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Electronic emission spectroscopy of Group IV tetrachloro molecular ions

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Two broad continuous bands are observed in the visible region following electron impact ionization of a He-seeded molecular beam of $SiCl_4$ or $GeCl_4$. By using tunable vacuum UV radiation from a synchrotron source to measure the threshold energy at which the fluorescence bands occur, it is shown that the bands are related to the initial formation of the $\tilde{C}\,^2T_2$ state of the parent ion $SiCl_4^+/GeCl_4^+$. By comparison with photoelectron data, the bands are assigned to bound–free transitions in $SiCl_4^+/GeCl_4^+$ $\tilde{C}\,^2T_2$–$\tilde{A}\,^2T_2$ and $\tilde{X}\,^2T_1$. The $\tilde{C}$ state of CCl_4^+ does not fluoresce. The results are compared with the electronic emission spectra of the three tetrafluoro molecular ions.

I. INTRODUCTION

In a series of papers,[1–3] two of us have reported observation of electronic emission spectra of three Group IV tetrafluoro molecular ions CF_4^+, SiF_4^+, and GeF_4^+ in the gas phase. The spectra are observed at a low rotational temperature in a crossed molecular beam/electron beam apparatus. For all three ions both continuous and discrete bands have been observed in the visible-UV region of the electromagnetic spectrum. From photoelectron spectroscopy, the ground and first two excited electronic states ($\tilde{X}$,$\tilde{A}$, and $\tilde{B}$) of MF_4^+ are known to dissociate rapidly to $MF_3^+ + F$ (M = C,Si,Ge), and the continuous bands arise from transitions to these states. These three states arise from electron removal from molecular orbitals in MF_4 which are essentially F $2p$ nonbonding in character. The third and fourth excited electronic states ($\tilde{C}$ and $\tilde{D}$) of CF_4^+ and SiF_4^+ give vibrational structure in their photoelectron spectra,[4–6] and hence are bound; these states of GeF_4^+ are also bound, but the vibrational structure is unresolved.[3] They arise from electron removal from t_2 and a_1 molecular orbitals in MF_4 that are essentially bonding in character. These are the upper states of the bound–free continuous transitions (e.g., CF_4^+ $\tilde{C}$–$\tilde{A}$ at 290 nm, SiF_4^+ $\tilde{D}$–$\tilde{A}$ at 304 nm, and GeF_4^+ $\tilde{D}$–$\tilde{A}$ at 255 nm).[7–9] The discrete bands arise from an allowed transition between the two bound states $\tilde{D}\,^2A_1$–$\tilde{C}\,^2T_2$, and this spectrum is described in detail in Refs. 1–3. From a spectroscopic point of view, interest has concentrated on the triply degenerate $\tilde{C}\,^2T_2$ state of these ions which show spin–orbit splitting, Coriolis splitting, and in SiF_4^+ and GeF_4^+[2,3] distortion from tetrahedral geometry via the Jahn–Teller effect. From a dynamics point of view, the interest is to understand why these excited electronic states fluoresce at all. They lie up to 10 eV above the lowest ionic dissociation channel,[10] and such states might be expected to decay nonradiatively rather than by a radiative channel. The observation of fluorescence decay from highly excited electronic states of these polyatomic ions is therefore a very surprising phenomenon.

In this paper we describe experiments to observe electronic emission spectra of the complementary Group IV tetrachloro molecular ions CCl_4^+, $SiCl_4^+$, and $GeCl_4^+$. Three different methods of ionization are used: nonselective electron impact ionization, Penning ionization using He* and Ne* metastables, and photoionization using tunable VUV radiation from the synchrotron storage ring at the SERC Daresbury Laboratory. No discrete bands are observed, but broad band (bound–free) transitions are observed with $SiCl_4$ and $GeCl_4$. The experiments confirm that these bands are due to fluorescence decay from the bound $\tilde{C}\,^2T_2$ state of the parent ion to lower-lying repulsive electronic states. The $\tilde{D}\,^2A_1$ states of $SiCl_4^+$ and $GeCl_4^+$ do not fluoresce, and neither $\tilde{C}$ nor $\tilde{D}$ of CCl_4^+ show fluorescence decay. These experiments are spectroscopic in nature, as the aim is to discover the emitter of particular fluorescence band systems. In the following paper we describe dynamic experiments to measure fluorescence quantum yields and radiative lifetimes of the fluorescing states of MF_4^+ and MCl_4^+.

II. EXPERIMENTAL

The electron impact and Penning ionization experiments were performed in Birmingham. The crossed molecular beam–electron beam apparatus has been described in detail elsewhere.[11] A rotationally cold supersonic beam of the appropriate tetrachloride seeded in helium is formed by expansion of the gas mixture through a 100 μm stainless-steel nozzle, collimated by a 0.5 mm diameter skimmer (Beam Dynamics Inc.), and crossed by an electron beam with an energy of approximately 200 eV and a beam current of 5–10 mA. It is noted that this method of ionization generally has a high cross section, but is not energy selective. Fluorescence from the crossing region is dispersed by a 1.26 m $f/9$ scanning monochromator (Spex 1269) equipped with a holographic grating (1800 ℓmm^{-1}) and a cooled RCA C31034 pm tube connected with single photon counting electronics. This detector has a uniform response between 300 and 830 nm. The scanning of the monochromator and fluorescence collection are controlled by a BBC microcomputer, and data is transferred to the University Mainframe Computer (Honeywell DPS-8/70M) for analysis. It is noted that in this apparatus a discrete spectrum of the parent molecular ion will be observed at a low rotational temperature,[1–3,11] but a broad band bound–free spectrum will not be affected by the reduced temperature of the emitter. CCl_4, $SiCl_4$, and $GeCl_4$ are all volatile liquids at room temperature, and the expansion mixture is obtained by passing helium over the liquid surface in a glass container outside the vacuum (nozzle) chamber. The liquids are used at 298 K, and the pressure of helium is typically 1 atm.

$SiCl_4$ and $GeCl_4$ were studied further in Birmingham by Penning ionization. Rare gas metastables A* (A = He and Ne) produced in a microwave discharge are used to ionize $SiCl_4/GeCl_4$ at room temperature. For example,

$$A^* + SiCl_4 \rightarrow A + SiCl_4^+ + e^- .$$

The total pressure is 15–20 Torr. Emitted light is focused onto the entrance slit of a 0.3 m $f/5$ scanning monochromator (Hilger and Watts), dispersed by a 600 ℓmm^{-1} grating blazed at 300 nm, and detected by an EMI 9635 QB pm tube used at room temperature in the dc mode. Experiments with two rare gas metastables He* and Ne* (excitation energies 19.82 and 16.72 eV, respectively) were performed. The cross sections for Penning ionization generally are smaller than for 200 eV electron impact ionization, but by varying the rare gas there is a limited degree of energy selectivity in the ionization process.

In the third experiment, a photoionization method is used to ionize CCl_4, $SiCl_4$, and $GeCl_4$ at room temperature, using tunable VUV radiation in the energy range 12–35 eV (100–35 nm) from the synchrotron storage ring at the SERC Daresbury Laboratory. This experiment is described in detail in the following paper. Briefly, an effusive spray of pure MCl_4 vapor at a pressure of $\sim 10^{-4}$ Torr is crossed by tunable VUV radiation dispersed from a 1 m VUV Seya monochromator. The photon flux in the apparatus is measured by an Al_2O_3 photocathode. Fluorescence from the ions initially produced or from fragment species is collected simultaneously by two pm tubes (an uncooled EMI 9883 QB and a red-enhanced Mullard 2254 with an S20 photocathode cooled to $-20\,^\circ$C) through optical filters. The signals are detected by single photon counting electronics. The scanning of the Seya monochromator, the recording of the incident photon flux and fluorescence collection are computer controlled, and data is transferred to the Daresbury Mainframe Computer (AS7000) for analysis.

III. ENERGETICS OF THE IONIC STATES OF MCl_4 AND DISSOCIATION CHANNELS

The description of the valence molecular orbitals in MCl_4 is very similar to that given for the tetrafluorides MF_4 in Sec. I. The valence molecular orbitals now arise from overlap of the 16 chlorine atom valence orbitals Cl $3s,3p$ with the central atom valence orbitals (e.g., C $2s,2p$). The central atom d orbitals have only a secondary role in the bonding. The electron configuration corresponding to the five highest occupied molecular orbitals of neutral MCl_4 is $\cdots (2a_1)^2(2t_2)^6(1e)^4(3t_2)^6(1t_1)^6$. The labeling used does not include core orbitals in the numbering scheme. He I and He II photoelectron (PE) spectroscopy show that five electronic states of the mono-positive ion MCl_4^+ exist below 21.2 eV,[12–14] $\tilde{X}\,^2T_1$, $\tilde{A}\,^2T_2$, $\tilde{B}\,^2E$, $\tilde{C}\,^2T_2$, and $\tilde{D}\,^2A_1$, corresponding to electron removal from the $1t_1$, $3t_2$, $1e$, $2t_2$, and $2a_1$ molecular orbitals, respectively. This assignment for the molecular orbital sequence also agrees with theoretical calculations.[15,16] Vibrational structure has only been resolved in the fifth band of $SiCl_4$ (ionization to $\tilde{D}\,^2A_1$:$\nu_1 \simeq 290$ cm^{-1} [14]), although Jahn–Teller and spin–orbit splittings are apparent in several other PE bands. However, it is noted that in the fourth PE band (ionization to $\tilde{C}\,^2T_2$) neither spin–orbit splitting nor Jahn–Teller splitting is observed in CCl_4^+, $SiCl_4^+$, or $GeCl_4^+$.

The three highest molecular orbitals $1e$, $3t_2$, and $1t_1$ are all nonbonding and composed mainly of pure chlorine $3p$ atomic orbitals. The $2t_2$ and $2a_1$ orbitals are largely the bonding orbitals between the chlorine atoms and the central atom. $2t_2$ is the bonding orbital between the valence p orbitals of the central atom and the $3p$ valence orbitals of the chlorine atoms. The bonding orbital $2a_1$ has s character of the central atom and $3s/3p$ character of the chlorine atoms. Semiempirical MNDO molecular orbital calculations[17] show that it is incorrect to label the $3t_2$ and $2t_2$ orbitals as π nonbonding and σ bonding where the Cl $3p$ orbitals are aligned perpendicular to and parallel to the M–Cl bonds, respectively. Both $3t_2$ and $2t_2$ are a mixture of σ- and π-type orbitals, and this is reflected in the magnitude and sign of the spin–orbit splitting constant in MCl_4^+ $\tilde{A}\,^2T_2$ and $\tilde{C}\,^2T_2$.[17]

The vertical ionization potentials (IPs) of these five ionic states of CCl_4^+, $SiCl_4^+$, and $GeCl_4^+$ taken from Ref. 12 are given in Table I, together with the energies of some of the neutral and ionic dissociation channels. The energies of the neutral dissociation channels of CCl_4 and $SiCl_4$ come from well-established heats of formation.[22,23] The energies of the $GeCl_4$ channels (e.g., $GeCl_4 \rightarrow GeCl_2 + Cl_2$) come from several sources and are probably less accurate.[24–26] The energies of the ionic fragments (e.g., $SiCl_4 \rightarrow SiCl_3^+ + Cl$) come from adding the appropriate neutral energy to the ionization potential (IP) of the fragment ($SiCl_3$ in this case). The IPs of MCl_n ($n = 1$–3) come from a variety of sources. A photoelectron spectrum, a direct electron impact measurement, or an analysis of the Rydberg series of the parent molecule/radical give the most accurate data. Thus the IP of CCl is 8.9 eV,[27] CCl_2 9.8 eV,[28] SiCl 6.8 eV,[29] $SiCl_2$ 10.1 eV,[30] GeCl 7.2 eV,[31] and $GeCl_2$ 10.2 eV[32]; the photoelectron values[30,32] are adiabatic IPs. The CCl_3, $SiCl_3$, and $GeCl_3$ free radicals are short lived, and no direct measurement of their IPs have been made. Data is only available from appearance potentials of MCl_3^+ from MCl_4, and this will give an upper limit to the IP of MCl_3. Thus we use IP values of 8.8, 7.9, and 9.5 eV for CCl_3, $SiCl_3$, and $GeCl_3$, respectively.[25,33,34]

Since some of the thermodynamic data and IP measurements are quite old, we quote only one decimal point in the energies of the dissociation channels in Table I, although the energies of some channels are more accurately known. Two particular points about these energetics are worth noting. First, for all three Group IV tetrachlorides the $MCl_3^+ + Cl$ threshold lies close to the ground electronic state of MCl_4^+, and in fact the MCl_3^+ ion is the strongest peak in the mass spectrum cracking pattern of MCl_4.[35] Second, there are a number of dissociation channels energetically "open" to the $\tilde{C}\,^2T_2$ and $\tilde{D}\,^2A_1$ states of the parent ion, and therefore any

TABLE I. Energetics of dissociation channels of MCl_4 and MCl_4^+ (M = C,Si,Ge) in eV.

Neutral/parent ion	Dissociation channel	Energy (eV)[a]
	$CCl + Cl^+ + Cl_2$	20.4
$CCl_4^+ \tilde{D}\,^2A_1$		20.4[b]
	$CCl + Cl + Cl_2^+$	18.9
$\tilde{C}\,^2T_2$		16.68
	$CCl^+ + Cl + Cl_2$	16.3
	$CCl_3 + Cl^+$	16.0
	$CCl_2 + Cl_2^+$	15.0
$\tilde{B}\,^2E$		13.37
	$CCl_2^+ + Cl_2$	13.3
$\tilde{A}\,^2T_2$		12.51
	$CCl_3^+ + Cl$	11.8
$CCl_4^+ \tilde{X}\,^2T_1$		11.64
	$CCl + Cl + Cl_2$	7.4
	$CCl_2 + Cl_2$	3.5
	$CCl_3 + Cl$	3.0
$CCl_4 \tilde{X}\,^1A_1$		0
	$SiCl + Cl^+ + Cl_2$	23.0
	$SiCl + Cl + Cl_2^+$	21.5
$SiCl_4^+ \tilde{D}\,^2A_1$		18.10
	$SiCl_3 + Cl^+$	17.8
	$SiCl^+ + Cl + Cl_2$	16.8
	$SiCl_2 + Cl_2^+$	16.6
$\tilde{C}\,^2T_2$		15.27
	$SiCl_2^+ + Cl_2$	15.2
$\tilde{B}\,^2E$		13.51
$\tilde{A}\,^2T_2$		13.03
	$SiCl_3^+ + Cl$	12.7
$SiCl_4^+ \tilde{X}\,^2T_1$		12.12
	$SiCl + Cl + Cl_2$	10.0
	$SiCl_2 + Cl_2$	5.1
	$SiCl_3 + Cl$	4.8
$SiCl_4 \tilde{X}\,^1A_1$		0
	$GeCl + Cl^+ + Cl_2$	20.9
	$GeCl + Cl + Cl_2^+$	19.4
$GeCl_4^+ \tilde{D}\,^2A_1$		18.38
	$GeCl_3 + Cl^+$	15.8
	$GeCl^+ + Cl + Cl_2$	15.1
$\tilde{C}\,^2T_2$		14.88
	$GeCl_2 + Cl_2^+$	14.8
	$GeCl_2^+ + Cl_2$	13.5
$\tilde{B}\,^2E$		13.05
$\tilde{A}\,^2T_2$		12.64
	$GeCl_3^+ + Cl$	12.3
$GeCl_4^+ \tilde{X}\,^2T_1$		12.17
	$GeCl + Cl + Cl_2$	7.9
	$GeCl_2 + Cl_2$	3.3
	$GeCl_3 + Cl$	2.8
$GeCl_4 \tilde{X}\,^1A_1$		0

[a] In addition to the thermodynamic and IP data in the text, we use $IP(Cl_2) = 11.5$ eV (Ref. 18), $IP(Cl) = 13.0$ eV (Ref. 19), and $D_0^0(Cl–Cl) = 2.5$ eV (Ref. 20).

[b] Reference 21.

fluorescence decay from these states is a surprising phenomenon.

IV. RESULTS

The emission spectra resulting from electron impact on supersonic beams of $SiCl_4$ and $GeCl_4$ seeded in helium are shown in Figs. 1 and 2. The optical resolution is 0.2 nm. The $SiCl_4$ spectrum (Fig. 1) between 350 and 670 nm shows no discrete molecular structure, but consists of two broad structureless bands with maxima at 410 and 570 nm. In addition there are many narrow atomic lines (assigned to Si, Cl, He, or N atomic transitions), and strong N_2^+ B–X bands at 391 nm(0,0) and 428 nm (0,1) from residual nitrogen in the apparatus. The $GeCl_4$ emission spectrum (Fig. 2) is very similar in appearance to the $SiCl_4$ spectrum. It consists of two continuous bands with maxima at 495 and 615 nm, and many narrow atomic lines due to Ge, Cl, He, or N. The N_2^+ B–X(0,1) band again is present. It is noted that the response of the RCA C31034 pm tube used is essentially flat over the spectral range 300–830 nm, and therefore no correction needs to be made to the observed fluorescence intensities in this region. The emission spectrum resulting from electron impact on a CCl_4/He supersonic beam was also recorded between 300 and 830 nm. No discrete or continuous bands could be identified above the noise from the electron gun filament, although many atomic lines are observed.

The emission spectra resulting from rare gas metastables impacting on $SiCl_4$ and $GeCl_4$ at room temperature have been recorded between 350 and 700 nm in the Penning ionization apparatus. Having corrected for the changes in grating efficiency and photomultiplier response over this wide range, with both He* and Ne* metastables both $SiCl_4$ and $GeCl_4$ give spectra very similar to those observed in the molecular beam/electron beam apparatus (Figs. 1 and 2). An initial experiment with N_2 showed that no species from the neon discharge had sufficient excitation energy to produce N_2^+ $B\,^2\Sigma_u^+$ ions (at 18.7 eV), since no N_2^+ B–X fluorescence at 391 nm was observed. This suggests that the neon discharge only produces Ne* $^3P_2$ and $^3P_0$ metastables with energies of 16.62 and 16.72 eV, respectively. By contrast, intense N_2^+ B–X fluorescence is observed with a helium discharge, confirming that this discharge produces helium metastables with an energy greater than 18.7 eV (i.e., He* ^3S with energy 19.82 eV). These experiments show that the emitting state of the emission bands in $SiCl_4$/$GeCl_4$ is related to the formation of an excited state with energy less than 16.62 eV above the ground state of $SiCl_4$/$GeCl_4$.

The results of the synchrotron-induced fluorescence experiments on $SiCl_4$ and $GeCl_4$ are shown in Figs. 3 and 4. Figure 3 shows the total undispersed fluorescence collected in the range 320–470 nm (EMI 9883 QB pm tube + Wratten 35 filter) when $SiCl_4$ is excited by VUV radiation with energy in the range 14–35 eV (i.e., 88–35 nm). The resolution of the Seya monochromator is 0.2 nm. The fluorescence signal has been normalized to photon flux, and full details are given in the following paper. Undispersed fluorescence is collected simultaneously in the range 505–750 nm (Mullard 2254 pm tube + Schott OG515 cut-on filter), and the fluorescence spectrum is identical to Fig. 3. These two wavelength ranges span the two broad bands observed in the molecular beam/electron beam apparatus, so the fluorescence function in Fig. 3 indicates the excitation energy at which the two continuous bands first appear. For $SiCl_4$, this energy is 15.1 ± 0.1 eV. The fluorescence spectrum shows a sharp increase at this threshold, and some weak structure between 16.5 and 18.0 eV (see Sec. V C). It is noted (Table I) that the vertical

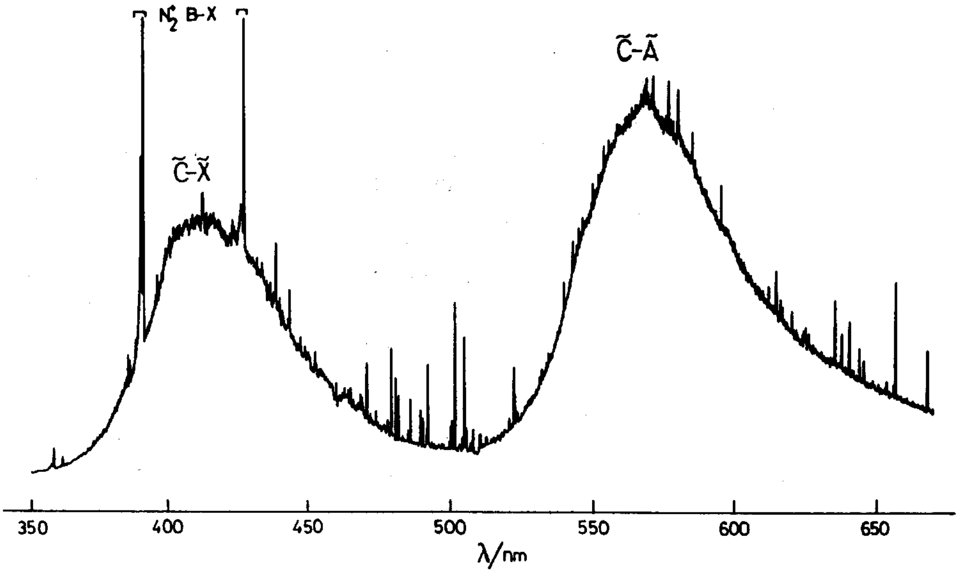

FIG. 1. Emission spectrum between 350 and 670 nm resulting from electron impact ionization of a He-seeded supersonic beam of $SiCl_4$. The continuous bands are due to emission of $SiCl_4^+$ from the bound $\tilde{C}\,^2T_2$ state to repulsive $\tilde{A}\,^2T_2$ and $\tilde{X}\,^2T_1$ states. The sloping background as the wavelength increases is due to increasing noise from the electron gun filament.

ionization potentials of $SiCl_4^+$ $\tilde{C}\,^2T_2$ and $\tilde{D}\,^2A_1$ are 15.27 and 18.10 eV, respectively[12]; the adiabatic ionization potential of $\tilde{C}\,^2T_2$ is 15.09 eV.[12] Figure 4 shows the result of the same experiment with $GeCl_4$, fluorescence being collected in the range 410–600 nm (EMI 9883 QB pm tube + Oriel LF42 cut-on filter). An identical fluorescence spectrum is obtained when fluorescence in the range 560–750 nm is collected (Mullar 2254 pm tube + Schott OG570 cut-on filter). These two spectral regions are approximately the same as those covered by the two continuous bands in the molecular beam/electron beam experiment with $GeCl_4$. The fluorescence function shows a sharp increase at 14.5 ± 0.1 eV, and we note that the adiabatic ionization potential of $GeCl_4^+$ $\tilde{C}\,^2T_2$ is 14.56 eV.[12] The fluorescence spectrum of CCl_4 was also studied in the energy range 14–35 eV (88–35 nm). Fluorescence is collected in the range 410–750 nm by the cooled Mullard 2254 pm tube + Oriel LF42 cut-on filter. Over this range of the synchrotron energy there is a very weak fluorescence signal (which is proportional to the synchrotron flux) detectable above the dark count of the pm tube, but no sharp turn on in the fluorescence is observed (as with $SiCl_4$ and $GeCl_4$).

V. ASSIGNMENT OF SPECTRA

The results reported in Sec. IV complement two other recent ionization studies on Group IV tetrachlorides. van Lonkhuyzen and Aarts[36] have observed the emission spectra produced by 1–25 keV H^+ impact on CCl_4, $SiCl_4$, and $GeCl_4$ at room temperature. The spectra are very similar to those observed in the molecular beam/electron beam apparatus: no discrete or continuous bands are observed with CCl_4, whereas the $SiCl_4$ and $GeCl_4$ spectra comprise two broad bands with the same maxima and spectral ranges as shown in Figs. 1 and 2. van Lonkhuyzen and Aarts measured the dependence of the cross section for fluorescence as a function of ion beam energy (cf. similar experiments on CF_4, SiF_4, and GeF_4[7–9]), but unfortunately they were unable to determine any information about the states of the ions initially formed in the excitation process. Toyoda *et al.*[37] have observed the emission spectra of MCl_4 under controlled electron impact excitation (300 eV) at 300 K. The $SiCl_4$ and $GeCl_4$ emission spectra are the same as those shown in Figs. 1 and 2, but the CCl_4 spectrum shows a single broad band with a maximum at 480 nm. The latter band was assigned to CCl_2, while the broad bands in the $SiCl_4$ and $GeCl_4$ spectra

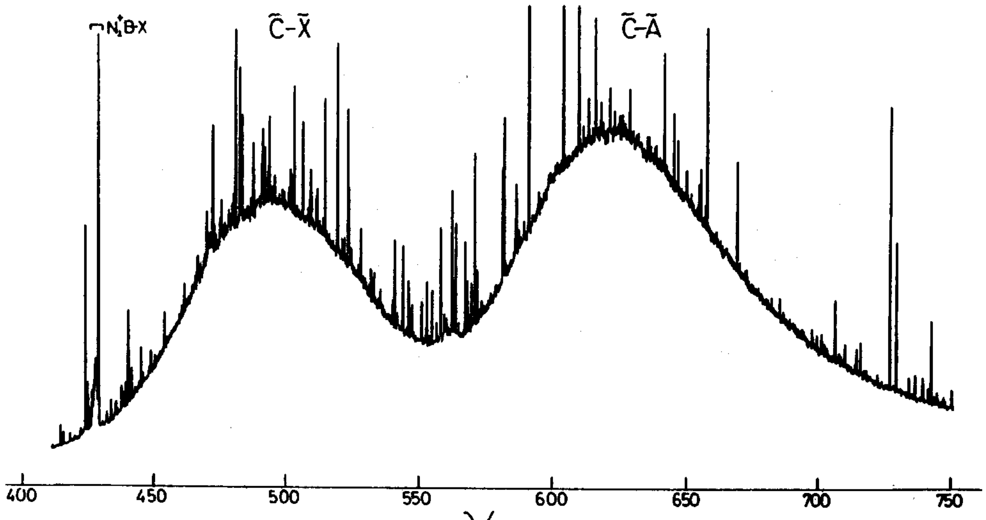

FIG. 2. Emission spectrum between 410 and 750 nm resulting from electron impact ionization of a He-seeded supersonic beam of $GeCl_4$. The continuous bands are due to emission of $GeCl_4^+$ from the bound $\tilde{C}\,^2T_2$ state to repulsive $\tilde{A}\,^2T_2$ and $\tilde{X}\,^2T_1$ states.

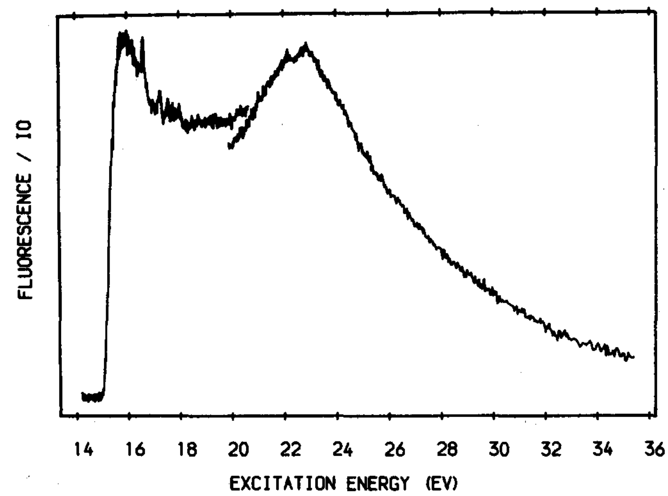

FIG. 3. Undispersed fluorescence of $SiCl_4$ excited by VUV radiation in the range 14–35 eV. The spectrum was recorded in two overlapping sections. Only photons in the range 320–470 nm are detected, and the photon count rate has been normalized to the synchrotron flux I_0.

were tentatively assigned to $SiCl_2$ and $GeCl_2$, respectively. We note that the gas pressure in these experiments is relatively high, and therefore the spectra are probably not being observed under single-collision conditions.

Thus the emission bands obtained with $SiCl_4$ and $GeCl_4$ in Figs. 1 and 2 are observed with several different ionization techniques (e^- impact, fast H^+ impact, Penning ionization, photoionization). In each technique the experimental conditions strongly favor the formation of ions. For example, experience on the molecular beam/electron beam apparatus has shown that the observation of emission from excited electronic states of the parent neutral molecule is rare.[38] Instead, emission from excited states of the parent molecular ion (or fragments) is usually seen. It is therefore instructive to compare these optical emission spectra with photoelectron data for $SiCl_4$ and $GeCl_4$. Table II shows calculated wavelengths for the band maxima of the transitions $SiCl_4^+$ and $GeCl_4^+$ $\tilde{C}\,{}^2T_2$–$\tilde{A}\,{}^2T_2$ and $\tilde{C}\,{}^2T_2$–$\tilde{X}\,{}^2T_1$ as obtained from differences between vertical IPs. It is noted that the band maximum for a transition from a bound to a dissociative electronic state of an ion can only be estimated in this way. Nevertheless, the predicted wavelengths for the band maxima fall within 0.2 eV of the observed positions, but all at a lower value. This same pattern is observed in CF_4^+ $\tilde{C}$–$\tilde{A}$,$\tilde{X}$ emission (Table I of Ref. 7), and furthermore this latter spectrum (Fig. 1 of Ref. 7) is remarkably similar to that found for electron impact on $SiCl_4$/$GeCl_4$: it consists of two broad structureless bands with the higher wavelength band ($\tilde{C}$–$\tilde{A}$) being of slightly greater intensity. This analysis therefore suggests that the emission bands observed in Figs. 1 and 2 are due to $SiCl_4^+$ and $GeCl_4^+$ $\tilde{C}$–$\tilde{A}$,$\tilde{X}$ transitions respectively, the large width of the bands being due to the repulsive nature of the $\tilde{A}$ and $\tilde{X}$ states. The fluorescence excitation functions obtained at Daresbury (Figs. 3 and 4) confirm this assignment.

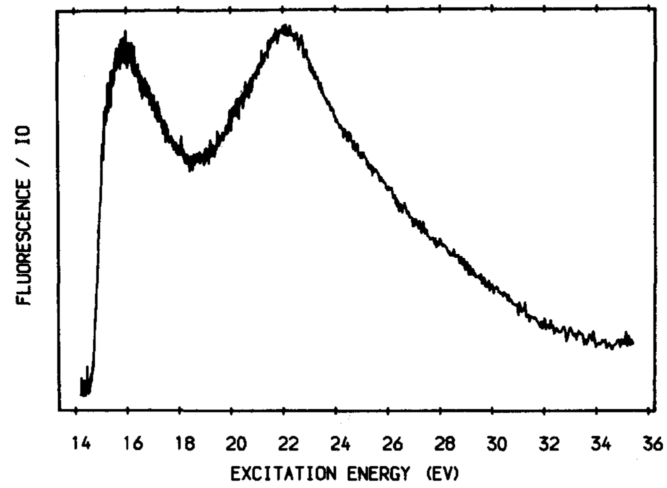

FIG. 4. Undispersed fluorescence of $GeCl_4$ excited by VUV radiation in the range 14–35 eV. The spectrum was recorded in two sections. Only photons in the range 410–600 nm are detected, and the photon count rate has been normalized to the synchrotron flux I_0.

TABLE II. Calculated wavelengths for transitions in $SiCl_4^+$ and $GeCl_4^+$ as deduced from photoelectron data. The observed maxima of emission bands resulting from electron impact on $SiCl_4$ and $GeCl_4$ are included for comparison. Wavelengths in nm.

	Transition	PE data[a]	e^- impact
$SiCl_4^+$	$\tilde{C}$–$\tilde{X}$	394	410
	$\tilde{C}$–$\tilde{A}$	553	570
$GeCl_4^+$	$\tilde{C}$–$\tilde{X}$	458	495
	$\tilde{C}$–$\tilde{A}$	554	615

[a] Vertical IP data from Table I, i.e., Ref. 12.

The absence of the two broad bands with CCl_4, however, is surprising, since it is not obvious why CCl_4 should behave differently from $SiCl_4$/$GeCl_4$. There is the possibility that the agreement between the PE data for $SiCl_4$/$GeCl_4$ and the observed emission bands (Table II) is coincidental, and the emissions are due to a fragment which is produced by rapid dissociation of the $\tilde{C}$ state of $SiCl_4^+$/$GeCl_4^+$. Although this seems unlikely, it is sensible to eliminate all fragments as emitters of the broad bands before their assignment to $SiCl_4^+$/$GeCl_4^+$ $\tilde{C}$–$\tilde{A}$,$\tilde{X}$ can be made definitive.

A. Emission from fragments of $SiCl_4^+$

Besides $SiCl_4^+$, the possible emitters of the 410 and 570 nm emission bands in Fig. 1 are the fragments $SiCl_n$ and $SiCl_n^+$ with $n = 1$–3. Since this spectrum is observed with neon metastables in the Penning ionization experiment, only fragments with dissociation energies below the Ne* recombination energy of 16.62 eV need be considered. From Table I, $SiCl^+$ is immediately eliminated. If $SiCl_2^+$ is the emitter, the photon energy corresponding to the band maximum must be added to the energy of the lowest channel to include $SiCl_2^+$ (i.e., 15.2 eV) to produce the minimum energy for the dissociative fragmentation of $SiCl_4$ to excited $SiCl_2^+$. For the 410 nm band ($\equiv$3.0 eV) this minimum energy is 18.2 eV, higher than the Ne* recombination energy of 16.6 eV. The same is true for the 570 nm band. Therefore, the observed emissions cannot be due to $SiCl_2^+$.

The possibility that the observed bands originate from neutral SiCl or $SiCl_2$ (which are candidates on energetic grounds) is also considered unlikely. SiCl has been comprehensively studied[20,29,39,40] and no continuous emission bands have been assigned to low-lying states of this molecule. Moreover, none of the known discrete SiCl bands are observed in the electron impact spectrum on $SiCl_4$ (Fig. 1). Only one electronic transition in $SiCl_2$ has definitely been assigned, the $\tilde{A}\ ^1B_1$–$\tilde{X}\ ^1A_1$ band system around 330 nm observed in both absorption[41] and emission.[42] This transition is between the two lowest energy states in $SiCl_2$, and therefore if this molecule is the emitter of the 410 and 570 nm bands, the transitions must be between highly excited electronic states. This is improbable. Furthermore, the $\tilde{A}$–$\tilde{X}$ band system is not observed in the electron impact spectrum.

The only remaining possibilities are $SiCl_3$ and $SiCl_3^+$, both possible on energetic grounds (Table I). No emission bands due to these free radicals are known. However, if either is the emitter of the 410 and 570 nm bands in Fig. 1, it might be expected that the same features be found in the spectra of electron impact on other $SiCl_3$-containing compounds. $SiCl_3 \cdot C_2H_5$, $SiCl_3 \cdot CH_3$, and $SiCl_3 \cdot H$ were therefore studied in the molecular beam/electron beam apparatus. With the first two compounds, no discrete or continuous bands are observed above the noise of the electron gun filament. With $SiCl_3H$ broad continuous bands with maxima at 360, 475, and 590 nm are observed (the latter two heavily overlapped),[38] but the bands in Fig. 1 are not detected. It therefore seems very unlikely that the 410 and 570 nm bands are due to $SiCl_3$ or $SiCl_3^+$. All the accumulative evidence is that they are due to $SiCl_4^+$ $\tilde{C}$–$\tilde{X}$,$\tilde{A}$.

B. Emission from fragments of $GeCl_4^+$

Besides $GeCl_4^+$, the possible emitters of the 495 and 615 nm bands in Fig. 2 are the fragments $GeCl_n$ and $GeCl_n^+$ with $n = 1$–3. Since both bands are observed with Ne* metastables in the Penning experiment, $GeCl^+$ can be ruled out on energetic grounds(Table I), but $GeCl_2^+$ is just possible. However, the synchrotron experiment (Fig. 4) shows that the fluorescence bands at 495 ($\equiv$2.5 eV) and 615 nm ($\equiv$2.0 eV) turn on at a threshold energy of 14.5 eV. Therefore, the ground state of the emitter must lie at an energy less than (14.5–2.5) or 12.0 eV. Thus $GeCl_2^+$ can also be eliminated on energetic grounds, since the lowest dissociation channel involving ground state $GeCl_2^+$ lies at 13.5 eV (Table I). There is strong circumstantial evidence to eliminate neutral GeCl and $GeCl_2$ as the emitters. Discrete electronic transitions in GeCl are well known,[20,43] and no continuous emission bands have been assigned as originating from excited electronic states of this radical. Furthermore, none of the discrete GeCl bands are observed in the electron impact spectrum on $GeCl_4$. The $^3B_1$–$^1A_1$ and $^1B_1$–$^1A_1$ transitions in $GeCl_2$ have been observed, but only in absorption.[44,45] If the emitter of the 495 and 615 nm bands is $GeCl_2$, then the transitions must be from highly excited electronic state(s). This seems improbable. Furthermore, neither of the two discrete $GeCl_2$ bands is seen in the electron impact spectrum of $GeCl_4$. Since the ground state of the emitting fragment must lie at an energy $\leqslant$12.0 eV, $GeCl_3^+$ can probably be eliminated on energetic grounds also (Table I), although the value of the $GeCl_3$ ionization potential (9.5 eV) comes from an appearance potential measurement of $GeCl_3^+$ from $GeCl_4$[25] and not from a direct measurement; the energy of the $GeCl_3^+ + Cl$ dissociation channel at 12.3 eV is therefore only an upper limit. The electronic spectroscopy of the $GeCl_3$ (and $GeCl_3^+$) free radical is unknown, and no experiments have been performed with other $GeCl_3$-containing compounds. As with $SiCl_4$, all the accumulative evidence is that the 495 and 615 nm bands in Fig. 2 are due to $GeCl_4^+$ $\tilde{C}$–$\tilde{X}$,$\tilde{A}$.

C. Rydberg structure in $SiCl_4$

The fluorescence function for $SiCl_4$ excited by VUV radiation (Fig. 3) shows structure between 16.5 and 18.1 eV, i.e., above the threshold energy for fluorescence. There is a discontinuity in the structure at 18.1 eV. An expansion of this part of the spectrum is shown in Fig. 5, and the peak positions are given in Table III. The peaks are assigned to transitions to Rydberg states of $SiCl_4$ lying above the $\tilde{C}$ state ionization potential (15.1 eV) which converge to the $\tilde{D}\ ^2A_1$ state of the ion at 18.1 eV (Fig. 5). These states autoionize to the $\tilde{C}$ state of $SiCl_4^+$, and hence are observed in fluorescence. The term values can be fitted to the normal Rydberg equation:

$$\nu = \nu^{\infty} - \frac{R_H}{(n-\delta)^2},$$

where ν^{∞} is the IP limit (18.1 eV), R_H is the Rydberg constant (13.59 eV), n is the quantum number of the Rydberg electron, and δ is the quantum defect. The first observed member of the series at 16.60 eV has $(n-\delta)^2 = 9.1$ (column 2 of Table III), hence $(n-\delta) \simeq 3.0$. These states arise from promotion of an electron from the $2a_1$ Si $3s$–Cl $3s/3p$ σ-bonding molecular orbital of $SiCl_4$ to a highly excited Rydberg orbital, and group theory shows that transitions to a p or d Rydberg orbital only are allowed. This state therefore is either the $n = 4$ level of a p Rydberg series (with $\delta \simeq 1.0$), the $n = 4$ level of a d Rydberg series (with $\delta \simeq 1.0$) or the $n = 3$ level of the d Rydberg series (with $\delta \simeq 0$). It is unlikely that the first member of a d Rydberg series would have $n = 3$, since the valence orbitals of $SiCl_4$ involve Si $3s/3p$ with Cl $3s/3p$. Second, d Rydberg states tend to have low quan-

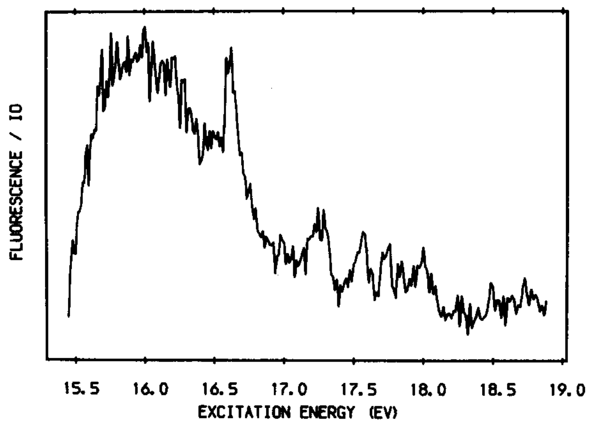

FIG. 5. Expansion of Fig. 3 in the range 15.5–19.0 eV.

TABLE III. Rydberg states of $SiCl_4$ converging to $SiCl_4^+$ $\tilde{D}\,^2A_1$.

Energy (eV)	$R_H/\nu^{\infty} - \nu^{a}$	$(n-\delta)_{\text{approx}}$
16.60	9.1	3
17.23	15.6	4
17.30	17.0	
17.56	25.2	5
17.72	35.8	6
17.83	50.3	7

[a] Calculated using $\nu^{\infty} = 18.10$ eV (Ref. 12) and $R_H = 13.59$ eV.

tum defects close to zero.[46,47] Therefore, the most likely assignment is a *p* Rydberg series with $n \geqslant 4$ and $\delta \simeq 1.0$.

VI. DISCUSSION

We believe that the assignment of the broad bands in Figs. 1 and 2 to bound–free emission in $SiCl_4^+/GeCl_4^+$ is almost definitive. The evidence is summarized below.

(1) The onset of the emission in both bands of $SiCl_4$/$GeCl_4$ (Figs. 3 and 4) occurs at the adiabatic IP of the $\tilde{C}$ state of the parent ion, i.e., 15.1 and 14.5 eV, respectively. The emission is therefore related to the initial formation of $SiCl_4^+/GeCl_4^+\,\tilde{C}\,^2T_2$.

(2) The sharp increase at the fluorescence thresholds suggests that the fluorescence is produced by a photoionization process. Similar observations have been made for $N_2^+\,B\,^2\Sigma_u^+$ at 18.7 eV, $CO^+\,B\,^2\Sigma^+$ at 19.7 eV, $N_2O^+\tilde{A}\,^2\Sigma^+$ at 16.4 eV,[48] and the $\tilde{C}\,^2T_2$ and $\tilde{D}\,^2A_1$ states of $CF_4^+/SiF_4^+/GeF_4^+$.[49] Fluorescence produced by a dissociative process is expected to show a smooth and slow increase at the threshold.[50]

(3) The excitation cross section of a neutral process usually depends on both the excitation energy and the excitation source (photon, electron, or photoion). For an ionization process, however, as long as the excitation energy is sufficient, the dependence on excitation source is not critical. The results in Sec. IV indicate that the excitation is not dependent on the source, and this suggests that the emitting species are ions.

(4) Partial ionization cross sections for the $2t_2$ molecular orbital of $SiCl_4$ have been measured as a function of excitation energy by angle-resolved photoelectron spectroscopy.[51] Ionization from this orbital gives $SiCl_4^+\,\tilde{C}\,^2T_2$. The shape of the fluorescence excitation function in Fig. 3 is the same as for the partial ionization cross section of this molecular orbital (Fig. 5 of Ref. 51). Again, the relation of the 410, 570 nm emission bands to the initial formation of $SiCl_4^+\,\tilde{C}\,^2T_2$ is confirmed.

(5) The excellent agreement of the observed emissions with photoelectron data for $SiCl_4/GeCl_4$ strongly suggests that the bands are due to $SiCl_4^+/GeCl_4^+\,\tilde{C}$–$\tilde{A}$,$\tilde{X}$. On energetic grounds, the only ion which is an alternative possibility for the carrier of the 410, 570 nm bands in the silicon tetrachloride experiment is $SiCl_3^+$. The synchrotron results mean that $SiCl_4^+\,\tilde{C}\,^2T_2$ would have to (pre)dissociate on a rapid time scale for this to be a possibility. Furthermore, the absence of these bands in the electron impact excitation of other $SiCl_3$-containing compounds suggests that $SiCl_3^+$ is not the emitter of the observed radiation. The assignment of the fluorescence to $SiCl_4^+/GeCl_4^+\,\tilde{C}\,^2T_2$, and the transitions to $\tilde{C}$–$\tilde{A}$,$\tilde{X}$ seems conclusive.

The main difference between the excited electronic states of the three fluorides $CF_4^+/SiF_4^+/GeF_4^+$ and the three chlorides $CCl_4^+/SiCl_4^+/GeCl_4^+$ is the decay properties of the $\tilde{D}\,^2A_1$ state. In MF_4^+ fluorescence is observed from this state both to the bound $\tilde{C}$ state and the repulsive $\tilde{A}$ and $\tilde{X}$ states. In MCl_4^+, however, fluorescence decay from $\tilde{D}$ is not observed. The reason(s) for this difference is not yet explained. The $\tilde{C}\,^2T_2$ state of the fluorides and chlorides also show differing spectroscopic and dynamic behavior. SiF_4^+ and $GeF_4^+\,\tilde{C}$ show dynamic Jahn–Teller distortion from T_d geometry,[2,3] and do not decay by a radiative process.[49] $CF_4^+\,\tilde{C}$ does not show Jahn–Teller distortion,[1] yet this state decays radiatively to the $\tilde{A}$ and $\tilde{X}$ states via broad band $\tilde{C}$–$\tilde{A}$,$\tilde{X}$ emission.[7] This paper has established that $SiCl_4^+$ and $GeCl_4^+\,\tilde{C}$ decay radiatively, but $CCl_4^+\,\tilde{C}$ does not, and it is tempting to speculate that there is a connection between the spectroscopic and dynamic decay properties of this state. It would be interesting, therefore, to observe the presence or absence of Jahn–Teller activity in the $\tilde{C}\,^2T_2$ state of CCl_4^+, $SiCl_4^+$, and $GeCl_4^+$. This information would normally be observed in the $\tilde{C}$ state photoelectron band, but at the low resolution of this technique no evidence for Jahn–Teller distortion can be observed.[14] It is difficult otherwise to understand why $CCl_4^+\tilde{C}$ exhibits different dynamic properties from $SiCl_4^+$ and $GeCl_4^+\,\tilde{C}$. The broad band emission in Toyoda's experiment on CCl_4[37] is almost certainly due to a neutral fragment (CCl_2 or CCl_3), and this would explain the unstructured background signal in our synchrotron experiment with CCl_4 (Sec. IV).

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