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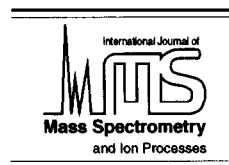
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Variation in ion-pair yields from CF_2Cl_2 photoexcited in the inner-shell excitation regions

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Abstract

Positively charged ion pairs produced from CF_2Cl_2 following soft X-ray absorption have been measured using a modified photoion–photoion coincidence technique and monochromatized synchrotron radiation. It was found that the modification specifying a particular fragment ion as the lighter partner is very useful for clarifying yields of ion pairs from the same molecular ion in polyatomic molecules. The ion pair F^+–Cl^+ produced the highest yield at most photon energies, with C^+–Cl^+ the second highest above the Cl $L_{2,3}$-edges. Partial yield spectra of individual ion pairs have been measured around the Cl $L_{2,3}$-edges, the C K-edge and the F K-edge and the features of many ion pairs are similar to those found using photoabsorption spectra. Some of the branching ratios obtained for the ion pairs, in particular for Cl^+–CF_2Cl^+, changed significantly near the Cl $L_{2,3}$-edges.

1. Introduction

Energy relaxation following the excitation of core electrons in a molecule ends in ionic fragmentation of the molecule after electronic de-excitation. Because core holes are strongly localized at the atoms fragmentation may depend on the site of the core hole, which can be selected by excitation of core electrons in the specified atom using monochromatized synchrotron radiation. This site selectivity has been demonstrated by the yield spectra of particular fragment ions from several molecules [1–4]. However, selectivity is not

so clear from a quantitative point of view because prior to fragmentation the molecular ion exists in a valence excited state and the valence orbital is not always localized at a specific site [2–6]. It is interesting to study the fragmentation of CF_2Cl_2 with respect to the site-selective process, because this molecule has three different atomic sites, with corresponding photon energy ranges in the Cl L-edge, the C K-edge, and the F K-edge.

Inner-shell excitation spectra of CF_2Cl_2 have been measured by several laboratories using monochromatized synchrotron radiation or an electron energy-loss technique [7–10]. The transitions of Cl 2p electrons to unoccupied molecular orbitals such as $13a_1$

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and $7b_2$, were found to split owing to spin–orbit coupling of these electrons in the Cl L-edge region. The pre-edge structures of the C 1s electron excitation and that of the shape resonance above the ionization threshold were found in the C K-edge region. Broad structures comprising transitions of F 1s electrons to unoccupied molecular orbitals and to the continuum were observed in the F K-edge region. Ionic fragmentation of freon molecules was studied in the inner-shell excitation region and in the vacuum ultraviolet [11–18]. Atomic ions were found to be prolific in these regions. However, molecular ions were produced in only a small quantity and doubly charged fragment ions hardly at all.

Auger transitions which happen just after core electron excitation usually render the molecule in a doubly or more highly charged state because this process accompanies electron emission [1–6]. In the soft X-ray region, radiative processes providing a singly charged molecule take place with a small probability, 1% or less. It is usual that a doubly charged molecular ion decomposes to give two ionic fragments, some of which may dissociate successively to ionic and neutral products, owing to Coulombic repulsion forces. In order to understand the mechanism of ionic fragmentation, it is very important to detect coincidently the ionic pair produced from a particular molecular ion [19–22]. For small molecules, the number of ion-pairs is limited and conventional photoion–photoion coincidence (PIPICO) techniques, which measure the difference in the flight time for each ion pair, can be utilized effectively. However, the number of ion pairs becomes very much greater as the number of atoms in the molecule increases, and the signals for ion pairs begin to overlap one another significantly. Some atoms are composed of a few stable isotopes and many ionic fragments often have large kinetic

energies [20–22]. These situations render the PIPICO technique unsuitable for the detection of ion-pair production.

In the present study, modification of the PIPICO technique using a time-of-flight mass spectrometer has been proposed and applied to the ionic fragmentation of CF_2Cl_2. Monochromatized synchrotron radiation was used for excitation of core electrons in the Cl L-shell, the C K-shell, and the F K-shell.

2. Experimental

Synchrotron radiation from the TERAS electron storage ring at the Electrotechnical Laboratory was dispersed using a Grasshopper monochromator to obtain monochromatic soft X-rays around the Cl L-edge, the C K-edge, and the F K-edge [23]. By selecting appropriate energies for the electron beam in the storage ring, the spectral distribution of the synchrotron radiation was modified to reduce the intensity of higher-order photons [24]. Thin films of beryllium, aluminium, indium, and mylar were used as filters to reduce the stray light and higher-order contribution to the monochromatized beam. Monochromatized synchrotron radiation passes through two differential pumping stages and enters an experimental chamber equipped with a time-of-flight (TOF) mass spectrometer [25]. The photon beam crosses an effusive beam of the sample gas at right angles in the center of the spectrometer. Electrons and ions produced were extracted in opposite directions and detected with microchannel plates. The electric field applied at this center was set at $80\,V\,mm^{-1}$ in order to collect ions of all kinetic energies. Since anisotropic dissociations may have a considerable effect on the measured PIPICO spectra, angular distributions of fragment ions were examined [26,27]. This examination showed that no
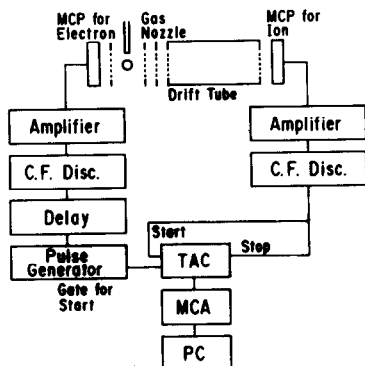
Fig. 1. Schematic drawing of the experimental set-up: MCP = tandem-type microchannel plates; C.F. disc. = constant fraction discriminator; TAC = time-to-amplitude converter; MCA = multichannel analyzer; PC = personal computer.

observable anisotropy was found under the present experimental conditions.

Fig. 1 shows schematically the experimental set-up for a modification of the conventional PIPICO technique, i.e. the selected PIPICO technique. Modification has been performed as follows. The signal from the microchannel plates for electron detection was processed by an amplifier and a constant fraction discriminator, and transferred to a pulse generator by way of a delay circuit. Appropriate selection of the delay time in this circuit specified the flight time of a fragment ion of interest. A signal for gating produced in the pulse generator was supplied to the input connector for a start signal in the time-to-amplitude converter (TAC). Only when this gating signal entered the TAC, was the TAC able to receive the start signal of an ion with a shorter flight time (lighter ion) from the ion detector. After the TAC was activated through the two types of signals, this device accepted a stop signal from a heavier ion. The time difference between the lighter ion and the heavier was converted to the signal having the corresponding pulse height, and this signal was accumulated in the multi-channel analyzer (MCA). When the specified lighter ion was changed, the delay time was
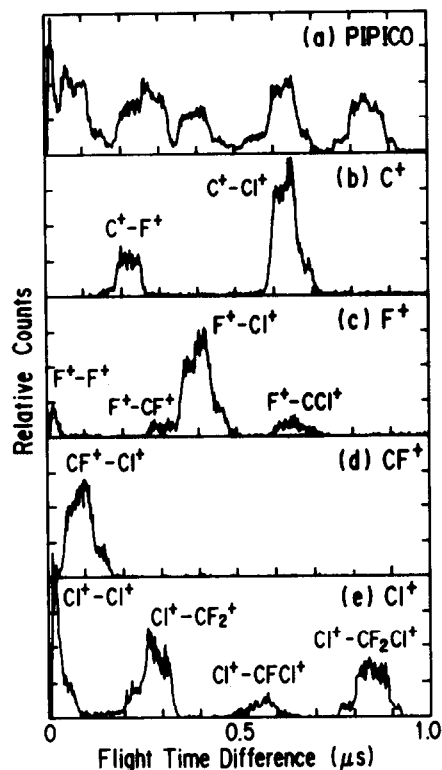

Fig. 2. Spectra of difference of flight times between fragment ions produced from CF_2Cl_2 at 214 eV using several measurement modes: (a) conventional photoion–photoion coincidence technique (PIPICO); (b) selected PIPICO when C^+ is selected; (c) selected PIPICO when F^+ is selected; (d) selected PIPICO when CF^+ is selected; (e) selected PIPICO when Cl^+ is selected.

tuned for the flight time of a second lighter ion.

Fig. 2. shows the spectra of ion–ion coincidence obtained using the selected PIPICO technique, for ion-pair production from CF_2Cl_2 at a photon energy of 214 eV. The conventional PIPICO spectrum is shown in Fig. 2(a). A number of structures are found in the difference spectrum of flight times from 0 to 1.0 μs. The structures around 0.05–0.1 μs are probably composed of the ion pair of CF^+-Cl^+ (mass difference $(\Delta M) = 3, 4, 5, 6$) and of tailings by the ion pairs of F^+-F^+ ($\Delta M = 0$) and Cl^+-Cl^+ ($\Delta M = 0.2$).

When we focused on the fragment ion C^+ as a lighter ion (faster ion), the spectrum was

measured with the selected PIPICO and is shown in Fig. 2(b). The spectrum indicates the presence of C^+–F^+ and of C^+–Cl^+ at a higher intensity. Since the incident photon energy is above the Cl $L_{2,3}$-edges, it is expected that the intensity of C–Cl^+ is considerably higher than that of C^+–F^+. Fig. 2(c), depicts the selected PIPICO spectrum when F^+ was selected. Signals due to F^+–F^+, F^+–CF^+, F^+–Cl^+, and F^+–CCl^+ are all evident. The ion pair F^+–Cl^+ has the highest intensity in this spectrum. In Fig. 2(d) the selected PIPICO spectrum is shown for the ion pair CF^+–Cl^+, when CF^+ was selected. In this instance only one ion pair is produced from this molecule; this finding is understandable since the structure of this molecule has a carbon atom at the center. When Cl^+ was selected as the lighter ion, a spectrum composed of four structures was obtained: Cl^+–Cl^+, Cl^+–CF_2^+, Cl^+–$CFCl^+$, and Cl^+–CF_2Cl^+ (Fig. 2(e)). Of these structures Cl^+–CF_2^+ seems to have the highest intensity and that of Cl^+–$CFCl^+$ the lowest.

As described above, the selected PIPICO technique provides an uncluttered spectrum in which we can easily assign each peak to the corresponding ion pair, even if the molecules studied are relatively large and signals for ion pairs overlap one another in conventional PIPICO spectroscopy. Thus this technique is powerful for clarifying ion-pair production and for determining the probability of production of each ion pair.

It is possible to obtain signals for ion-pair production using a time-to-digital converter (TDC), as Eland illustrated for clarification of the dissociation mechanism of photoionized polyatomic molecules [28]. However, it is not so easy to process the data collected in a memory system combined with the TDC and to derive ion–ion coincidence data for individual ion pairs. It is a difficult job to assess and then subtract the noise from observed signals. The TDC system is expensive and requires a long measurement period in order to obtain reliable data. Moreover it is difficult to examine observed spectra in real time in order to find optimum experimental conditions in measurements using a TDC. In contrast, the selected PIPICO technique proposed here provides a simple method for obtaining reliable data for ion-pair production.

3. Results and discussion

Selected PIPICO spectra at several photon energies have been transformed to branching ratios for ion-pair production through the calibration of the photon intensity using a monitor of gold-coated nickel mesh. Table 1 lists these branching ratios at photon energies around the Cl $L_{2,3}$-edges, the C K-edge, and the F K-edge.

3.1. Cl $L_{2,3}$-edges region

Below the transition energy of the Cl 2p electrons, the ion pair having the highest branching ratio is F^+–Cl^+ (Table 1). These ions probably originate from the doubly charged molecular ion. As discussed previously, double photoionization is very likely even below the threshold of core electron excitation [12,13,18,24]. The measurement of single fragment ions showed that the intensities of atomic ions such as Cl^+ are relatively high even below 200 eV for CF_2Cl_2 [13]. These atomic ions, which possibly originate from double photoionization, are presumed to be one of the partners constituting the ion pair. Typical examples of fragmentation pathway are shown in Eq. (1).
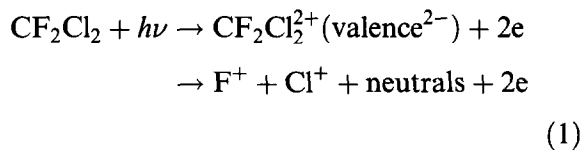
$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl_2^{2+}(\text{valence}^{2-}) + 2e$$

$$\rightarrow F^+ + Cl^+ + \text{neutrals} + 2e$$

$$(1)$$

Table 1
Branching ratios (%) of ion-pair production from CF_2Cl_2 photoexcited around the inner-shell ionization thresholds

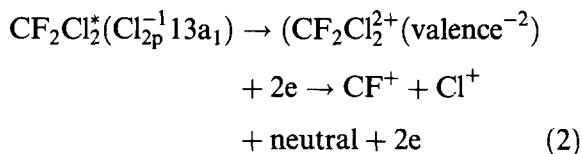| Energy (Ev)	Assignment	C–F	C–Cl	F–F	F–CF	F–Cl	F–CCl	CF–Cl	Cl–Cl	Cl–CF$_2$	Cl–CFCl	Cl–CF$_2$Cl
198	below $Cl_{2p}^{-1} U^1$	7.8	17.9	1.7	1.3	22.2	3.8	13.9	10.5	12.2	4.8	3.6
201	$Cl_{2p}^{-1} U^1$	6.8	18.6	1.4	1.5	20.3	3.1	17.2	11.4	11.7	4.0	4.1
216	above the Cl_{2p} edges	4.9	16.2	0.9	1.2	14.0	1.8	16.8	11.2	14.9	4.5	13.7
290	below $C_{1s}^{-1} U^1$	8.4	18.9	1.5	1.4	22.4	1.6	15.6	12.8	8.9	2.3	6.1
295	$C_{1s}^{-1} U^1$	8.7	19.5	1.6	1.3	22.8	2.4	14.7	11.9	9.7	2.2	5.2
308	above the C_{1s} edge	8.9	19.5	1.6	1.4	23.1	2.1	15.1	12.5	8.6	1.9	5.2
680	below $F_{1s}^{-1} U^1$	11.6	19.7	2.4	1.6	25.6	2.0	12.8	11.1	7.4	1.8	4.2
692	$F_{1s}^{-1} U^1$	12.1	21.0	2.5	1.4	25.5	2.5	11.7	10.7	7.7	1.9	3.0
720	above the F_{1s} edge	11.7	21.4	2.5	1.4	25.9	2.7	11.3	10.9	7.6	1.6	2.9

U denotes unoccupied molecular orbitals.

Since the branching ratio of Cl^+ was found to have the highest intensity in our previous work [13], it follows that the ion pairs in which Cl^+ participates show relatively high branching ratios.

The second highest branching ratio at 198 eV is found for the ion pair C^+–Cl^+. This observation is peculiar because the fragment ion originating from the center of the molecule, C^+, contributes to this ion pair in spite of the energy being below that of inner-shell electron transition. The ion pair CF^+–Cl^+ shows the third highest intensity. It is important to note that the branching ratios of ion pairs having Cl^+ as a partner are always higher than those of the corresponding F^+ pairs, e.g. the C^+–Cl^+ branching ratio is higher than that of C^+–F^+. This finding is probably connected with the result that the branching ratio of Cl^+ is considerably higher than that of F^+ in single-ion measurement [13]. This fact also seems related to the phenomena that the branching ratio of CCl^+ is lower than that of CF^+ and that no CCl_2^+ was produced.

The branching ratios for CF^+–Cl^+, Cl^+–Cl^+, and C^+–Cl^+ are higher at 201 eV than those at 198 eV. Those for C^+–F^+, F^+–Cl^+, F^+–CCl^+, Cl^+–CF_2^+, and Cl^+–$CFCl^+$ decreased, compared to those below the Cl 2p excitation energy. At a photon energy of 201 eV, the electron in the $2p_{3/2}$ orbital of the Cl atom is excited to unoccupied molecular orbitals, $13a_1$ and $9b_2$. After the excitation, Auger-type decay generally occurs with electron emission and the molecule transforms into either a state having a valence orbital hole or a state having two valence holes and an electron in an unoccupied molecular orbital. Fluorescent soft X-ray emission is negligible owing to its low probability at these photon energies. Auger-like transition is occasionally accompanied by a second electron emission, i.e. Auger shake-off or successive Auger transition, yielding a doubly charged molecular ion. This molecular ion

decomposes to two ionic fragments. One of the probable decomposition pathways is shown schematically in Eq. (2).

$$CF_2Cl_2^*(Cl_{2p}^{-1}13a_1) \rightarrow (CF_2Cl_2^{2+}(valence^{-2})$$

$$+ 2e \rightarrow CF^+ + Cl^+$$

$$+ neutral + 2e \qquad (2)$$

Since the initial excited state is due to the loss of a C–Cl slightly bonding electron and the addition of a C–Cl anti-bonding electron, bond rupture is expected to happen easily at the C–Cl bond while the C–F bond is maintained. This theory should lead to lower intensities for C^+ and F^+ and higher intensities for Cl^+ and CF^+. The results obtained at 201 eV in the branching ratios of the ion pairs are in accord with this expectation.

Above the ionization threshold of the Cl 2p electron, 216 eV, the branching ratios of Cl^+–CF_2^+ and Cl^+–CF_2Cl^+ became significantly higher than those at 198 eV. Some of the molecular ion states after the Auger transition are different from those at 201 eV, because some ion pairs show different branching ratios from the latter case of the $Cl_{2p} \rightarrow 13a_1$ transition. The ratios for C^+–F^+, C^+–Cl^+, and F^+–Cl^+ decreased considerably compared to those at the excitation of Cl 2p → unoccupied molecular orbitals. The ion pairs CF^+–Cl^+, Cl^+–Cl^+, F^+–F^+, F^+–CF^+, and F^+–CCl^+ show slightly smaller branching ratios than those at 201 eV. The most interesting change is a sharp increase in the branching ratio for Cl^+–CF_2Cl^+ above the Cl $L_{2,3}$-edges. The threshold energy of the formation of this ion pair is presumed to be the lowest of all possible ion pairs due to thermochemical considerations. This threshold energy cannot be approached using the present monochromator system, but Codling et al. reported that the ion pair generated through only one bond breaking, F^+–CF_3^+, shows the lowest

threshold energy (37.6 eV) for CF_4 [29]. The Cl 2p electron is localized on the Cl atom and some of the highest occupied molecular orbitals are Cl lone pairs [10]. This situation often induces Auger transition within these orbitals, which produces a doubly charged molecular ion in the ground or lower excited states. This molecular ion dissociates to Cl^+ and CF_2Cl^+ without release of a neutral fragment. This supposition agrees with the increase in the branching ratio of Cl^+–CF_2^+, generated through two bond breakings, above the Cl L-edges. This ion pair is probably produced from the doubly charged molecular ion in a relatively low excited state.
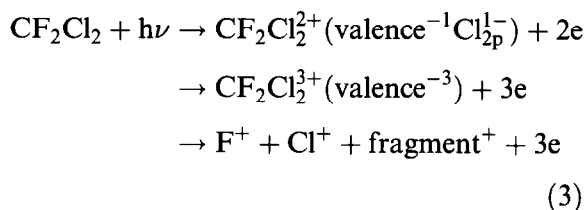
Fig. 3 shows partial yield spectra for ion-pair production around the Cl $L_{2,3}$-edges. The bars with hatching denote the ionization thresholds for Cl 2p electrons, the L_3-edge and L_2-edge. The total ion spectrum has a profile close to that of the photoabsorption spectrum [7,8,10]. The yield curves for C^+–F^+, C^+–Cl^+, F^+–Cl^+, and Cl^+–Cl^+ show similar characteristics to the total yield spectrum. Those for CF^+–Cl^+ and Cl^+–CF_2^+ have a slightly different feature, showing little increase at high Rydberg orbital transitions.

The yield spectrum for Cl^+–CF_2Cl^+ shows a slight increase at the unoccupied molecular orbital excited states and a clear onset near the ionization threshold. This feature probably causes a rise in the branching ratio for this ion pair above the thresholds. The yield curve for Cl^+–$CFCl^+$ exhibits a similar trend to that of Cl^+–CF_2Cl^+, although the curve is not shown here. Those for other ion pairs show a relatively large scatter in signal intensity but a monotonous increase across the Cl $L_{2,3}$-edges.

3.2. C K-edge region

It can be seen in Table 1 that the F^+–Cl^+ ion pair exhibits the highest branching ratio at 290 eV, slightly below the C K-shell excitation energy. The branching ratio for C^+–Cl^+ is the second highest and that for CF^+–Cl^+ is the third. The ratios for F^+–Cl^+ and C^+–Cl^+ become significantly higher at 290 eV than those just above the Cl 2p ionization edges, 216 eV. This large change is probably ascribable to a relative decrease in probability of Cl 2p ionization against valence ionization, and also to double photoionization consisting of electron ejection from the valence orbital and the Cl 2p orbital. The former phenomenon makes the branching ratios become close to those at 198 eV. The latter gives rise to a triply charged molecular ion through an Auger transition, as illustrated below.

$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl_2^{2+}(\text{valence}^{-1}Cl_{2p}^{1-}) + 2e$$

$$\rightarrow CF_2Cl_2^{3+}(\text{valence}^{-3}) + 3e$$

$$\rightarrow F^+ + Cl^+ + \text{fragment}^+ + 3e$$

$$(3)$$

The ratio for CF^+–Cl^+ increased slightly, in comparison with that below the Cl $L_{2,3}$-shell excitation energy, but this ratio decreased slightly from that at 216 eV. The ratio for Cl^+–CF_2^+, which has the fifth highest intensity, decreased by about 3% from that below the Cl $L_{2,3}$-shell transition energy, and show a decrease of about 6% from that just above the Cl 2p edges. The ion pair of Cl^+–CF_2Cl^+ exhibited a sharp decrease in the branching ratio from that at 216 eV. This decrease is probably due to the same reason as that for the increase in the F^+–Cl^+ ratio.

At the energy of the C K-shell to unoccupied molecular orbital excitation (295 eV), branching ratios for several ion pairs did not change, showing similar values to those at 290 eV. Decreases seen are those for CF^+–Cl^+, Cl^+–Cl^+, and Cl^+–CF_2Cl^+. After the excitation of the C K-shell electron, an
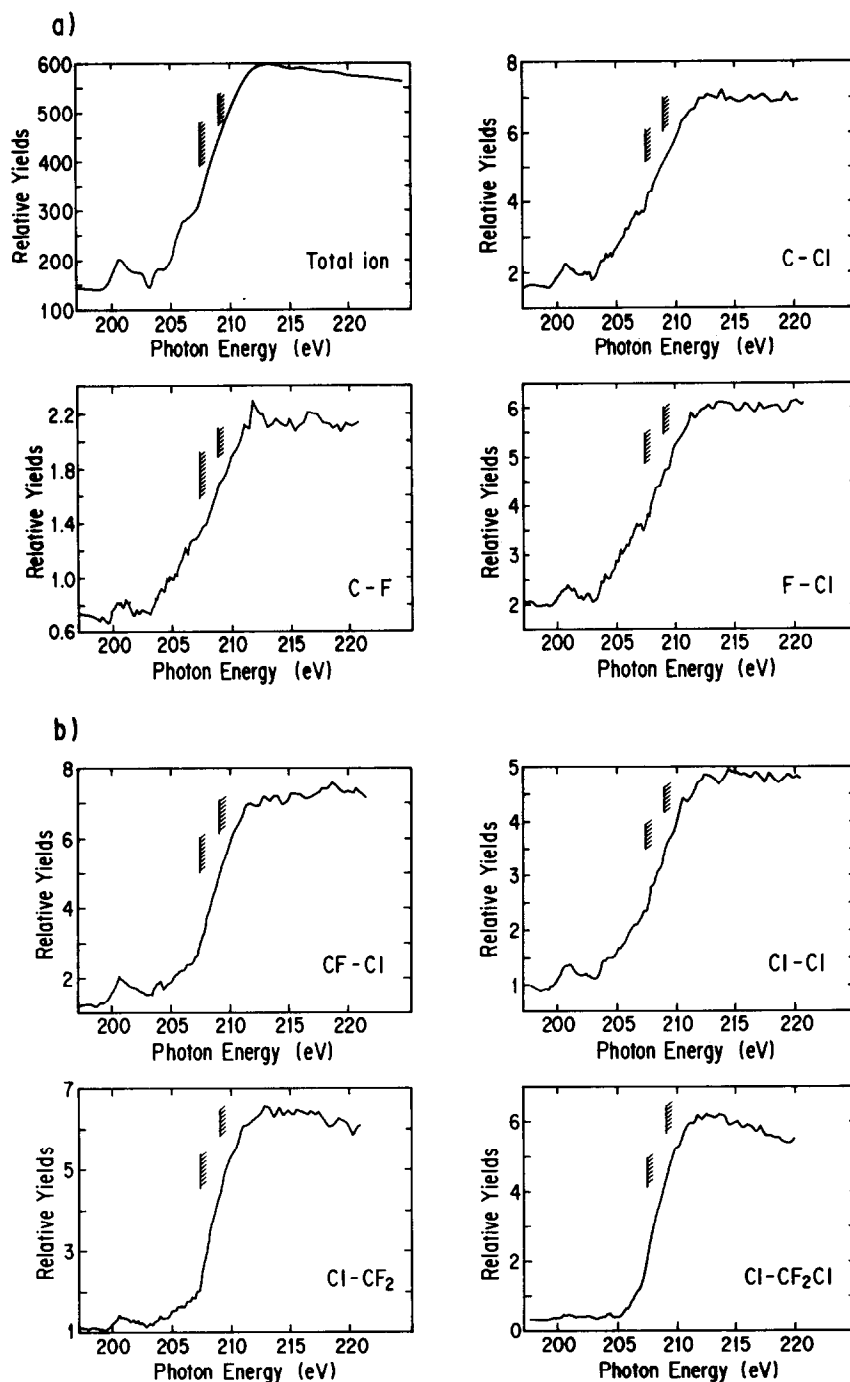
Fig. 3. Partial yield spectra for ion-pair production from CF_2Cl_2 around the Cl 2p ionization thresholds. (a) Total ion, C^+–Cl^+, C^+–F^+, and F^+–Cl^+; (b) CF^+–Cl^+, Cl^+–Cl^+, Cl^+–CF_2^+, and Cl^+–CF_2Cl^+. Total ion denotes the summation of the yields of all ions. Bars with hatching denote the Cl $L_{2,3}$-edges. Note that the lowest figure at each ordinate is not always zero.
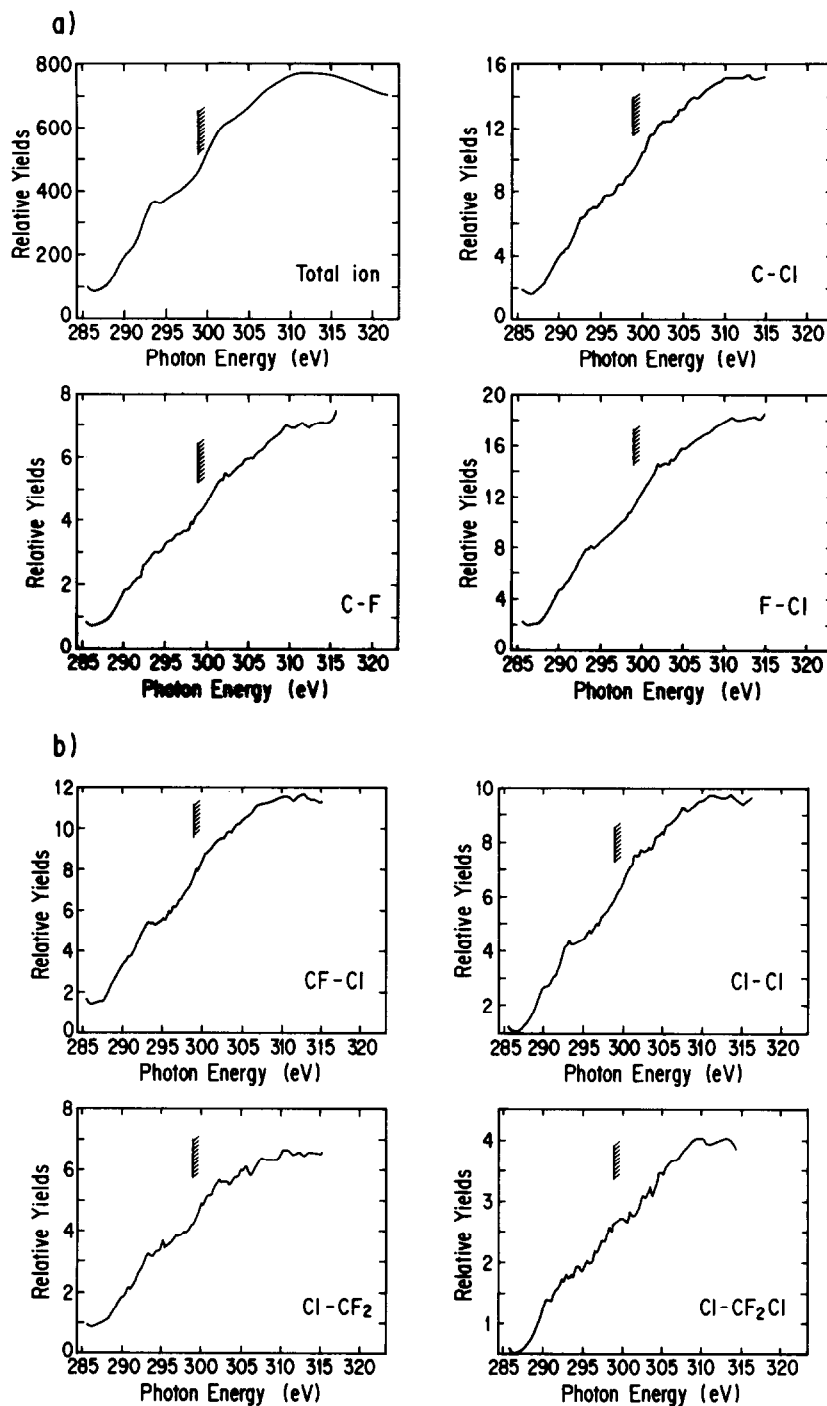
Fig. 4. Partial yield spectra for ion-pair production from CF_2Cl_2 around the C 1s ionization threshold. (a) Total ion, C^+-Cl^+, C^+-F^+, and F^+-Cl^+; (b) CF^+-Cl^+, Cl^+-Cl^+, $Cl^+-CF_2^+$, and $Cl^+-CF_2Cl^+$. Total ion denotes the summation of the yields of all ions. Bar with hatching denotes the C K-edge. Note that the lowest figure at each ordinate is not always zero.

Auger transition takes place, probably yielding a molecular ion having a valence hole in the C–F bonding orbitals and in the C–Cl bonding orbitals. This phenomenon seems to bring about rupture of the C–F bond, causing decreases in the branching ratios for these ion pairs. Above the K-shell ionization edge, 308 eV, branching ratios for all ion pairs are essentially the same as those below this edge.

The partial yield spectra for ion-pair production around the C K-edge are shown in Fig. 4, together with the total ion yield spectrum. (Note that the incident photon intensity monotonously increases with the photon energy in this region.) The total yield shows a spectrum similar to the photoabsorption spectrum [9,10]. The ion pairs having large branching ratios (C^+–F^+, C^+–Cl^+, F^+–Cl^+, CF^+–Cl^+, Cl^+–Cl^+, Cl^+–CF_2^+) exhibit yield curves close to the total yield. The ion pairs with small branching ratios, including Cl^+–CF_2Cl^+, exhibit featureless curves due to appreciable scatter of the measured data. The F^+–CCl^+ ion pair exhibits an intensity increase at the energies of the transition of the K-shell electron to unoccupied molecular orbital and of the shape resonance although the yield curve shows large scattering (not shown here).

3.3. F K-edge region

Branching ratios for ion-pair production near the F K-edge are listed in Table 1. The F^+–Cl^+ ion pair shows the highest branching ratio, about 25%, which is higher than that below the C K-edge. Compared to the branching ratios just above the C K-edge, the feature at the energy below the F K-shell transition, 680 eV, is a decrease in the branching ratios of CF^+–Cl^+, Cl^+–Cl^+, Cl^+–CF_2^+, and Cl^+–CF_2Cl^+. This intensity decrease is mainly compensated by an increase in the branching ratios of C^+–F^+ and F^+–Cl^+.

At the energy of the transition of the F 1s electron to unoccupied molecular orbital (692 eV), the branching ratio for C^+–Cl^+ exhibits an increase of about 1.5% in comparison with that at 680 eV. The ratios for CF^+–Cl^+ and Cl^+–CF_2Cl^+ exhibit a decrease of 1% or more. The decrease in the Cl^+–CF_2Cl^+ branching ratio may be related to a decrease in production of doubly charged low excited-state molecular ions, produced via Auger transition. The increase in the ratios for C^+–F^+ and C^+–Cl^+ probably arises from the phenomenon that the higher the energy the molecule has, the more completely the molecule decomposes.

Above the F K-edge, 720 eV, the branching ratios of C^+–Cl^+ and F^+–Cl^+ increased slightly, compared to those at 692 eV. Those for CF^+–Cl^+ and Cl^+–$CFCl^+$ exhibit a slight decrease. This trend can be explained by an increase in the intensity of F^+ in single-ion measurement [13]. The molecule with a hole at the F atom site probably decays to a molecular ion having valence holes in the C–F bonding orbitals [11]. The molecular ion possibly dissociates to F^+, an ionic fragment and neutrals. The probability of maintaining the C–F bond is presumed to be lowered.

Fig. 5 shows partial yield spectra for ion-pair production around the F K-edge, together with the total yield spectrum. The total yield spectrum is very similar to the inner-shell excitation spectrum [10]. The partial yield curves for C^+–F^+, F^+–Cl^+, and Cl^+–Cl^+ show essentially the same characteristics as those of the total yield, although the signals flucutate noticeably. The yield spectra for C^+–Cl^+, CF^+–Cl^+, and Cl^+–CF_2^+ show the highest intensities at the ionization threshold, and are different from those of the total ion. This finding suggests that the yields of these ion pairs are larger just above the threshold than at the excitation energies of F_{1s} electrons to unoccupied molecular orbitals. The curve for
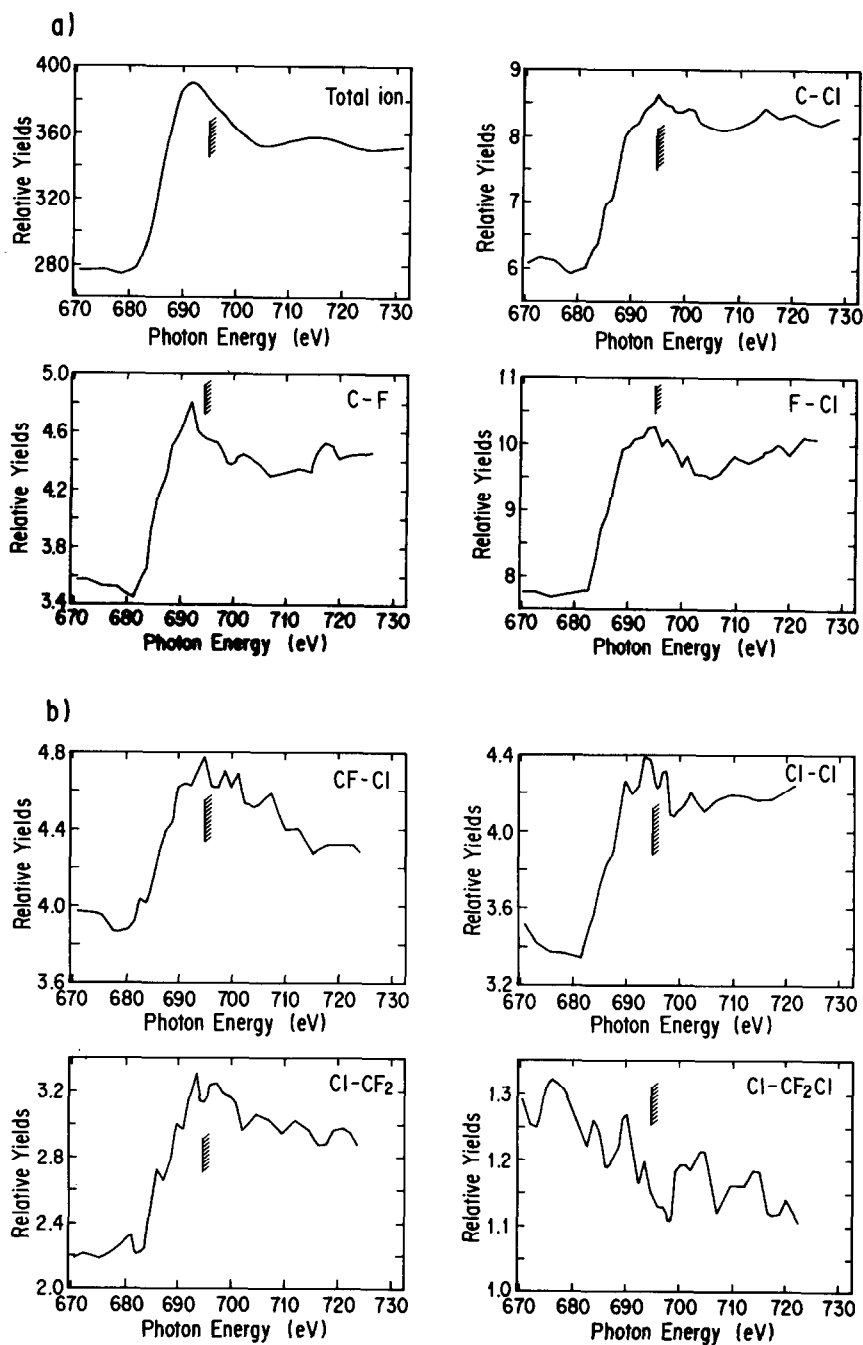
Fig. 5. Partial yield spectra for ion-pair production from CF_2Cl_2 around the F 1s ionization threshold. (a) Total ion, C^+-Cl^+, C^+-F^+, and F^+-Cl^+; (b) CF^+-Cl^+, Cl^+-Cl^+, $Cl^+-CF_2^+$, and $Cl^+-CF_2Cl^+$. Total ion denotes the summation of the yields of all ions. Bar with hatching denotes the F K-edge. Note that the lowest figure at each ordinate is considerably higher than zero.

Cl^+–CF_2Cl^+ features a constantly decreasing intensity across the F K-edge. The yield for Cl^+–$CFCl^+$ exhibits an intensity increase at the transition energies to the unoccupied molecular orbitals although the measured data show large scattering (not shown here). The spectra for F^+–F^+ and F^+–CF^+ show little change in this energy region.

3.4. Relative weight of double photoionization in the production of each fragment ion

A few doubly charged fragment ions were produced with very small probabilities in the photoexcitation of CF_2Cl_2, over the soft X-ray range [13]. If only double photoionization occurs and two singly charged fragments are produced at a certain photon energy, then half of the sum of the branching ratios of ion-pair production for a specified fragment ion can be approximated by the branching ratio for this fragment ion in single-ion measurement, as shown in Eq. (4).

$$B.R.(A) = 1/2 \sum_B I.P.B.R.(A-B) \qquad (4)$$

In this equation, B.R.(A) denotes the branching ratio for fragment A in single-ion measurement, I.P.B.R.(A–B) indicates the branching ratio for the ion pair A–B, and Σ_B denotes the summation of all fragment ions having the A ion as a partner. When single photoionization is the dominant process, i.e. below the Cl $L_{2,3}$-edges, Eq. (4) does not hold; the value of the right-hand term is larger than that of the left-hand term for some ions and the reverse is true for other ions. When a certain fragment ion is produced mainly through single photoionization, this ion should have a larger value for the left-hand term than that of the right hand. The fragment ion produced mainly through double photoionization exhibits a smaller value for the left hand than that of the right hand. Thus it is interesting to calculate the summation of the branching

ratios of ion-pair production for each ion and to compare it with that obtained by single-ion measurement.

Table 2 lists the branching ratios for fragment ions of CF_2Cl_2, both observed using the single-ion technique [13] and calculated from those of ion-pair production. Below the Cl 2p electron transition energy, 198 eV, the single ionization mainly occurs and double ionization is presumed to be the less important process. The calculated branching ratios for Cl^+, F^+, and C^+ are considerably larger than the measured data, whereas the calculated ratio for CF_2Cl^+ is much smaller than that measured by the single-ion technique. Other ions such as CF^+ have a smaller calculated value than a measured value. Since the fragment ion $CFCl_2^+$ was detected at a very low intensity using the photoion–photoion coincidence technique, this ion has a value of essentially zero for the calculated branching ratio. It is discovered that atomic ions such as Cl^+ are produced largely through double photoionization.

At a photon energy of 201 eV (Cl 2p → unoccupied molecular orbitals), the trend shown in Table 2 is not very different from that at 198 eV. The atomic ions exhibit larger values when calculated from ion-pair production than they do from single-ion measurement. The difference between calculated and measured values becomes larger for the ions of CCl^+ and CF_2^+ than that at 198 eV.

Above the Cl 2p ionization threshold, 216 eV, the difference between calculation and measurement becomes smaller, only a few percent or less. The atomic ions, C^+ and F^+, still exhibit larger calculated values than those measured. The fragment ions, Cl^+, CF^+, CF_2^+, and $CFCl^+$, have essentially the same values from calculation and measurement, and these ions are produced mainly through double photoionization at this excitation

Table 2
Comparison of measured[a] and calculated (values in parentheses)[b] branching ratios of fragment ions from CF_2Cl_2

Energy (eV)	C^+	F^+	CF^+	Cl^+	CCl^+	CF_2^+	$CFCl^+$	CF_2Cl^+	$CFCl_2^+$
198	7.3	9.2	9.2	40.0	5.1	7.6	3.7	14.1	3.9
	(12.9)	(19.4)	(7.6)	(47.8)	(1.9)	(6.1)	(2.4)	(1.8)	(< 0.2)
201	9.6	8.8	10.6	43.7	5.8	8.5	2.4	8.6	2.1
	(12.7)	(17.4)	(9.4)	(49.4)	(1.6)	(5.8)	(2.0)	(2.0)	(< 0.2)
216	7.6	6.9	8.8	51.6	3.1	7.2	2.6	11.7	0.6
	(10.6)	(11.9)	(9.0)	(51.3)	(0.9)	(7.4)	(2.2)	(6.9)	(< 0.2)
290	10.0	11.6	8.1	53.0	2.8	4.9	1.8	7.3	0.4
	(13.6)	(18.4)	(8.5)	(49.9)	(0.8)	(4.5)	(1.1)	(3.0)	(< 0.1)
295	10.9	13.0	8.7	52.6	3.8	3.6	1.5	5.5	0.3
	(14.1)	(19.2)	(8.0)	(49.0)	(1.2)	(4.9)	(1.1)	(2.6)	(< 0.1)
308	10.8	13.5	8.0	52.6	3.2	4.3	1.2	6.1	0.2
	(14.2)	(19.4)	(8.3)	(49.2)	(1.0)	(4.3)	(0.9)	(2.6)	(< 0.1)
680	12.5	15.8	7.5	51.1	2.8	3.8	1.2	5.0	0.2
	(15.6)	(22.8)	(7.2)	(46.9)	(1.0)	(3.7)	(0.9)	(2.1)	(< 0.1)
692	13.8	17.0	7.7	51.0	4.3	2.0	1.3	2.6	0.3
	(16.6)	(23.3)	(6.6)	(46.1)	(1.2)	(3.8)	(0.9)	(1.5)	(< 0.1)
720	14.3	17.7	7.2	49.4	5.0	2.2	1.1	2.7	0.3
	(16.6)	(23.4)	(6.3)	(46.3)	(1.3)	(3.8)	(0.8)	(1.4)	(< 0.1)

[a] Measured data from Ref. [13]. Note that all values here shown sum to 100% for each photon energy.

[b] Calculated values are from the branching ratios observed with the selected photoion–photoion coincidence technique.

energy. The CF_2Cl^+ ion is produced mainly through single ionization.

In the energy region close to the C K-edge the single ionization of a valence electron may be considered as a negligibly important process, because the cross-section for this type of transition becomes much smaller than those for inner-shell transitions, owing to the excitation energy being far away from valence ionization thresholds. A difference between the left-hand value and that of the right hand in Eq. (4) probably originates from triple ionization, i.e. production of three singly charged fragments. The three fragment ions can contribute to three types of ion–ion coincidence signals although the two fragment ions from double photoionization provide only one coincidence signal. Therefore triple photoionization yields a larger value for the right-hand term, the calculated value, than the value found by single-ion measurement.

At an excitation energy of 290 eV, the difference between calculation and measurement is most noticeable for F^+ (Table 2). This ion exhibits a much larger calculated value and this suggests that F^+ is produced substantially through triple ionization. At about 100 eV above the ionization threshold, a photoionization shake-off process takes place to a large extent for many atoms and molecules [12,13,24,30]. In CF_2Cl_2, the photoionization shake-off probably yields a doubly charged molecular ion with a valence hole and a Cl L-shell hole around 290 eV. This ion becomes triply charged through Auger transition, and the resultant molecular ion decomposes to three ionic fragments (see Eq. (3)). A double Auger transition occasionally happens after inner-shell ionization and the molecule becomes a triply charged ion. The probability that the final state of the fragment ion is doubly charged is very low because single-ion measurement showed low yields for doubly charged fragments in the photo-excitation of CF_2Cl_2; 3% or less below the F K-edge [13].

The branching ratios calculated for many fragment ions are similar to those obtained by measurement. The calculated ratios for Cl^+, CCl^+, and CF_2Cl^+ are smaller, while the calculated ratios for C^+ and CF^+ are slightly larger than those obtained by measurement. The ions of the latter group are presumed to be produced to a certain extent by triple photoionization; the partners are probably two F^+ ions.

At the energy of the transition of the C 1s electron to an unoccupied molecular orbital (295 eV), the trend in the difference between calculation and measurement is similar to that at 290 eV. The calculated branching ratio for F^+ is larger than the measured value. Those for C^+ and CF_2^+ are slightly larger, but those for the other ions are smaller than the measured values. When the excitation energy becomes greater than the C K-edge, the trend in the difference is close to that at 295 eV.

Just below the energy of the F 1s electron transition, 680 eV, the branching ratio for F^+ calculated from the data for ion-pair production is larger by 7% than that obtained by single-ion measurement. The triple photoionization process probably contributes to the production of F^+ here. The calculated ratio for C^+ is larger, while those for Cl^+, CCl^+, and CF_2Cl^+ are smaller than the measured ones.

At the energy of the transition of the F 1s electron to an unoccupied molecular orbital (692 eV) and above the F 1s ionization threshold, 720 eV, the trend in the difference between calculated and measured values is similar to that at 680 eV. However, the difference between calculation and measurement was larger for CCl^+, becoming smaller for C^+, F^+, and Cl^+. The relative importance of triple ionization for C^+ and F^+ yields becomes lower than that below the F 1s transition energy. The calculated branching ratio for CF_2^+ showed higher values at 692 and 720 eV than those observed. Triple ionization contributes substantially to the formation of CF_2^+ in the instance of F 1s excitation.

4. Summary

Ion-pair production from CF_2Cl_2 photoexcited around the Cl $L_{2,3}$-edges, the C K-edge, and the F K-edge has been observed using the selected photoion–photoion coincidence technique. The F^+–Cl^+ ion pair was the most intense at all the excitation energies except at 216 eV. At most energies the C^+–Cl^+ ion pair was the second most intense. The branching ratios for ion-pair production changed significantly near the Cl $L_{2,3}$-edges, especially that for Cl^+–CF_2Cl^+ which exhibited a change from about 4% below these edges to about 14% above them. The ratios, however, showed little variation around the C K-edge and the F K-edge. These findings suggest that excitation of the shallowest inner-shell electrons plays a critical role in ion-pair formation related to double photoionization of the molecule, whereas that of deeper-shell electrons has little effect on ion-pair formation.

Acknowledgments

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