C) \)

5. SiCl₄ \( (E \rightarrow D) \)

6. SiCl₄ \( (F \rightarrow E) \)

7. SiCl₄ \( (G \rightarrow F) \)

8. SiCl₄ \( (H \rightarrow G) \)

9. SiCl₄ \( (I \rightarrow H) \)

10. SiCl₄ \( (J \rightarrow I) \)

11. SiCl₄ \( (K \rightarrow J) \)

12. SiCl₄ \( (L \rightarrow K) \)

13. SiCl₄ \( (M \rightarrow L) \)

14. SiCl₄ \( (N \rightarrow M) \)

15. SiCl₄ \( (O \rightarrow N) \)

16. SiCl₄ \( (P \rightarrow O) \)

17. SiCl₄ \( (Q \rightarrow P) \)

18. SiCl₄ \( (R \rightarrow Q) \)

19. SiCl₄ \( (S \rightarrow R) \)

20. SiCl₄ \( (T \rightarrow S) \)

21. SiCl₄ \( (U \rightarrow T) \)

22. SiCl₄ \( (V \rightarrow U) \)

23. SiCl₄ \( (W \rightarrow V) \)

24. SiCl₄ \( (X \rightarrow W) \)
the 10–15 eV range originate from the $^3B_1 \rightarrow \bar{X}^1A_1$ and $A^1B_1 \rightarrow \bar{X}^1A_1$ transitions of the SiCl$_4$ radical, as discussed in the previous section.

The valence shell electron configuration of the SiCl$_4$ molecule is $(2a_1)^2(2t_2)^6(1e)^2(3t_2)^6(1t_1)^6$ 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. 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. Figure 5 shows the expanded photoabsorption and fluorescence cross sections of 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, while Robin has claimed that this band is the $4s \rightarrow 3t_2$ Rydberg transition by comparing the photoabsorption bands of the group IV tetrachlorides. He has also assigned the peaks at 9.77 and 10.07 eV to the $4p$- and $4p' \rightarrow 3t_2$ 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. who have performed an ab initio calculation of SiCl$_4$. They re-assigned the 8.84 eV band as two overlapped transitions composed of the $3a_1 \rightarrow 3t_2$ and $4t_2 \rightarrow 1t_1$ valence transitions. 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 experimental one is at 13.0 eV. In addition, peak assignments in the previous papers were based on the photoabsorption data obtained in the photon energy region below 11.27 eV (110 nm).

### Table I. The Rydberg assignments for SiCl$_4$ in the 7.5–15 eV region.

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

$^a$Peak positions were determined by deconvoluting the photoabsorption spectrum (see Fig. 5).

$^b$Ionization potentials from Ref. 25. $\Delta(4s) = 2.15 \pm 0.06$, $\Delta(np) = 1.78 \pm 0.22$, and $\Delta(np) = 1.76 \pm 0.04$. 

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FIG. 4. Emission cross sections of SiCl$_4$ in the 7–31 eV region. The total and partial emission cross sections are shown for the SiCl$_4$(B$_1$ and B$_2$) radical at $h\nu<15$ eV and for the SiCl$_4$(C$^2T_2$) molecular ion at $h\nu>15$ eV. The emission intensity of the C$^2T_2 \rightarrow \bar{A}^2T_1$ transition relative to that of the C$^2T_2 \rightarrow \bar{X}^2T_1$ transition is given in the top panel. Partial formation cross sections of the SiCl$_4$(C) state reported in Ref. 24 are also depicted. See text for details.

FIG. 5. Expanded photoabsorption and emission spectra at 7.5–14 eV.
Since the \(s\rightarrow t_1\) transition is forbidden in a \(T_d\) symmetry,\(^2^6\) we assign the first broadband at 8.84 eV as the \(4s\rightarrow3t_2\) Rydberg transition as did Robin.\(^2^7\) The second broad photoabsorption band at 9.68 eV, which seems to correspond to the weak band at 9.5 eV in the \(\text{SiCl}_4 (A\, ^1B_1\rightarrow X\, ^1A_1)\) 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 \(4s\rightarrow2t_2\) Rydberg transition. The quantum defects for these \(4s\) excitations lie at \(\delta=2.15\pm0.06\). This \(\delta\) value can be compared with the quantum defects for the Rydberg transitions of the \(\text{Cl}(3p)\) atom. That is, \(\delta=2.14\pm0.04\), 1.68\pm0.07, and 0.63\pm0.14 for the 4s, \(np(n=4\rightarrow6)\), and \(4d\) levels, respectively.\(^2^9\) The other photoabsorption and emission peaks observed are mostly assigned as the \(p\)- or \(p'\)-terminating Rydberg bands of the 3\(t_2\) and 1e MOs. The band at 12.29 eV is assigned as the \(4p\rightarrow2t_2\) Rydberg transition. The \(\delta\) values for the \(np\)- and \(np'\)-bands are deduced to be 1.88\pm0.19 and 1.67\pm0.16, respectively, which show good consistency with those of the Cl atom.\(^2^9\) 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 \(6p\rightarrow3t_2\) Rydberg transitions are strongly correlated to a potential curve releasing the triplet \(\text{SiCl}_2 (^3B_1)\) radical. Since the thermochromic onset of \(\text{SiCl}_4 (^3B_1)\) is 9.71 or 10.06 eV as given in reactions (2) and (3), the emission of \(\text{SiCl}_4 (^3B_1\rightarrow^1A_1)\) is energetically insufficient at the 4s \(\rightarrow3t_2\) Rydberg excitation at 8.84 eV. The 1e Rydberg series seems to be correlated to singlet \(\text{SiCl}_2 (A\, ^1B_1)\) radical generation. The onsets of emissions from the \(\text{SiCl}_4^+\) molecular ion give a vertical IP of 15.04 \pm0.03 eV for \(\text{SiCl}_4^+ (C\, ^2T_2)\), which agrees with the recently reported IP of 15.0 eV.\(^5\)

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.\(^3\) who have assigned it as the \(np\rightarrow2a_1\) transition with \(\delta=1.0\). Kameta et al.\(^1^0\) 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 \(nd\rightarrow2a_1\) Rydberg series (\(\delta=0.12\pm0.09\)) with \(n=4\).\(^1^0\)

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.

**TABLE II.** The Rydberg assignments for \(\text{SiCl}_4\) in the 16–18.5 eV region. The \(np(n\geq6)\) bands may be overlapped by the \(nd(n\geq6)\) Rydberg bands. \(\Delta(nd)=0.22\pm0.16; \Delta(np)=1.10\pm0.10.\)

<table>
<thead>
<tr>
<th>Peak (eV)</th>
<th>Term value</th>
<th>Quantum defect</th>
<th>Assignment</th>
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<tr>
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<td>17.231</td>
<td>0.94</td>
<td>0.12</td>
<td>(4d\rightarrow2a_1)</td>
</tr>
<tr>
<td>17.291</td>
<td>0.87</td>
<td>0.99</td>
<td>(5p\rightarrow2a_1)</td>
</tr>
<tr>
<td>17.551</td>
<td>0.61</td>
<td>0.17</td>
<td>(5d\rightarrow2a_1)</td>
</tr>
<tr>
<td>17.591</td>
<td>0.58</td>
<td>1.01</td>
<td>(6p\rightarrow2a_1)</td>
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<td>17.731</td>
<td>0.43</td>
<td>1.20</td>
<td>(7p\rightarrow2a_1)</td>
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<tr>
<td>17.841</td>
<td>0.33</td>
<td>1.24</td>
<td>(8p\rightarrow2a_1)</td>
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<tr>
<td>17.921</td>
<td>0.25</td>
<td>1.14</td>
<td>(9p\rightarrow2a_1)</td>
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<tr>
<td>17.971</td>
<td>0.20</td>
<td>1.06</td>
<td>(10p\rightarrow2a_1)</td>
</tr>
<tr>
<td>18.001</td>
<td>0.17</td>
<td>1.14</td>
<td>(11p\rightarrow2a_1)</td>
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</table>

\(2a_1\)^1

**FIG. 6.** Expanded photoabsorption and emission spectra at 16–18.5 eV.
the adiabatic IP for the $\left(1a_1\right)^{-1}$ or $\text{SiCl}_4^+ (\bar{D})$ state. This agrees well with the previously reported 18.1 eV. 3

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

The $\text{SiCl}_4^+ (\bar{C})$ molecular ion formed by direct photoionization decays completely through radiative processes into the ground $X^2T_1$ and $A^2T_2$ ionic states. The probability of the transition from the $\bar{C}$ state into the lower $A$ state relative to the transition to the $X$ state is constant as shown at the top of Fig. 4: The ratio is 2.2±0.2 over the wide energy range 15–31 eV. The relative fluorescence intensity of the $\bar{C}$ ionic state is not affected even in the region where the $\text{SiCl}_4^+ (\bar{D} 2A_1)$ state is formed at $h\nu=18.17$ eV. The open circles with error bars in Fig. 4 are the partial formation cross sections of $\text{SiCl}_4^+$ relative to that for the $\text{SiCl}_4^+$, $\text{SiCl}_3^+$ + Cl, and $\text{SiCl}_4^+$ along the $X^2T_1$ states 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 $A^1B_1$ and triplet $^3B_1$ states of the $\text{SiCl}_2$ radical and the $\text{SiCl}_4^+ (\bar{C} 2T_2)$ molecular ion. Forma-

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 $A^1B_1$ and triplet $^3B_1$ states of the $\text{SiCl}_2$ radical and the $\text{SiCl}_4^+ (\bar{C} 2T_2)$ molecular ion. Forma-

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