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Ionic Fragmentation of CF_3Cl Photoexcited in the Cl L-Shell, C K-Shell, and F K-Shell Transition Regions

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Fragment ions produced from CF_3Cl have been measured in the soft X-ray region using monochromatized synchrotron radiation and a time-of-flight mass spectrometer. The yield ratios for ion production were determined from the TOF spectra over the energy range of 44 through 1200 eV, and the partial yield spectra for the individual ions were observed around the Cl $L_{2,3}$-edges, the C K-edge, and the F K-edge. The atomic chlorine ion, Cl^+, has the greatest intensity between 100 and 700 eV, and exhibits a steep increase at the Cl $L_{2,3}$-edges. The yield ratios of F^+ and C^+ decrease sharply at the Cl $L_{2,3}$-edges and greatly increase at the C K-edge and F K-edge. Some fragment ions, e. g. CF^+, have distinctive yield changes upon excitation of the inner-shell electron to unoccupied molecular orbitals.

A number of studies have been performed for obtaining information concerning the spectroscopic property and chemical reactivity of freon molecules.[1—8] This is partly because these molecules play a large role in the depletion of the earth's ozone layer through photochemical processes. Another reason is that those studies are important for clarifying the electronic structures and dynamical behavior in small molecules, because these molecules are able to take a variety of geometries only by the substitution of one atom. The production of fragment ions from CF_3Cl was observed in the vacuum ultraviolet radiation region,[2,3] indicating that the parent molecular ion is only slightly produced, while CF_2Cl^+ and $CF_3{}^+$ are produced in large quantity. Zhang and co-workers performed several studies of simulated photon impact onto these molecules using a high-energy electron beam; they proposed a breakdown scheme for the ionic fragmentation of CF_3Cl in the region of valence-electron ionization.[4] Photoelectron measurements were carried out for determining the asymmetry parameters and partial cross sections for the ionization of individual valence electrons.[5,6,8]

On the other hand, energy relaxation following the excitation of core electrons in a molecule ends in a multiply ionic decomposition of the molecule after electronic de-excitation. Since core holes are strongly localized at the atoms, the decomposition pattern depends on the site of the core hole, which can be selected by excitation of the core electrons in the specified atom using a monochromatic soft X-ray. This site selectivity has attracted much attention around the world for the realization of complete control of the chemical reaction site. Several studies exhibited a clear selectivity for a particular fragment ion, but others did not show this effect distinctively.[9—12] It is important to study the ionic fragmentation of CF_3Cl with respect to the site-selective process, because this molecule has three different atomic sites, with corresponding photon energy ranges in the Cl L-edges, the C K-edge, and the F K-edge.

Excitation spectra of core electrons of CF_3Cl have been measured using monochromatized synchrotron radiation and an electron energy-loss technique.[13—15] Pre-edge structures, which consist of transitions into the $11a_1$ unoccupied molecular orbital, the $(8e+12a_1)$ molecular orbitals and high Rydberg orbitals, were identified below the Cl $L_{2,3}$-edges ($2p_{3/2}$ ionization energy$=$207.83 eV; that of $2p_{1/2}=209.44$ eV) using a high-resolution technique. Some peaks below the C K-edge (300.31 eV) and a broad intensity increase above this edge were observed, which correspond to the transitions to the unoccupied molecular orbitals and to the shape resonance owing to temporal trapping of a photoelectron by the anisotropic molecular field. The excitation spectrum near the F K-edge (695.04 eV) shows only a broad band composed of overlapping transitions to neutral excited states and to the ionization continuum. The fragmentation of freon molecules in inner-shell excited states was studied using monochromatized synchrotron radiation by several laboratories, including our group.[16—21] The intensities of several fragment ions were found to change significantly both below and above the core-edge, suggesting that site-specific fragmentation occurs for those ions. In particular, the yield ratio of atomic ion Cl^+ steeply increased at the Cl L-edges and that of F^+ greatly decreased at the Cl L-edges, and sharply increased at the F K-edge. It is nat-

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ural that the molecule to be studied as the next step is CF_3Cl for obtaining a comprehensive understanding on the site-selective fragmentation.

In the present study, the fragment ions produced from CF_3Cl irradiated by monochromatic soft X-rays have been measured using a time-of-flight (TOF) mass spectrometer. The yield ratios for these ions were determined as a function of photon energy from 44 to 1200 eV, and the yield spectra for individual fragment ions were observed in detail near the Cl L-edges, the C K-edge, and the F K-edge. A comparison with the results of other freon molecules was made on the yield ratios and partial yield spectra of individual fragment ions around the inner-shell edges.

Experimental

Synchrotron radiation from the TERAS electron storage ring at the Electrotechnical Laboratory was dispersed using a Grasshopper monochromator to obtain monochromatic soft X-ray from 44 to 1200 eV.[22] By selecting appropriate energies for the electron beam in the storage ring, the spectral distribution of the synchrotron radiation was modified so as to reduce the intensity of higher energy photons in the "white" light, and thereby minimize higher order contributions to the monochromaized beam.[23] Thin films of Be, Al, In, and mylar were also used as filters in order to reduce any stray light and higher order contributions. Monochromatized synchrotron radiation passed through two differential pumping stages and entered an experimental chamber equipped with a TOF mass spectrometer. The photon beam crossed an effusive beam of the sample gas at the center of the spectrometer, and the electrons and ions produced were extracted in opposite directions and detected with microchannel plates. The electric field applied at this center was set to be 80 $\mathrm{V\,mm^{-1}}$ in order to collect ions of all kinetic energies. The sample pressure in the ionization region was estimated to be about 1×10^{-2} Pa.

Since anisotropic dissociations may have a considerable effect on the measured TOF spectra,[24,25] the angular distributions of fragment ions were examined at photon energies corresponding to Cl L-shell excited states. This examination showed that no observable anisotropy was found under the present experimental conditions. The axis of the TOF spectrometer was set in the horizontal direction during the measurement. The flight times of the photoions were determined using two time-to-amplitude converters (TAC's).[20] When two ionic fragments result from a single ionization event, a single TAC can measure the arrival of the first ion, the lighter ion, but can not detect the second heavier ion with the same detection efficiency as the lighter one. Thus, two appropriately gated TAC's were used in the experiment to overcome the loss of signals from the heavier ions, in which the second TAC can accept the signal of the heavier ion only after the first TAC has received that of the lighter. The outputs of both TAC's were summed electronically and supplied to the same input of the pulse-height analyzer (see the details given in Ref. 20).

Results and Discussion

Yield Ratios of Fragment Ions. The time-of-flight mass spectra of fragment ions from CF_3Cl were measured at a number of photon energies in the vacuum ultraviolet through soft X-ray regions. Typical TOF spectra are shown in Fig. 1 at photon energies of 50, 200, 300, and 800 eV. These correspond to the energies of only the valence electron transition, just below the Cl L-shell transition, just below the C K-shell ionization threshold, and above the F K-edge, respectively. The assignment of each peak in the TOF spectra to its corresponding ion species is indicated on the figure. Since natural chlorine atom consists of two main stable isotopes, ^{35}Cl and ^{37}Cl, the peaks for ions including a Cl atom are split into two components. The relative intensities of the peaks change dramatically with a photon energy over this energy range. The relative intensities of atomic ions are much larger in the spectrum measured at 800 eV than in the spectrum at 50 eV. The widths of the peaks increase at higher photon energies in the TOF spectra in Fig. 1, resulting in a lower apparent mass resolution. The increased peak width results from a greater release of kinetic energy in the ionic fragmentation of CF_3Cl at the higher incident photon energies. The parent molecular ion, CF_3Cl^+, was not appreciably produced at these photon energies.[4]

The yield ratios for the fragment ions of CF_3Cl were determined from the areas of the peaks in the TOF mass spectra measured across the photon energy range, 44—1200 eV. The areas of the fully resolved peaks (C^{2+},

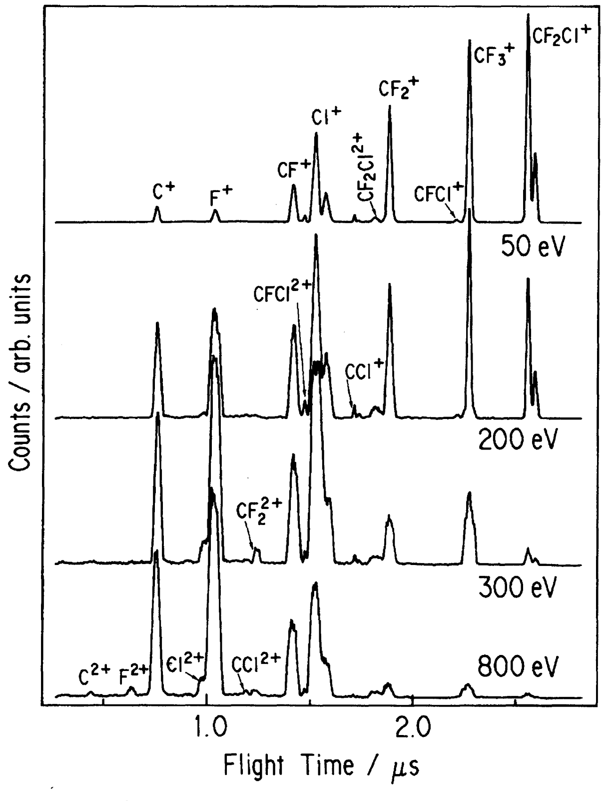

Fig. 1. TOF spectra of CF_3Cl measured with photon energies of 50, 200, 300, and 800 eV.

F^{2+}, C^+, CF^+, CCl^+, $CF_3{}^+$, $CFCl^+$, and CF_2Cl^+) were determined by summing the signal across the peak and subtracting a liner baseline. For the overlapping peaks (Cl^{2+} and F^+, $CF_2{}^{2+}$ and CCl^{2+}, Cl^+ and $CFCl^{2+}$, and CF_2Cl^{2+} and $CF_2{}^+$), the peak areas were determined by fitting a series of Gaussian-Lorentzian lines to the peaks. A $^{35}Cl:{}^{37}Cl$ intensity ratio of 0.324 and a mass difference of 2 amu were used in the fitting procedure. The resulting yield ratios for ions having considerable intensities are shown as a function of photon energy in Fig. 2 and summarized for selected photon energies in Table 1. Although the peaks for C^{2+}, CF^{2+}, CCl^{2+}, $CF_2{}^{2+}$, CF_2Cl^{2+}, and $CFCl^+$ were observed in the TOF mass spectra, they were very weak, with yield ratios of less than 1%. The peak areas could not be determined with high accuracy. The yield ratios obtained here are presumed to be close to the intrinsic branching ratios for fragment ion production, although no clear experimental evidence has been obtained at present for a uniform detection efficiency of all ions regardless of m/z and the kinetic energies of the ions and energies of electrons generating a start signal for the TOF spectra. This subject was discussed elsewhere for the instance of ionic fragmentation of CF_4.[20)]

The yield ratios of CF_2Cl^+, $CF_3{}^+$, and $CF_2{}^+$ decrease with an increase in the photon energy below the Cl L-edges, as shown in Fig. 2(a). CF_2Cl^+ has the highest intensity below 80 eV; the yield ratio of this ion exhibits a steep decrease at the Cl L-edges, and shows a considerable decrease between the Cl L-edges and the C K-edge, followed by a slowly decreasing trend above the C K-edge. The ratio for $CF_3{}^+$ has a small shoulder around 100 eV in the decreasing curve below the Cl L-edges, exhibits a sharp increase at the Cl L-edges, and again shows a decrease between the Cl L-edges and the C K-edge. This ion has a sharp drop at the C K-edge and F K-edge. The fragment ion, $CF_2{}^+$, shows a small plateau above 130 eV in the decreasing curve below the C K-edge. The yield ratio of this ion exhibits a sharp drop at every inner-shell threshold.

The yield ratio of diatomic ion CF^+ exhibits a steep increase below 100 eV, and reachs a saturation value of about 10% near the Cl L-edges (Fig. 2(b)). The ratio shows a sharp peak near the Cl L-edges and the C K-edge, which is probably ascribed to transitions into neutral inner-shell excited states. The CF^+ ratio gives a maximum around the F K-edge. That of CCl^+ seems to show a relatively constant value all over the energy regions of interest, although we cannot make a conclusive statement due to the low intensity of this ion. However, the ratio changes considerably in the inner-shell transition regions, peaking at the Cl L-shell and C K-shell transition energies and increasing sharply at the F K-shell ionization.

In Fig. 2(c), the ion Cl^+ shows the highest intensity among atomic ions below the F K-edge; the yield ratio of this ion becomes higher than the molecular ion, CF_2Cl^+, at a photon energy of about 80 eV. The ratio considerably increases with increasing photon energy below the Cl L-edges, except for small saturation around 120 eV, and exhibits a sharp increase to about 40% at the Cl L-shell excitation energies. Above the Cl L-edges, the yield ratio considerably decreases with increasing photon energy; this ratio shows a step-down of the intensity slightly above the F K-edge. The yield ratio of F^+ shows a steep increase below the Cl L-edges, and exhibits a drop at these edges. The ratio again shows a steep increase between the Cl L-edges and the C K-edge, and has a peak at C K-shell excited neutral states, e. g. $C_{1s}\rightarrow 8e$ molecular orbital.[14,15)] The F^+ yield exhibits a gradual increase with increasing photon energy, and reaches a plateau in the region above both the C K-edge and the F K-edge. This ion has the highest intensity among all ionic species above 750 eV. The atomic ion C^+ has a similar feature to the F^+ in all photon energy regions, although the yield ratio of this ion is about half, or lower than, that of F^+. However, the change in the ratio for this ion is steeper in the three inner-shell edge regions than that of F^+, when the feature of the ratio curve is examined closely.

The doubly charged fragment ions were not produced in great quantity, as shown in Fig. 1. The ion $CF_2{}^{2+}$ has a yield ratio of about 1% between the Cl L-edges and the F K-edge and shows a value of about 0.5% above the F K-edge, although the yield-ratio curve for this ion was not drawn in Fig. 2. The ion Cl^{2+} has a yield-ratio rising to about 1% at the Cl L-edges, increasing to about 2.5% between the Cl L-edges and the C K-edge, and showing a gradual increase to about 3.5% below the F K-edge. This yield ratio exhibits a drop down to about 2% at the F K-edge and a slowly increasing trend above this edge. The ion F^{2+} has a considerably lower yield ratio than 1% below the F K-edge, and shows a value of about 1% above this edge.

It is interesting to find that the yield ratios of the fragment ions consisting of 3 and 4 atoms considerably decrease, and that those of atomic ions and CF^+ steeply increase below the Cl L-edges. Similar results were measured below the Cl L-edges in CF_2Cl_2 and below the C K-edge in CF_4.[18,20)] This phenomenon probably originates from fragmentation pathways which become open at or above incident photon energies of 50 eV. It can be ruled out that the molecular-ion states related to these pathways are single valence hole states, because the binding energy of the deepest valence orbital, $6a_1$, was reported to be 42.5 eV.[4,5)] These fragmentation pathways are presumably related to excited states having two valence holes. A molecular ion with two holes in the valence shell has a greater probability of yielding a higher degree of decomposition, i. e. higher intensities of atomic ions, than that having only a single valence hole. In rare gases, considerable yields of the doubly charged ions are obtained at excitation energies above their valence ionization thresholds but below their in-

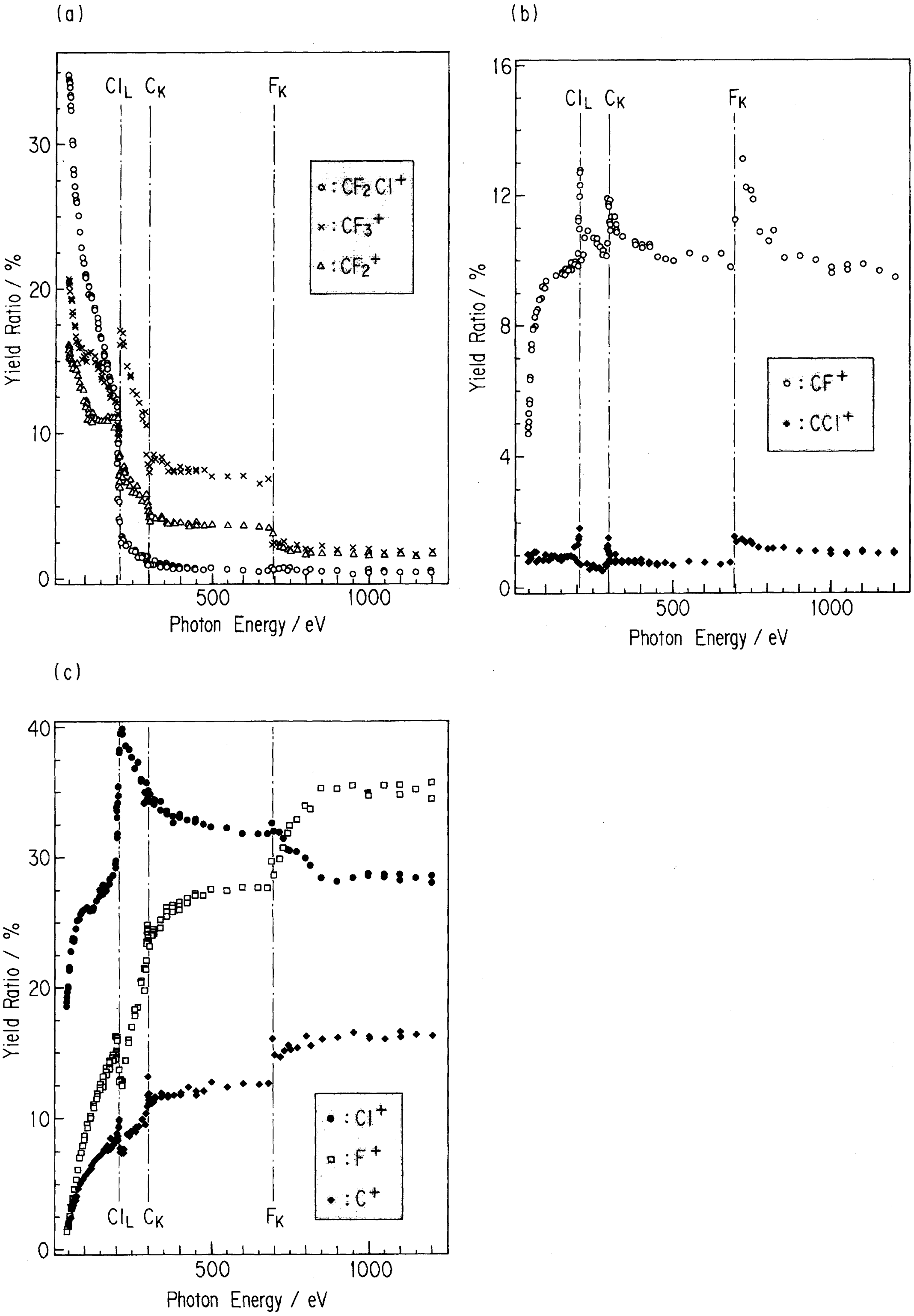

Fig. 2. Yield ratios of the fragment ions of CF_3Cl as a function of the photon energy of 44 eV through 1200 eV. (a) CF_2Cl^+, CF_3^+, and CF_2^+. (b) CF^+ and CCl^+. (c) Cl^+, F^+, and C^+. The broken vertical lines indicate the Cl $L_{2,3}$-edges, the C K-edge, and the F K-edge.

ner-shell excitation energies.[26)] The ratio of double-to-single photoionization depends on the number and binding energies of the valence electrons in atoms as well as the photon energy. In the instance of molecules, the number of valence electrons is much larger and their binding energies are usually less than those of atoms. In CF_3Cl, two electrons are probably excited to unoccupied molecular orbitals and/or ionized to the continuum (i. e. shake-off) at photon energies above 50 eV, as interpreted in instances of CF_2Cl_2 and CF_4.[18,20)] On

Table 1. Yield Ratios of the Fragment Ions Produced from CF_3Cl over the Photon Energy Range of 44 eV through 1200 eV

Energy eV	C^+	Cl^{2+}	F^+	CF_2^{2+}	CF^+	Cl^+	CCl^+	CF_2^+	CF_3^+	CF_2Cl^+
44	2.2	0.2	1.5	0.0	4.9	18.5	1.0	15.9	20.3	34.7
44[a]	2.28	—	1.48	—	5.56	15.83	1.03	16.17	20.88	35.98
50	2.0	0.2	1.9	0.0	6.4	19.9	0.9	15.2	20.1	32.7
50[a]	2.03	—	1.84	—	6.81	16.66	0.97	15.15	21.10	34.70
80	4.7	0.1	6.0	0.0	8.8	25.1	0.9	13.6	16.0	24.0
80[a]	3.72	—	5.37	—	8.57	18.82	1.04	14.86	19.07	27.74
120	6.4	0.1	10.1	0.1	9.3	26.0	1.1	11.2	15.5	19.5
200	8.4	0.3	14.8	0.1	10.0	29.4	1.2	10.8	11.8	12.3
220	7.7	1.1	12.6	0.7	10.8	39.6	0.4	7.5	16.1	2.8
290	9.9	2.4	20.3	1.2	10.2	34.9	0.7	5.8	11.3	1.6
300	11.6	2.2	24.3	1.1	11.0	34.6	1.1	4.4	7.5	1.0
320	11.6	2.5	24.3	1.1	11.0	34.0	0.9	4.2	8.2	1.0
680	12.7	3.7	27.6	1.2	9.8	31.7	0.8	3.6	6.9	0.6
800	15.7	2.1	33.6	0.4	10.7	29.8	1.2	1.8	2.1	0.5
900	16.1	2.4	35.2	0.5	10.1	28.1	1.1	1.8	2.0	0.5
1000	16.0	2.4	34.8	0.6	9.8	28.6	1.0	1.7	2.0	0.4
1200	16.2	2.5	34.9	0.6	9.8	28.3	1.1	1.7	1.9	0.4

a) Denotes the branching ratios obtained with the (e, e+ion) technique (Ref. 4).

the basis of the consideration described above, it is reasonable that the steep increase in the yield ratios for atomic ions below the Cl L-edges originates from the molecule being excited into an electronic state containing two valence holes.

It is important to note the following general observations from the photon energy dependences of the yield ratios described above:
(1) The yield ratio of Cl^+ is considerably higher than that of F^+ below the F K-edge, although the number of Cl atoms is a third of that of F atoms in this molecule.
(2) The yield ratio of CF_2^+ is significantly higher than that of $CFCl^+$ in all the energy regions (see TOF spectra in Fig. 1).
(3) The ion CF^+ is observed with considerable intensity, but the ion CCl^+ has a small intensity in the energy region studied here.
These findings are observed in the vacuum ultraviolet region where only valence electrons can be excited, together with inner-shell transition regions. These phenomena can be ascribed to the different bonding characteristics of the two elements, in particular their bonding characteristics in the various ionic species, e. g. the appearance potential of Cl^+ from this molecule is 19.5 eV, considerably lower than that of F^+, 34 eV.[4] Inner-shell holes are usually filled with valence electrons through an Auger transition, resulting in a molecule with two valence holes prior to the fragmentation. Some of these states are the same as the doubly excited or ionized states formed through photoionization in the vacuum ultraviolet region. This can explain the validity of the above general observations, independent of the photon energy.

Sharp changes in the yield-ratio curves across the inner-shell ionization edges have been found for several fragment ions in Fig. 2. These changes may originate from different relative populations of two valence hole states being accessed by double ionization directly and indirectly. Inner-shell ionized states of the molecule usually decay to doubly charged molecular-ion states through an Auger transition, and the molecular ions turn into two or more ionic fragments. Radiative processes take place with a negligibly low probability in the energy region of the present study. Thus the fragmentation processes are schematically expressed as follows:

$$CF_3Cl^+ \text{ (inner-shell}^{-1}) \to CF_3Cl^{2+} \text{ (valence orbital}^{-2}) + e \to \text{Fragment}(1)^+ + \text{Fragment}(2)^+ + \text{Fragment}(3) + e \quad (1)$$

The valence orbitals which are involved in the Auger decay are determined in part by the spatial overlap of the orbitals with the atomic site of the core hole, i. e. valence orbitals which have a greater amplitude in the region of the core hole have a greater probability of being involved in the Auger transition. Since the fragmentation of the molecular ion depends significantly on which valence orbitals the two holes are created in, the bonds to be broken probably depend on the location of the initial excitation. This dependence of the fragmentation on the location of the valence holes, and hence the site of the core hole, results in different patterns between different core holes within the same molecule.

Table 1 lists the yield ratios of fragment ions at several photon energies, together with the branching ratios obtained with the (e, e+ion) coincidence technique by Zhang et al.[4] Although the present results are similar to their data, the yield ratio of Cl^+ is higher, and those of CF_2Cl^+ and CF_3^+ are slightly lower, than those in

Table 2. Comparison of Yield Ratios of Fragment Ions among Three Freon Molecules Irradiated in the Soft X-Ray Region (Units of %)

Molecule	Energy eV	1 atom ions	2 atom ions	3 atom ions	4 atom ions
CF_4	50	9.4	3.5	7.5	79.5
CF_3Cl	50	24.0	7.3	15.2	52.8
CF_2Cl_2	50	23.7	14.5	20.8	41.2
CF_4	200	47.8	12.7	6.9	32.4
CF_3Cl	200	52.9	11.2	10.9	24.1
CF_2Cl_2	190	56.5	14.0	11.3	18.1
CF_4	294	55.3	12.9	6.8	25.0
CF_3Cl	290	67.5	10.9	7.0	12.9
CF_2Cl_2	280	74.8	10.6	6.6	8.0
CF_4	317.5	70.0	18.8	3.6	7.9
CF_3Cl	320	72.4	11.9	5.3	9.2
CF_2Cl_2	320	77.2	10.8	5.5	6.4
CF_4	684	75.4	15.7	3.7	5.5
CF_3Cl	680	75.7	10.6	4.8	7.5
CF_2Cl_2	680	80.0	9.9	4.8	5.3
CF_4	800	77.6	16.0	4.7	1.7
CF_3Cl	800	81.2	11.9	2.2	2.6
CF_2Cl_2	800	84.1	10.0	3.0	3.1

The previously reported results are cited for CF_4 (Ref. 20) and CF_2Cl_2 (Ref. 18).

their previous results at a photon energy of 80 eV. This discrepancy possibly results from discrimination against the detection of high kinetic-energy ions and electrons. Fragment ions having high kinetic energy hold a higher probability of escaping from the detector than do those with low kinetic energy, even in the high electric field in the previous study.[4] When double photoionization occurs, one or two slow electrons are ejected, which may increase the probability of their detection in the present experimental apparatus. These effects may result in small differences in the ion yield ratios measured in different experimental apparatuses. This table includes the yield ratios for fragment ions which have low intensities in all the energy regions studied and thus are not shown as a photon-energy dependence in Fig. 2.

It is interesting to compare the yield ratios of ions from CF_3Cl with those from other freon molecules.[18,20] This comparison is shown in Table 2, where the number of atoms constituting a fragment ion is adopted as a measure instead of the fragment ion itself. The ratio of 1-atom ions means the summation of those of all singly and doubly charged atomic ions. Several photon energies are selected because those photons induce typical electronic transitions.

Below the Cl L-edges, the yield ratios of 4-atom ions from CF_4 show the greatest among the three molecules and those of 1-atom ions exhibit the lowest. One reason for these results is presumed to be the fact that the ionization energies of the valence orbitals of CF_4 are higher than those of the corresponding orbitals of CF_3Cl and CF_2Cl_2. This is mainly because the 2s and 2p orbitals of the fluorine atom have higher ionization energies than do the 3s and 3p orbitals of the chlorine atom. The partial photoionization cross sections of inner valence orbitals usually show maxima considerably above their ionization thresholds, and the decrease in the yield ratios of 4-atom ions and the increase in those of 1-atom ions are largely governed by the magnitude in the population of inner valence hole states generated. Another reason is probably the following. The valence double photoionization of CF_4 takes place with a lower probability than do those of CF_3Cl and CF_2Cl_2. This is because the CF_4 has deeper valence orbitals than do the other two molecules. The molecular ion having two valence holes decomposes to form atomic ions, yielding a lower intensity of 4-atom ions. The appreciable difference in the yield ratios of 4-atom ions and of 1-atom ions between CF_3Cl and CF_2Cl_2 is consistent with the above reasoning.

Above the Cl L-edges but below the C K-edge, around 290 eV, the feature of the difference in the yield ratios among the molecules are similar to that at the photon energies below the Cl L-edges. The ratio of 4-atom ions from CF_4 is the highest and that of 1-atom ions shows the lowest. This finding is reasonable because inner-shell excitation does not occur in CF_4, though the others have a possibility that multiple ionization accompanying fragmentation is induced by the Cl L-shell ionization. The yield ratios of 2-atom and 3-atom ions are relatively close to one another among the three molecules.

The yield ratios of 2-atom ions from CF_4 exhibit the

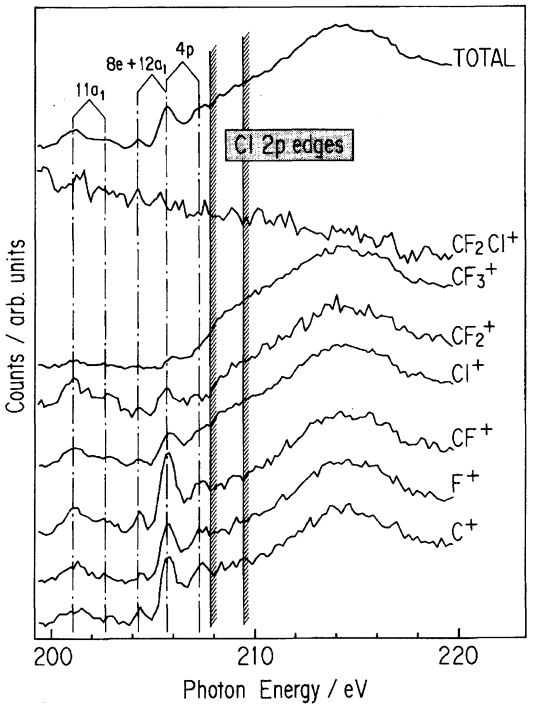

Fig. 3. Partial yield spectra of the fragment ions of CF_3Cl around the Cl $L_{2,3}$-edges. The broken vertical lines and those with hatching indicate the energy positions of transitions to the $11a_1$ and ($8e+12a_1$) unoccupied molecular orbitals, the 4p Rydberg orbital, and the ionization thresholds.

highest and those of 1-atom ions show the lowest among these molecules at the photon energies above the C K-edge. The differences are considerably large in the ratios of 2-atom ions, but relatively small in the 1-atom ions ratios. The ratios of 1-atom and 2-atom ions from CF_3Cl range between those for CF_4 and for CF_2Cl_2. These findings seem to be related to the previous and above-mentioned results, i. e. the yield ratios of Cl^+ and CF^+ are much higher than those of F^+ and CCl^+, respectively, in the ionic fragmentation of CF_3Cl and CF_2Cl_2 if the numbers of F and Cl atoms constituting the relevant molecule are taken into account.

A systematic trend is not clearly found for the yield ratios of 3-atom and 4-atom ions above the C K-edge. In comparison with the ratios in CF_2Cl_2, however, the results in CF_3Cl and CF_4 exhibit a distinct change in the ratios of 3-atom and 4-atom ions through the excitation of F_{1s} electrons. In particular, the ratios of 4-atom ions decreased to about 0.3 and 0.34 of the values below the F K-edge in CF_4 and CF_3Cl, respectively, in which the change in the intensities of $CF_3{}^+$ played a major role in both molecules.

Yield Spectra of Fragment Ions in the Inner-Shell Excitation Regions. Figure 3 shows detailed yield spectra of singly charged fragment ions produced from CF_3Cl in the region of the Cl L-edges. The broken vertical lines and the lines with hatching denote the energy positions of transitions to the $11a_1$ unoccupied molecular orbital, the ($8e+12a_1$) molecular orbitals, the 4p Rydberg orbital and the ionization thresholds.[13,14] When the yield ratio curves were plotted, the intensity of the incident soft X-rays was not calibrated, because only relative variations among these curves were closely examined in the present study. The $11a_1$ molecular orbital is primarily C–Cl antibonding in character, while the 8e and $12a_1$ orbitals are primarily C–F antibonding. The characteristics of the valence orbitals of this molecule are listed in Table 3, together with their ionization energies.[4—8] The Cl 2p orbital has two ionization thresholds, $2p_{3/2}^{-1}$ (207.8 eV) and $2p_{1/2}^{-1}$ (209.4 eV) due to spin orbit splitting. The total ion-yield curve, simply a summation of the individual fragment ion yields, shows a spectrum similar to the photoabsorption spectrum reported previously.[14]

Table 3. Valence Orbitals of CF_3Cl

Occupied orbital	Ionization energy eV	Major component
$6a_1$	42.5	F_{2s}
3e	40.0	F_{2s}
$7a_1$	26.9	Cl_{3s}
$8a_1$	23.8	C_{2s}, C–F bonding
4e	21.2	C–F bonding
$9a_1$	20.2	F_{2p} lone-pair
5e	17.7	F_{2p} lone-pair
6e	16.7	F_{2p} lone-pair
$1a_2$	15.8	F_{2p} lone-pair
$10a_1$	15.2	C–Cl bonding
7e	13.1	C_{3p} lone-pair
Unoccupied Orbital		
$11a_1$		C–Cl anti-bonding
8e		C–F anti-bonding
$12a_1$		C–F anti-bonding

The atomic ion Cl^+ has a yield spectrum similar to the photoabsorption spectrum. Although the other two atomic ions, F^+ and C^+, show a similar feature to that of the total yield, the peaks of these ions corresponding to the transition into the 4p Rydberg orbital are more prominent than that of the total. The spectrum of CF^+ is very close to those of F^+ and C^+. The feature of the $CF_2{}^+$ yield curve is the peaks having higher relative intensities at the $11a_1$ orbital transitions than those at other transitions. The fragment ion, $CF_3{}^+$, exhibits a yield spectrum different from those of the ions mentioned above. Although this ion does not seem to be appreciably produced at the transition to the unoccupied molecular orbitals, its yield increases to some extent at the photon energies of transitions into high Rydberg orbitals, and largely above the ionization thresholds. The yield spectrum of the CF_2Cl^+ shows a profile that is much different from those of other ions. The yield decreases monotonically in this energy region, although an appreciable fluctuation of ion signals is seen due to the low intensity of this ion. This finding means that this ion is not produced through excitation of the Cl 2p electron.

After the transition of the Cl 2p electron to the $11a_1$ orbital, an autoionization generally takes place; the core-excited neutral molecule then turns into a molecular ion with one valence hole or two valence holes and an electron in the unoccupied molecular orbital. The former process is called a participator Auger decay because the excited electron takes part in this decay process; the latter process is called a spectator Auger decay, because of no participation of the excited electron during this decay process.[10,11,27] These decay processes are occasionally accompanied by the emission of a second electron, i. e. an Auger shake-off process, or successive Auger transitions, rendering the molecule in a doubly charged state. There are a number of molecular ion states accessible from the core-excited states. However, based on a consideration of the bonding characters of the valence orbitals as well as the fragmentation patterns of the molecules following ionization of these orbitals, it is partly possible to make assignments of the probable electronic states of the molecular ion. At the photon energy of 201 eV, one of probable processes for Cl^+ production is given by the following:

$$\begin{aligned}\mathrm{CF_3Cl^*(Cl_{2p}^{-1}11a_1)} &\rightarrow \mathrm{CF_3Cl^+(4e^{-1})+e}\\ &\rightarrow \mathrm{Cl^+ + neutrals + e} \qquad (2)\end{aligned}$$

The $11a_1$ orbital is antibonding at the C–Cl site and the 4e orbital is bonding. It is reasonable that the molecular ion having a 4e hole decomposes to give Cl^++neutral fragments, according to the study concerning the breakdown scheme of the CF_3Cl^+ by Zhang and co-workers.[4] As shown in Fig. 3, the $CF_2{}^+$ has a high production yield at 201 eV. This indicates that the inner-shell excited state of Cl_{2p}^{-1} $11a_1$ turns considerably into a valence hole state, like $9a_1^{-1}$, which is transformed to CF_2^++neutral fragments.

The inner-shell excited Rydberg state of Cl_{2p}^{-1} Cl_{4p}, on the other hand, considerably decays to the valence hole states, like $6a_1^{-1}$, $3e^{-1}$, and $8a_1^{-1}$. These orbitals are mainly F 2s and C 2s orbitals, which are essentially bonding. The Rydberg orbital having a non-localization character is presumably able to appreciably overlap with a molecular orbital mainly consisting of the F 2s orbital, one of the inner-valence orbitals. There is a possibility that these inner valence orbitals have some character of the Cl 3s orbital or C 2s owing to a configuration interaction among the states having the same symmetry. The singly charged molecular ion with an inner-valence hole dissociates to yield C^+ or F^++other fragments,[4] occasionally accompanying a second electron ejection because of sufficient energy for the conversion to doubly charged states. One probable pathway is as follows:

$$\begin{aligned}&\mathrm{CF_3Cl^*(Cl_{2p}^{-1}4p)} \rightarrow \mathrm{CF_3Cl^+(3e^{-1})+e}\\ &\qquad \rightarrow \mathrm{F^+\ (or\ C^+) + neutrals\ (or\ ion) + e\ (or\ 2e)} \qquad (3)\end{aligned}$$

Another possibility of the yield increase in the F^+, C^+, and CF^+ at the Cl_{2p}^{-1} Cl_{4p} state is as follows. The spectator Auger transition occurs at this energy more frequently than other inner-shell excited states. At the next step, the spectator electron, Cl4p, is emitted from the singly charged molecular ion in a highly excited state, which yields a doubly charged ion. The formed molecular ion decomposes to F^+ (C^+, or CF^+) and an ionic fragment.

Little increase in the $CF_3{}^+$ yield at the transition to the unoccupied molecular orbitals is possibly due to the following. The participator Auger transition from the Cl_{2p}^{-1} $11a_1$ state does not render the molecule into a valence hole state, like the $7e^{-1}$ or $6e^{-1}$ state. Although these states considerably induce the formation of $CF_3{}^+$, other one-hole states do not result in the decomposition into $CF_3{}^+$+Cl.[4] The ion states generated through the spectator Auger transition are those having two valence holes; the fragmentation is thus supposed to proceed more completely than the one-hole states, in which little yield of $CF_3{}^+$ is expected to result.

In comparison with the yield spectra of fragment ions from CF_2Cl_2,[18] a similarity is found between CF_2Cl^+ from CF_3Cl and $CFCl_2{}^+$ from CF_2Cl_2, between $CF_3{}^+$ from CF_3Cl and CF_2Cl^+ from CF_2Cl_2, between $CF_2{}^+$ from CF_3Cl and $CFCl^+$ (or $CF_2{}^+$) from CF_2Cl_2, and between CF^+ from CF_3Cl and CF^+ from CF_2Cl_2. These ions are of the same ionic species or the remaining ions after a detachment of the same species. The atomic ions have, of course, the same feature in this two molecules.

Detailed yield spectra for individual fragment ions in the C K-edge region are shown in Fig. 4, together with that of the total ion. The broken vertical lines and the line with hatching denote the energies for transitions to the $11a_1$ unoccupied molecular orbital, the ($8e+12a_1$) orbitals, high Rydberg orbitals (mainly 5p), the ionization threshold, and the shape resonance.[14,15] The spectrum of the total ion is close to the photoabsorption spectrum obtained at moderate resolution. Those of atomic ions, C^+, F^+, and Cl^+, are similar to that of the total. The diatomic ion CF^+ shows a yield curve similar to the total ion spectrum, but exhibits a slightly more prominent increase at the shape resonance. The ion $CF_2{}^+$ has a feature similar to those of the other ions, but shows a slightly higher peak at excitation into the ($8e+12_1$) orbitals.

The fragment ion CF_3^+ has a yield spectrum different from that of the total ion, indicating no peak at the ($8e+12a_1$) orbital transition and no intensity increase at the shape resonance. That of CF_2Cl^+ exhibits a feature much different from the total ion curve, showing a peak only at the ($8e+12a_1$) orbital excitation. After excitation of the C_{1s} electron into the ($8e+12a_1$) orbitals, a participator Auger transition usually takes place, rendering the molecule into an ionic state having a valence hole. A part of this valence hole is probably positioned

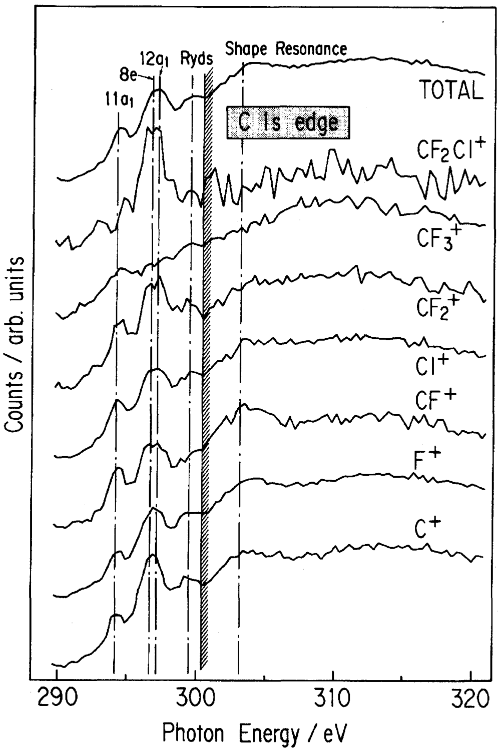

Fig. 4. Partial yield spectra of the fragment ions of CF_3Cl around the C K-edge. The broken vertical lines and that with hatching indicate the energy positions of transitions to the $11a_1$ and $(8e+12a_1)$ unoccupied molecular orbitals, high Rydberg orbitals, the ionization threshold, and the shape resonance.

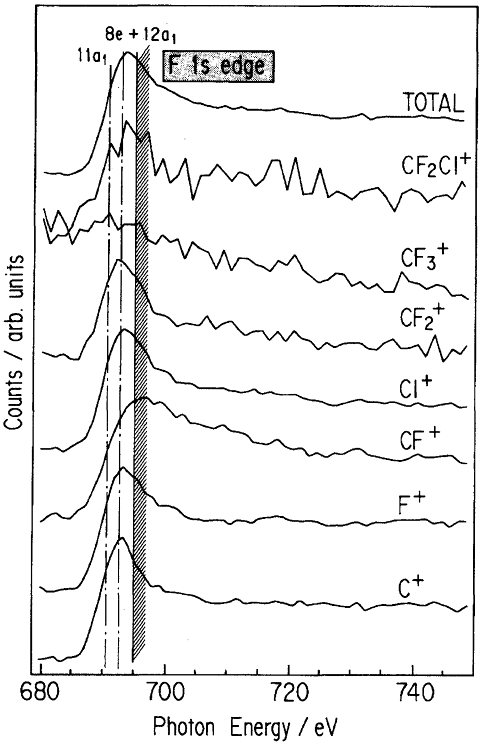

Fig. 5. Partial yield spectra of the fragment ions of CF_3Cl around the F K-edge. The broken vertical lines and that with hatching indicate the energy positions of transitions to the $11a_1$ and $(8e+12a_1)$ unoccupied molecular orbitals, and the ionization threshold.

at the $10a_1$ orbital, $1a_2$ orbital, or $9a_1$ orbital. These orbitals are largely populated at the F atom site owing to mainly lone-pair orbital of F 2p. The states having a hole in these orbitals induce the dissociation into CF_2Cl^++F or CF_2^++neutrals, according to the work by Zhang et al.[4] One of these processes is schematically expressed with the following:

$$CF_3Cl^*(C_{1s}^{-1}8e) \rightarrow CF_3Cl^+(1a_2^{-1}) + e \rightarrow CF_2Cl^+ + F + e \quad (4)$$

The inner-shell excited states $(C_{1s}^{-1}8e/12a_1)$ do not seem to turn into the single-valence hole states of $7e^{-1}$, $6e^{-1}$, and $5e^{-1}$ through the participator Auger decay. The molecular ion in these states decomposes to CF_3^++Cl, as postulated by Zhang et al.[4] No peak at the $(8e+12a_1)$ orbital transition in the CF_3^+ yield spectrum indicates this specific character in the Auger decay process.

Compared with the results of CF_2Cl_2,[18] a similarity in the yield curves near the C K-edge is found between CF_2Cl^+ from CF_3Cl and $CFCl_2^+$ from CF_2Cl_2, between CF_2^+ from CF_3Cl and $CFCl^+$ from CF_2Cl_2, and between CF^+ from CF_3Cl and CCl^+ (or CF^+) from CF_2Cl_2.

Figure 5 shows the yield spectra of individual fragment ions in the F K-edge region. The broken vertical lines and the line with hatching denote the photon energies of transitions to the $11a_1$ orbital, the $(8e+12a_1)$ orbitals, and the ionization threshold.[14] The total ion curve is close to the photoabsorption spectrum obtained at moderate resolution. The atomic ions, Cl^+, F^+, and C^+, show spectra similar to the total ion curve. The spectrum of CF^+ exhibits a feature slightly different from the total; the maximum of CF^+ yield appears at the ionization threshold. This finding indicates that this ion is not produced considerably through transitions into the unoccupied molecular orbitals. This result shows a clear contrast to the yield spectra obtained around the Cl L-edges and the C K-edge.

The fragment ion CF_2^+ shows a yield curve similar to that of the total ion. The yield spectrum of CF_3^+ exhibits a feature that is much different from those of other ions, indicating little change in the yield in this energy region. This ion is not formed by the excitation and ionization of the F_{1s} electron. This finding differs from the results observed near the Cl L-edges and the C K-edge. The CF_3^+ was produced considerably through the ionization of Cl 2p and C 1s electrons, although this ion is hardly formed through excitation into the unoccupied molecular orbitals. Although the signals greatly fluctuate, the CF_2Cl^+ seems to have essentially the same feature as the total ion. This finding also shows a distinct difference in the formation of the

CF_2Cl^+ among the three inner-shell transitions. This ion is largely produced at the excitation of C 1s electron into the (8e+12a$_1$) orbital, although no yield is observed through the excitation and the ionization of the Cl 2p electron.

Compared with the yield curves of ions from CF_2Cl_2,[18] the fragment ions having a large intensity in CF_3Cl show a similar curve to the counterpart ions from CF_2Cl_2. Further minor yield ions have a similarity in the yield spectra near the F K-edge, e. g. between CF_3^+ from CF_3Cl and CF_2Cl^+ from CF_2Cl_2 and between CF^+ from CF_3Cl and CCl^+ from CF_2Cl_2.

Summary

Although the fragment ions consisting of 4 atoms show great yield ratios in the vacuum ultraviolet region, above 100 eV up to the F K-edge the atomic ion Cl^+ exhibits the highest intensity. The yield ratio of F^+ shows the second highest from about the Cl L-edges to the F K-edge, and becomes the greatest above the F K-edge. Some of the photon energy dependences of the yield ratios show a large change at the inner-shell transition energies; in particular, CF^+ exhibits a steep increase in the yield ratio at the transition energies into the unoccupied molecular orbitals around the Cl L-edges and a considerable rise through the ionization of the F 1s electron. A general feature in the yield ratios of fragment ions from this molecule is very similar to that of CF_2Cl_2 if the difference in the number of halogen atoms is taken into account.

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