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To cite this article: K Okada *et al* 2011 *J. Phys.: Conf. Ser.* **288** 012021

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Dissociative photoionization of perfluorocyclobutane and *cis*-1,1,2,2,3,4-hexafluorocyclobutane

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Abstract. Ion yield spectra produced by the photoionization of perfluorocyclobutane (*c*-C₄F₈) and *cis*-1,1,2,2,3,4-hexafluorocyclobutane (*cis*-*c*-C₄H₂F₆) have been measured in the photon energy range of 25–170 eV. For the *c*-C₄F₈ photoionization, the C₃F₅⁺ and C₂F₄⁺ fragments are most abundant at all the energies, but the yields decline with the energy, giving at 170 eV about 30% of the yields at 30 eV. The C₃H₂F₃⁺ and C₂HF₃⁺ ions are the most dominant fragments for the *cis*-*c*-C₄H₂F₆ photoionization, with their yield curves similar to the C₃F₅⁺ and C₂F₄⁺ counterparts for *c*-C₄F₈, respectively. Photoelectron–photoion–photoion coincidence spectra were also acquired to study the breakdown pathways.

1. Introduction

Molecular photoionization and ionic fragmentation processes are of fundamental importance in the upper-atmospheric chemistry and plasma physics. Perfluorocyclobutane (*c*-C₄F₈, FC-c318) is extensively used as a reagent for dry etching of semiconductors. However, the use of the gas in industry has atmospheric implications for global warming because *c*-C₄F₈ has a high global warming potential (GWP) of 8700 [1]. The estimated atmospheric lifetime depends on the sink mechanism: Ravishankara *et al* [2] reported that the lifetime of this molecule in the atmosphere is 3200 years. Later, Morris *et al* [3] argued that it is reduced to 1400 years if considering the atmospheric removal of *c*-C₄F₈ by electron interactions. The knowledge of its chemical processes in the upper atmosphere is eagerly required to evaluate the GWP of *c*-C₄F₈.

The photochemical process of *c*-C₄F₈ has not been fully established yet. Tuckett's group [4,5] reported the threshold photoelectron and threshold-photoelectron–photoion coincidence (TPEPICO) spectra of *c*-C₄F₈ in the photon energy range of 10–27 eV. Ion yield curves and branching ratios were

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determined for the C_3F_5^+ , C_2F_4^+ , CF_3^+ , CF_2^+ and CF^+ fragment ions. More recently, Limão-Vieira *et al* [6] studied the electron spectroscopy of *c*- C_4F_8 and derive a precise value of 12.291 eV for the vertical ionization energy. As far as we are aware, however, no study has been reported on the ion yield curves above 27 eV. We therefore measured in this study the yield spectra of the fragment ions produced by the photoionization of *c*- C_4F_8 in the 25–170 eV region. The region covers the multiply-charged molecular states, because the appearance energy for the *c*- $\text{C}_4\text{F}_8^{2+}$ ion is estimated as ~ 34 eV according to the rule of thumb given in ref. [7].

In recent years, significant effort has been devoted to develop the most promising alternative chemicals to perfluorocarbons (PFCs) for etching and chamber cleaning processes. While a practical use in semiconductor device fabrication requires good etching characteristics of the alternatives comparable to the PFCs as well as lower cost, the alternatives have short atmospheric lifetime and low GWP. Thus, we also carried out the same measurements for *cis*-1,1,2,2,3,4-hexafluorocyclobutane (*cis*-*c*- $\text{C}_4\text{H}_2\text{F}_6$, HFC-c336ee), a candidate for replacing *c*- C_4F_8 , to provide the photochemical data.

In addition, ion pairs originating from charge separation of the multiply-charged molecular ions were detected with a photoelectron-photoion-photoion coincidence (PEPIPICO) technique to obtain information on the breakdown pathways. A demonstration of this technique for the *c*- $\text{C}_4\text{F}_8^{2+}$ dissociation was given by Hsieh and Eland [8], but was illustrated only for the reaction *c*- $\text{C}_4\text{F}_8^{2+} \rightarrow \text{CF}_3^+ + \text{C}_2\text{F}_4^+ + \text{CF}$ at 30.4 nm; The PEPIPICO spectrum itself has already been provided in an earlier, separate paper [9]. A more detailed investigation is necessary for discussing the breakdown pathways.

The next section describes our experimental setup and methods. We then discuss the ion yields obtained by the dissociative photoionization of *c*- C_4F_8 and *cis*-*c*- $\text{C}_4\text{H}_2\text{F}_6$. Several breakdown pathways are deduced from their PEPIPICO spectra. Finally, we summarize the conclusions of this study.

2. Experimental

The experiments have been performed on the beamline BL2B at the UVSOR facility, Institute for Molecular Science in Japan. The experimental setup has been described in previous papers [10,11], except a minor change for the purpose of this study: A thickness monitor was removed and a needle for gas inlet was installed. Synchrotron radiation was irradiated at right angles to the effusive beam of the sample gas. Fragment ions produced in the ionization region were extracted toward a time-of-flight (TOF) spectrometer by a pulsed electric field applied at its extractor plate. A microchannel plate (MCP) operated in pulse-counting mode served for the detection of the ions. The pulse and ion-detection signals were fed into the start and stop inputs of a multi-stop time-to-digital converter (FAST ComTec, model P7888), respectively, to record the TOF signals. Partial ion yield (PIY) spectra were obtained by measuring a series of TOF spectra while scanning the photon energy. The spectra were obtained over the energy range of 25–170 eV which can be covered by three gratings installed on the beamline [12]. Ion signal counts were integrated over the respective TOF mass peaks. The integrated ion counts were normalized with the fluxes of synchrotron radiation at the each photon energy.

Breakdown pathways of the multiply-charged molecular ions were also investigated by applying a PEPIPICO technique for detecting a pair of fragment ions resulting from the same ionization event. In this measurement mode continuous electrostatic field was applied over the ionization region. Emitted electrons were detected with another MCP which was set in the opposite direction to the ion TOF tube. The start of the multi-stop time-to-digital converter was triggered by the electron signals instead of the electric pulses.

The chemicals *c*- C_4F_8 and *cis*-*c*- $\text{C}_4\text{H}_2\text{F}_6$ for this study were purchased from SynQuest Laboratories, Inc. The sample of *c*- C_4F_8 was used as provided while that of *cis*-*c*- $\text{C}_4\text{H}_2\text{F}_6$ was carefully degassed under vacuum by repeated freeze–pump–thaw cycles before use. The pressure in the chamber during the measurements was kept at $\sim 2 \times 10^{-6}$ Torr (1 Torr = 133.2 Pa).

3. Results and discussion

TOF spectra were measured to study the yield of fragment ions formed by the VUV photoabsorption.

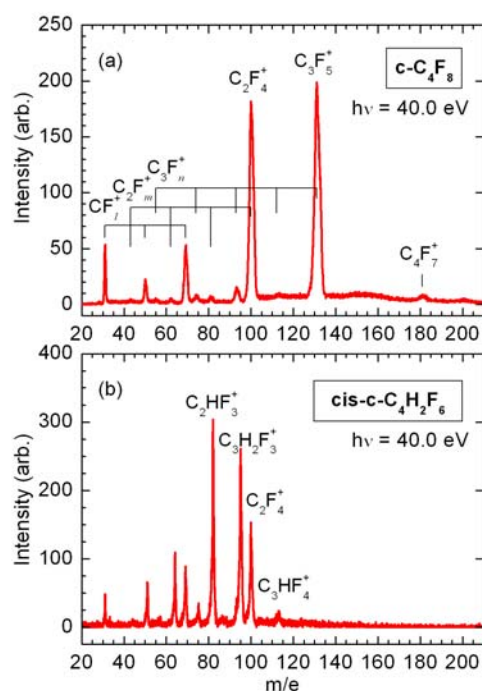


Figure 1. Typical mass spectra obtained by the photoionization of (a) *c*-C₄F₈ and (b) *cis-c*-C₄H₂F₆ measured at 40.0 eV. Virtually no peaks are seen in the range $m/e \leq 20$.

Figure 1a displays a typical mass spectrum measured at 40.0 eV. The abscissa has been converted from the flight time of ions to the mass/charge ratio. A variety of fragment ions were detected, i.e., CF_l^+ ($l = 1-3$), $C_2F_m^+$ ($m = 1-4$), $C_3F_n^+$ ($n = 1-5$) and $C_4F_7^+$. This is in accordance with the results by Eland *et al* (figure 3a of ref. [9]). However, it is slightly different from the report by Jarvis *et al* [4], in which $C_4F_7^+$ could not be detected by the measurement of TPEPICO spectra acquired at photon energies of 10–27 eV. The production of $C_4F_7^+$ is reasonable as observed in this study, if we consider the fragmentation of other perfluorocarbon compounds, for example, perfluoro-2-butene (2-C₄F₈) [4].

Figure 2 gives PIY curves of the fragment ions. A reasonable agreement is obtained between the curves in the regions which two gratings can cover. While the $C_3F_5^+$ and $C_2F_4^+$ fragments are most

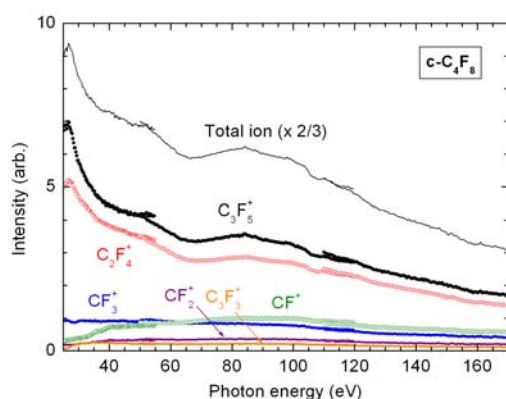


Figure 2. Partial ion yield curves of the fragment ions produced by the photoionization of *c*-C₄F₈. The total ion yield is also shown and is scaled by two-thirds.

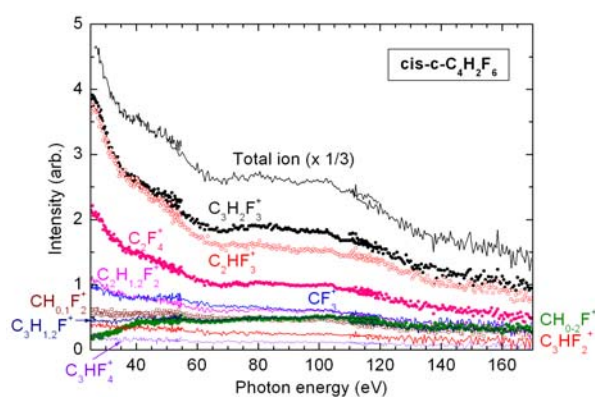


Figure 3. Partial ion yield curves of the fragment ions produced by the photoionization of *cis-c*-C₄H₂F₆. The total ion yield is also shown and is scaled by a third.

abundant at all the energies studied here, the yield of these ions decreases greatly with the photon energy. The yield at 170 eV becomes about 30% of that at 30 eV. The yield of CF_3^+ gives an approximately constant value up to 55 eV and decreases monotonically at the higher energies. The yield of CF^+ increases with the photon energy up to ~ 90 eV and then gradually decreases. Table 1 summarizes the branching ratio of the fragment ions at selected excitation energies. The ions are listed in order of abundance at 30.0 eV. Relative increase of the CF^+ and C_3F_2^+ ion yields is found with the energy. This indicates that at higher energies the larger C_3F_5^+ and C_2F_4^+ fragments further decompose to emit F atoms or CF/CF^+ fragments.

Similar yield curves were observed for the photofragmentation of *cis-c*- $\text{C}_4\text{H}_2\text{F}_6$. Figure 1b shows a typical mass spectrum measured at 40.0 eV. A variety of fragment ions were detected, such as CH_kF^+ ($k = 0-2$), $\text{CH}_{0.1}\text{F}_2^+$, $\text{C}_2\text{H}_{1.2}\text{F}_2^+$, CF_3^+ , C_2HF_3^+ , $\text{C}_3\text{H}_2\text{F}_3^+$ and C_2F_4^+ . The peak of C_3HF_4^+ is discernible, but that of C_3F_5^+ is not. This infers that the C–H bond in the CHF group is not scissile. Figure 3 exhibits the PIY curves of the fragment ions. The $\text{C}_3\text{H}_2\text{F}_3^+$ and C_2HF_3^+ fragments are most abundant at all the photon energies and their yields decline with the energy, just like the yield curves of the C_3F_5^+ and C_2F_4^+ fragments from *c*- C_4F_8 , respectively. Yield curves are highly similar between CF_3^+ from *c*- C_4F_8 and CHF_2^+ from *cis-c*- $\text{C}_4\text{H}_2\text{F}_6$. In the tail of the intense $\text{C}_3\text{H}_2\text{F}_3^+$ peak the C_3HF_3^+ component might exist, but its relative contribution is small, judging from the peak shape. Careful determination was made in this way for the higher mass peaks $m/e \geq 50$.

Table 2 outlines the branching fraction of the fragment ions of *cis-c*- $\text{C}_4\text{H}_2\text{F}_6$ at selected excitation energies. Increase in the fraction of the $\text{CH}_{0.2}\text{F}^+$ and $\text{C}_3\text{H}_{1.2}\text{F}^+$ ions is found, showing that at higher energies the abundant $\text{C}_3\text{H}_2\text{F}_3^+$, C_2HF_3^+ and C_2F_4^+ fragments further decompose to form these ions. The approximately constant value of 17 for the PIY ratio between $\text{C}_3\text{H}_2\text{F}_3^+$ and C_3HF_4^+ reveals that the loss of a CF_2 group is about 17 times easier than that of a CHF group irrespective to the photon energy, if we assume that the CHF/CF_2 dissociation is initiated by removal of a fluorine atom. This fact also explains the lower branching fraction of the $\text{C}_3\text{H}_2\text{F}_3^+$ and C_3HF_4^+ fragments compared to the branching fraction of C_3F_5^+ for *c*- C_4F_8 . Reversely, the total branching fraction for $\text{C}_2\text{H}_k\text{F}_{4-k}^+$ ($k = 0-2$) production is larger for *cis-c*- $\text{C}_4\text{H}_2\text{F}_6$, being 1.2 times as much as the branching fraction of C_2F_4^+ from *c*- C_4F_8 .

In addition, PEPICO spectra were acquired to study the breakdown pathways of the multiply-charged *c*- $\text{C}_4\text{F}_8^{n+}$ and *cis-c*- $\text{C}_4\text{H}_2\text{F}_6^{n+}$ ($n \geq 2$) molecular ions. Figure 4 depicts a typical spectrum obtained for *c*- C_4F_8 at the excitation energy of 45.0 eV. The flight time of the ions arrived at the ion detector first was taken as the abscissa, while that of the ions detected afterwards as the ordinate. Several coincidence islands can be found in the spectrum, along with ridges arising from false coincidences with background noises. They are $\text{C}_3\text{F}_5^+/\text{CF}_2^+$, $\text{C}_3\text{F}_4^+/\text{CF}_2^+$, $\text{C}_2\text{F}_4^+/\text{CF}_2^+$, $\text{C}_3\text{F}_3^+/\text{CF}_2^+$, $\text{CF}_3^+/\text{CF}_2^+$, $\text{C}_2\text{F}_4^+/\text{CF}_3^+$, $\text{C}_3\text{F}_3^+/\text{CF}_3^+$, $\text{C}_2\text{F}_4^+/\text{CF}^+$, $\text{CF}_3^+/\text{CF}^+$ and $\text{CF}_2^+/\text{CF}^+$ fragment pairs. The following breakdown pathways can be identified from these pairs:

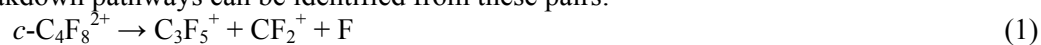


Table 1. Branching fraction (%) of the fragment ions formed by the dissociative photo-ionization of *c*- C_4F_8 .

Ion	Photon energy (eV)					
	30.0	40.0	70.0	100.0	130.0	170.0
C_3F_5^+	46.2	40.6	37.8	37.2	37.5	36.3
C_2F_4^+	37.5	35.0	31.1	30.8	31.5	30.0
CF_3^+	7.2	8.2	9.6	8.9	8.3	8.8
CF^+	3.1	6.4	10.4	11.3	11.2	12.6
CF_2^+	1.7	3.1	3.9	4.1	3.9	4.2
C_3F_3^+	1.7	2.3	2.3	2.3	2.2	2.5
C_4F_7^+	1.1	0.8	0.6	0.8	0.8	0.6
C_3F^+	0.2	0.4	0.9	0.9	1.0	1.1
C_3F_2^+	0.2	1.0	1.2	1.3	1.4	1.6

Table 2. Branching fraction (%) of the fragment ions formed by the dissociative photo-ionization of *cis-c*-C₄H₂F₆.

Ion	Photon energy (eV)					
	30.0	40.0	70.0	100.0	130.0	170.0
C ₃ H ₂ F ₃ ⁺	26.3	24.3	23.2	23.2	23.3	22.4
C ₂ HF ₃ ⁺	25.6	23.7	20.4	19.5	20.8	18.7
C ₂ F ₄ ⁺	15.1	13.6	12.7	12.9	12.8	11.3
C ₂ H _{1,2} F ₂ ⁺	7.5	7.7	7.5	7.6	8.1	7.3
CF ₃ ⁺	7.3	7.4	8.5	7.9	8.0	10.1
CH _{0,1} F ₂ ⁺	4.7	5.3	6.2	6.3	5.4	6.3
C ₃ H _{1,2} F ⁺	3.5	4.5	5.8	6.5	6.1	6.2
C ₃ HF ₂ ⁺	2.8	3.2	3.2	3.0	3.2	4.2
CH ₀₋₂ F ⁺	2.0	3.8	5.7	6.4	6.6	6.5
C ₃ HF ₄ ⁺	1.5	1.7	1.6	1.4	1.3	1.2

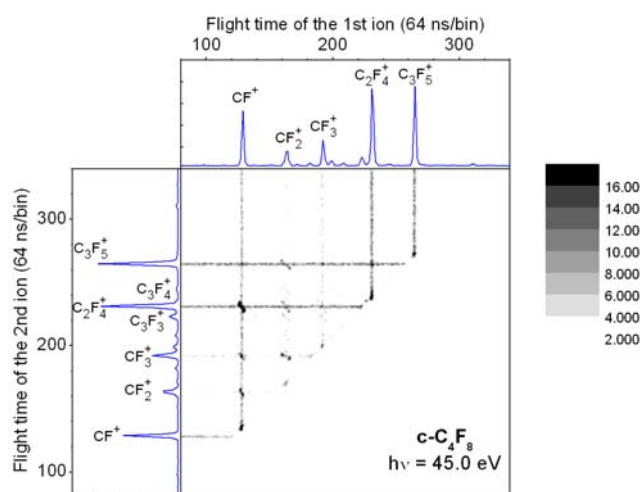
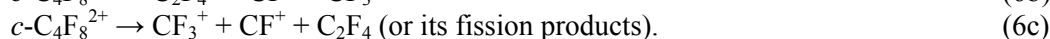
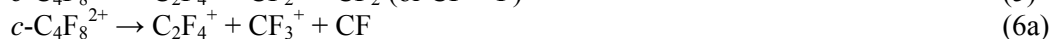
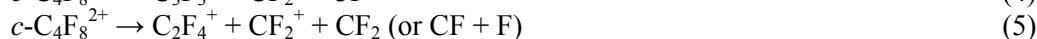
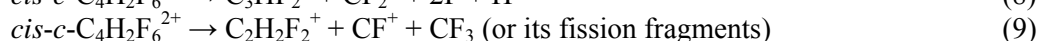


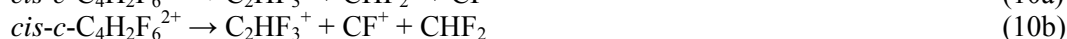
Figure 4. Overview of a typical PEPICO map for *c*-C₄F₈ measured at 45.0 eV. The top and left panels indicate the corresponding TOF spectrum.



Reaction channel 6a has already been discussed by Hsieh and Eland [8]. We presume that in reactions 1–4 the charge separation follows fluorine atom fission(s), i.e., deferred charge separation.

Similar spectra were obtained for *cis-c*-C₄H₂F₆ as well. Coincidence islands identified are C₂HF₃⁺/CHF₂⁺, C₃HF₂⁺/CF₂⁺, CF₃⁺/CF₂⁺, C₂HF₃⁺/C₂HF₂⁺, C₂HF₃⁺/CF⁺, CF₃⁺/CF⁺, C₂H₂F₂⁺/CF⁺ and CHF₂⁺/CF⁺ fragment pairs at 45.0 eV. The pairs to the C₃H₂F₃⁺ ion are left unassigned due to a relatively high ridge appearing in our spectra. The following breakdown pathways can be identified:





If one formally replaces the Hs with Fs, reactions 8, 9 and 10a–c correspond to reactions 4, 6b and 6a–c for the *c*-C₄F₈ fragmentation, respectively. The *c*-C₄F₈ counterpart for reaction 7 is hardly seen due to the low yield of C₂F₃⁺, implying that the C₂F₃⁺ ion is more reactive than C₂HF₂⁺. Thermochemical stability of the ions is not the factor because the heat of formation is 812 kJ/mol for C₂F₃⁺ and 916 kJ/mol for C₂HF₂⁺ [13].

Analyzing the slope of the islands allows us to deduce the fission dynamics [14,15] and is now in progress. The results will be published elsewhere.

4. Summary

Dissociative photoionization of *c*-C₄F₈ in the energy range of 25–170 eV produces CF_{*l*}⁺ (*l* = 1–3), C₂F_{*m*}⁺ (*m* = 1–4), C₃F_{*n*}⁺ (*n* = 1–5) and C₄F₇⁺ as fragment ions. The C₃F₅⁺ and C₂F₄⁺ ions are most abundant at all the energies studied here, but their yields decrease significantly with the photon energy: The yield at 170 eV becomes about 30% of that at 30 eV. Similar yield curves were obtained for the *cis-c*-C₄H₂F₆ photoionization. The most dominant fragments are C₃H₂F₃⁺ and C₂HF₃⁺, giving a total yield of 52% at 30 eV. The PIY curves of C₃H₂F₃⁺ and C₂HF₃⁺ closely resemble those of C₃F₅⁺ and C₂F₄⁺ produced by the *c*-C₄F₈ photoionization, respectively. Several breakdown pathways were also identified by applying a PEPICO technique. Comparison of the pathways between both molecules implies that the C₂F₃⁺ ion is more reactive than C₂HF₂⁺.

Acknowledgments

The authors are grateful to the staff of the UVSOR facility for stable operation of the storage ring. This study was supported in part by the Joint Studies Program of the Institute for Molecular Science. KO also acknowledges the financial support from the Japan Society for the Promotion of Science through its Grant-in-Aid for Scientific Research.

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