

7. Poster Presentation (1)

7.1 Variation in Yield Ratios of Fragment Ions and of Ion-pairs from CF_2Cl_2 Following Monochromatic Soft X-ray Absorption

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Abstract Fragment ions produced from CF_2Cl_2 have been measured from 44 to 1200 eV using a time-of-flight mass spectrometer and monochromatized synchrotron radiation. Positively charged ion pairs from this molecule were observed in the inner-shell excitation regions using a Selected photoion-photoion coincidence technique. Obtained yield ratios of fragment ions indicate that the atomic chlorine ion, Cl^+ , has the greatest intensity at all photon energies above 60 eV and exhibits a steep increase at the $\text{Cl L}_{2,3}$ -edges. Some fragment ions, in particular CF_2^+ , have a clear intensity increase at the transitions of inner-shell electrons to unoccupied molecular orbitals. The ion pair $\text{F}^+ - \text{Cl}^+$ exhibits the highest yield at most photon energies, and some of the branching ratios for ion-pair production changed significantly near the $\text{Cl L}_{2,3}$ -edges.

INTRODUCTION

When a molecule is irradiated with a soft X-ray, an inner-shell electron in the molecule is excited to unoccupied molecular orbitals, Rydberg orbitals or ionized continuum. Produced inner-shell holes are usually filled through the Auger transition, and the molecule turns into a highly excited molecular ion. Then the molecular ion decomposes to ionic fragments. Since the core hole is strongly localized around the particular atom, core-electron excitation in the molecule is expected to result in selective bond breaking. Several studies were carried out for understanding this site-selective reaction in molecules excited in core-hole states (Nagaoka et al., 1993). Since the molecule CF_2Cl_2 has three inner-shells in the soft X-ray region, it is very interesting to examine the fragmentation pattern of this molecule photoexcited using monochromatic soft X-rays. On the other hand, ionic fragmentation was studied in the vacuum ultraviolet radiation region, indicating that CF_2Cl^+ has the highest yield (Zhang et al., 1991). Inner-shell excitation spectra were also reported to show some pre-edge structures and ionization continuum transition (Chen and Sette, 1990 and Zhang et al., 1992). In the present study, ionic products from CF_2Cl_2 following selective inner-shell excitation have been measured using a time-of-flight (TOF) mass spectrometer and monochromatized synchrotron radiation.

EXPERIMENTAL

Synchrotron radiation from the electron storage ring at the Electrotechnical Laboratory was dispersed using a Grasshopper monochromator in the soft X-ray region (Saito et al., 1994, Suzuki et al., 1994a and Suzuki et al., 1994b). In order to reduce the stray light and higher-order contributions, the energy for the electron beam in the storage ring was appropriately selected and thin films of Be, Al, In and mylar were inserted into the soft X-ray beam. The monochromatic soft X-ray beam crossed an

effusive beam of the sample gas at right angles in the center of the TOF spectrometer. The electrons and ions produced were extracted in opposite directions and detected with micro-channel plates. The electric field applied at this center was set to be 80 V/mm in order to collect ions of all kinetic energies.

The spectrometer was operated in two measurement modes; TOF mass spectrum mode and Selected photoion-photoion coincidence (PIPICO) spectrum mode. In the TOF mode, two time-to-amplitude converters (TAC's) were used for minimizing detection loss of heavier fragment ions because two ionic products are usually formed in the present photon energies and because the conventional technique usually detects only lighter fragment ions. In the Selected PIPICO mode, the conventional PIPICO technique was modified for obtaining a well separated PIPICO peak for each ion-pair. A gating signal was supplied to the TAC for selecting a particular fragment ion as the lighter partner of ion pairs.

RESULTS AND DISCUSSION

1) Time-of-flight spectra

Figure 1 shows TOF spectra of CF_2Cl_2 measured at photon energies of 50, 220, 320 and 800 eV. These photon energies correspond to those being capable to induce ionizations of only valence electron, Cl 2p electron, C 1s electron and F 1s electron, respectively. The parent molecular ion CF_2Cl_2^+ was not observed here, which agrees with the result by Zhang et al. (1991). Since natural chlorine atom consists of two main stable isotopes, the peaks for the ions including one or two atoms are split into two or three components. The relative intensities of the peaks change dramatically with photon energy over this energy range. The widths of the peaks increase at higher photon energies, and this increase results from a greater release of kinetic energy in the ionic fragmentation of CF_2Cl_2 at the higher photon energies. Yield ratios for the production of fragment ions were determined from the areas of the peaks in the TOF mass spectra measured over the energy range 44–1200 eV (Suzuki et al., 1994a).

2) Selected photoion-photoion coincidence spectra

For ion-pair production from CF_2Cl_2 , the Selected PIPICO technique was used. Typical examples of ion-ion coincidence spectra are shown in Fig. 2 for a photon energy of 214 eV. The conventional PIPICO spectrum is shown at the top panel of Fig. 2, where a number of structures are found in the difference spectrum of flight times. When we focused on the fragment ion C^+ as a lighter ion (faster ion), the spectrum measured with the Selected PIPICO is shown in Fig. 2 (b). The spectrum indicates the presence of $\text{C}^+ - \text{F}^+$ and of $\text{C}^+ - \text{Cl}^+$ clearly. Since the photon energy is above the Cl L_{2,3}-edges, it is natural that the intensity of $\text{C}^+ - \text{Cl}^+$ is considerably higher than that

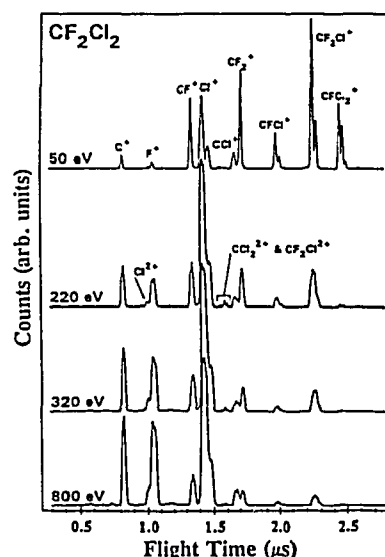


Fig. 1 Time-of-flight spectra of CF_2Cl_2 measured with some photon energies.

of $C^+ - F^+$. The central panel of the figure, Fig. 2 (c), depicts the Selected PIPICO spectrum when F^+ was selected, where the ion-pair of $F^+ - Cl^+$ has the highest intensity. The Selected PIPICO spectra for the selection of CF^+ and Cl^+ are given in Fig. 2 (d) and (e), respectively. As described here, the Selected PIPICO technique provides a clear spectrum in which we can easily assign each peak to the corresponding ion pair (Suzuki et al., 1994b).

3) Yield ratios of fragment ions

Yield ratios of fragment ion production are shown as a function of photon energy in Fig. 3 (a) and (b) (Suzuki et al., 1994a). Molecular ions composed of 3 and 4 atoms have high yield ratios below 100 eV but show a steeply decreasing trend with increasing photon energy below the Cl L_{2,3}-edges. The atomic ions have the yield ratios exhibiting a significantly increasing curve below these edges. The ratio of Cl^+ suddenly increases at these edges, but that of F^+ shows a drop at these edges and a considerable increase at the F K-edge.

It is interesting to note that the yield ratios of molecular ions decrease below the Cl L_{2,3}-edges and that those of atomic ions increase. This phenomenon probably originates from fragmentation pathways which become open at or above excitation energies of 50 eV. These pathways are presumably connected to excited states involving two valence electrons. A molecular ion with two holes in the valence shell has a greater probability of yielding a higher degree of fragmentation than the one with only a single valence hole.

Sharp changes in the yield ratios of the fragment ions across the inner-shell ionization edges may result from the different relative probabilities of two valence hole states being populated by double valence

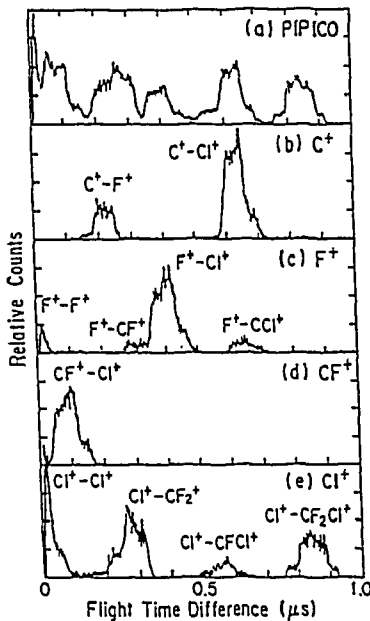


Fig. 2 Spectra of difference of flight times between fragment ions produced from CF_2Cl_2 using the Selected PIPICO technique.

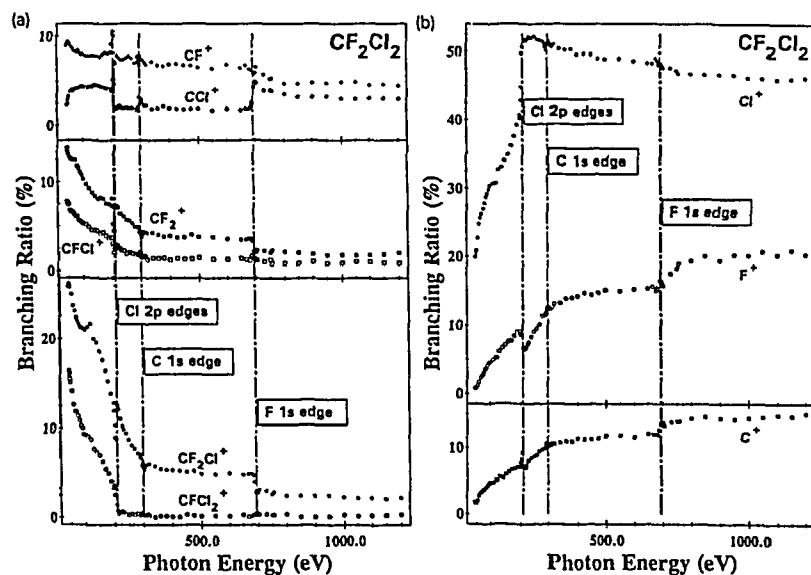


Fig. 3 Yield ratios of the fragment ions of CF_2Cl_2 over the photon energy range of 44 to 1200 eV. (a) Molecular ions. (b) Atomic ions.

excitation or by the Auger decay of a core hole. The valence orbitals holding the spatial overlap with the core-hole have a greater probability of being involved in the Auger transition. Then the excitation of Cl 2p electron tends to bring about the bond breaking near the Cl atom, i.e. the Cl⁺ has a higher probability to be produced. A similar effect is found through the increase in the yield ratio of F⁺ around the F K-edge, as shown in Fig. 3.

Measured partial yield spectra for fragment ions around inner-shell ionization edges show that atomic ions have a spectrum close to the total ion curve, which approximates the photoabsorption spectrum (Chen and Sette, 1990 and Zhang et al., 1992). The fragment ions CF₂⁺ and CF⁺ show a large peak at the excitation of Cl 2p electron into the unoccupied molecular orbital, 13a₁. The CFCI₂⁺ has a constantly decreasing curve across the Cl L_{2,3}-edges, indicating no production of this ion through the Cl 2p electron transition. The feature in the partial yield curves around the C K-edge is that the CFCI₂⁺ exhibits a broad peak at the excitation into the molecular orbitals of 7b₁+14a₁. The ions CF₂Cl⁺ and CF₂⁺ have partial yield spectra of constantly decreasing intensity around the F K-edge.

4) Yield ratios of ion-pairs

Yield ratios obtained at several photon energies are listed in Table 1 (Suzuki et al., 1994b). The ion pair F⁺ - Cl⁺ has the highest yield ratios at all the photon energies except 216eV, slightly above the Cl L_{2,3}-edges, and C⁺ - Cl⁺ shows the second highest. The most interesting finding is that the ratio of Cl⁺ - CF₂Cl⁺ exhibits a sharp increase at 216eV. This phenomenon is presumed to come from the following. The Auger transition following the Cl 2p electron ionization yields a number of low excited states of doubly charged molecular ions. These ions decompose to fragment ion pairs with a single bond breaking. If the molecular ion is produced in a highly excited state, the decomposition should take place more completely; Lower yield of the Cl⁺ - CF₂Cl⁺ and higher yield of the ion-pairs composed of only atomic ions are expected than the measured results. This presumption is supported by the increase in the yield ratio of Cl⁺ - CF₂⁺ at 216eV. It is desirable that the Auger electron spectra are precisely measured from the inner-shell hole states of interest in the near future. The ion-pairs including F⁺ show an increase in the yield ratio near the F 1s electron excitation. This finding is interpreted as a site specific effect; The chemical bond around the fluorine atom is loosened to break and the atomic fluorine ion is yielded largely.

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. The spectra for many ion pairs show a similar curve to the photoabsorption spectra (Chen and Sette, 1990 and Zhang et al., 1992). Some spectra, however, exhibit a feature different from the photoabsorption; Relative intensity of excitation into unoccupied molecular orbitals, compared to that of ionization, is very low for Cl⁺ - CF₂Cl⁺ near the Cl L_{2,3}-edges, for Cl⁺ - CF₂⁺ near the F K-edge. The yield of Cl⁺ - CF₂Cl⁺ shows a constantly decreasing trend near the F K-edge, indicating no production of this ion pair through the F 1s electron transition.

Table 1. Yield ratios (%) of ion-pair production from CF_2Cl_2 photoexcited around the inner-shell ionization thresholds. U denotes unoccupied molecular orbitals.

Energy	C-F	C-Cl	F-Cl	CF-Cl	Cl-Cl	Cl-CF ₂	Cl-CF ₂ Cl
198	7.8	17.9	22.2	13.9	10.5	12.2	3.6
201(Cl _{2p} ⁻¹ U)	6.8	18.6	20.3	17.2	11.4	11.7	4.1
216	4.9	16.2	14.0	16.8	11.2	14.9	13.7
290	8.4	18.9	22.4	15.6	12.8	8.9	6.1
295(C _{1s} ⁻¹ U)	8.7	19.5	22.8	14.7	11.9	9.7	5.2
308	8.9	19.5	23.1	15.1	12.5	8.6	5.2
680	11.6	19.7	25.6	12.8	11.1	7.4	4.2
692(F _{1s} ⁻¹ U)	12.1	21.0	25.5	11.7	10.7	7.7	3.0
720	11.7	21.4	25.9	11.3	10.9	7.6	2.9

CONCLUSIONS

Variation in yield ratios of fragment ions and ion-pairs from CF_2Cl_2 have been found around the Cl L_{2,3}-edges, the C K-edge and the F K-edge. The yield ratio of Cl⁺ increases steeply at the C L_{2,3}-edge, and F⁺ exhibits an increase above the F K-edge. The yield ratio of Cl⁺ - CF₂Cl⁺ shows a significant change near the Cl L_{2,3}-edges.

REFERENCES

- Chen C. T. and Sette F. (1990) High resolution soft X-ray spectroscopies with the Dragon beam line. *Physica Scripta* **T31** 119.
- Nagaoka S., Oshita J., Ishikawa M., Masuoka T. and Koyano I. (1993) Ionic fragmentation processes following Si : 2p core level photoexcitation and photoionization of 1, 1, 1-trimethyltrichlorodisilane. *J. Phys. Chem.* **97** 1488.
- Saito N., Bozek J. D. and Suzuki I. H. (1994) Ionic fragmentation of CF₄ in the vacuum ultraviolet through the soft X-ray region. *Chem. Phys.* (in press).
- Suzuki I. H., Bozek J. D. and Saito N. (1994) Ionic dissociation of CF₂Cl₂ photoexcited using monochromatic soft X-rays. *Chem. Phys.* **182** 81.
- Suzuki I. H., Saito N. and Bozek J. D. (1994) Variation in ion-pair yields from CF₂Cl₂ photoexcited in the inner-shell excitation regions. *Int. J. Mass Spectrom. Ion Processes* (in press).
- Zhang W., Cooper G., Ibuki T. and Brion C. E. (1991) Excitation and ionization of freon molecules. III. Absolute oscillator strengths for the photoabsorption (8.5-200eV) and the ionic photofragmentation (11.5-70eV) of CF₂Cl₂. *Chem. Phys.* **151** 357.
- Zhang W., Ibuki T. and Brion C. E. (1992) Absolute dipole differential oscillator strengths for inner shell spectra from high resolution electron energy loss studies of the freon molecules CF₄, CF₃Cl, CF₂Cl₂, CFCl₃ and CCl₄. *Chem. Phys.* **150** 435.