

Growth of Neutral Species in the Downstream Region of Perfluorocarbon Plasmas

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The mass analysis of neutral molecules using a Li^+ ion attachment ionization technique was conducted at a position 90 cm downstream from the generating area of Ar/CF_4 , $\text{Ar}/\text{C}_2\text{F}_6$ and $\text{Ar}/\text{C}_3\text{F}_8$ plasmas. $\text{C}_n\text{F}_{2n+2}$ ($n = 1-7$), C_nF_{2n} ($n = 4-8$) and $\text{C}_n\text{F}_{2n-2}$ ($n = 8$) were commonly observed in their plasmas, whereas C_nF_{2n} ($n = 2$ and 3), $\text{C}_n\text{F}_{2n-2}$ ($n = 4-7$), $\text{C}_n\text{F}_{2n-4}$ ($n = 8$ and 9), $\text{C}_n\text{F}_{2n+1}$ ($n = 6$ and 7) and $\text{C}_n\text{F}_{2n-1}$ ($n = 7$ and 8) were observed only in the $\text{Ar}/\text{C}_3\text{F}_8$ plasma. Quantum chemical calculations using the GAUSSIAN 03 program package were conducted to estimate the Li^+ affinity, which is closely related to the Li^+ attaching probability, to several species concerned. It has been found that the reactions between radicals, each of which contains more than three carbon atoms, play an important role in the growth of the neutral species.

Keywords: CF_4 , C_2F_6 , C_3F_8 , Li^+ ion attachment, mass spectrometry, molecular growth

1. Introduction

Perfluorocarbon (PFC) plasmas have been used for selectively etching away Si and SiO_2 wafers and cleaning chambers after chemical vapor deposition in the semiconductor industry. Recently, they are also applied to form new materials such as carbon nanowall [1] and low- k films [2]. Controlling the concentration and the kind of radicals and neutral species in these plasmas is significant for improving the properties of the new materials. However, little has been known about the initial stage of formation of the materials in the plasmas. Several experimental results have demonstrated that CF_2 -surface interactions are largely governed by other species in the plasma and not by the chemistry of CF_2 alone [3]. Some researchers have pointed out that high-mass species produced in the gas phase play an important role in the PFC plasma processes [4,5]. To optimize the plasma processes and explore new materials, it is necessary to investigate the reaction mechanisms of molecular growth in the gas phase in detail.

Positive and negative ions in plasmas can easily be identified by mass spectrometry, leading to better understanding of the growth mechanisms of the high-mass ions. We have recently clarified the growth mechanisms of the high-mass positive ions existing in the downstream region of the Ar/CF_4 plasma [6]. In contrast, identifying neutral species contained in the plasmas by mass spectrometry is difficult because of the existence of various unidentified neutral species in the plasmas and because of the fragmentation induced by ionization of the neutral species.

The Li^+ attachment ionization is a powerful method. It is fragment-free in many cases and then makes it

possible to identify undoubtedly neutral species contained in plasmas [7-11]. In particular, most of the positive and negative ions of saturated, open-chain perfluorocarbon molecules are unstable, and only their fragment ions are observed in mass spectra [5,11]. In contrast, the Li^+ adducts of such PFCs are stable, and fragmentation does not take place. Using this method, we have recently found that there are various neutral species in the down stream region of the Ar/CF_4 plasma [12].

In this paper, we show the mass analysis results of high-mass neutral molecules in the downstream region of the Ar/CF_4 , $\text{Ar}/\text{C}_2\text{F}_6$ and $\text{Ar}/\text{C}_3\text{F}_8$ plasmas. The kind of the species observed was dependent strongly on the mixing ratio of C_3F_8 to Ar in the case of the C_3F_8 plasma. This finding provides fundamental information on the growth mechanisms of the high-mass neutral molecules.

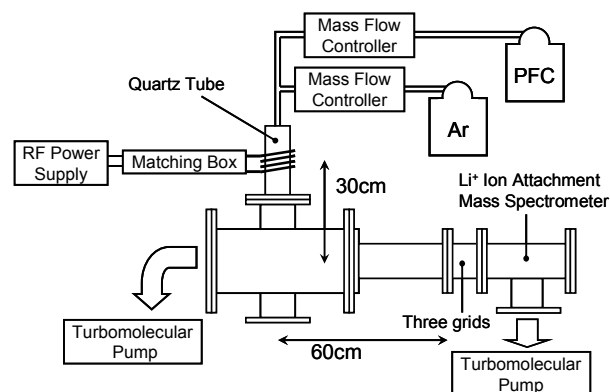


Fig. 1. Schematic view of the experimental setup. PFC represents CF_4 , C_2F_6 or C_3F_8 .

2. Experimental Procedure

An inductively coupled low-pressure plasma was generated in a quartz tube of 50 mm in diameter by supplying an RF (13.56 MHz) power of 150 W (ARIOS, ERF5-511). The chamber was evacuated by a $550 \text{ l}\cdot\text{s}^{-1}$ turbomolecular pump. The neutral molecules were analyzed using a low-pressure type Li^+ attachment mass spectrometer (CANON ANELVA, L-241G-IA). This equipment consists of a Li^+ attachment compartment and an ordinary quadrupole mass spectrometer. The mass spectrometer was separated by an aperture 0.8 mm in diameter from the Li^+ attachment compartment and was differentially pumped with a $220 \text{ l}\cdot\text{s}^{-1}$ turbomolecular pump [12]. The natural abundance of ^6Li is 7.6%, and then would disturb the assignment of mass peaks observed through the Li^+ ion attachment. This Li^+

attachment compartment contains a simple magnetic mass filter for selecting $^7\text{Li}^+$, reducing the $^6\text{Li}^+/\text{Li}^+$ ratio to 3.3%. The HFLi^+ and H_2OLi^+ peaks appeared strongly in the Li^+ attachment mass spectra (Li^+ -IAMS) because of the high affinity of Li^+ to HF and H_2O even if there is a very small amount of H_2O in the chamber. We then baked the chamber at 100°C for ten hours before starting experiment.

In ordinary ion-attachment ionization, a third body such as N_2 is additionally supplied into the ion-attachment compartment at the order of 100 Pa to stabilize the Li^+ adducts. In the present low-pressure type one, no third body was additionally supplied, although the probability of attaching Li^+ was very low.

CF_4 (Carbon tetrafluoride, 99.999%, TAKACHIHO TRADING), C_2F_6 (Hexafluoroethane, 99.995%, NIPPON

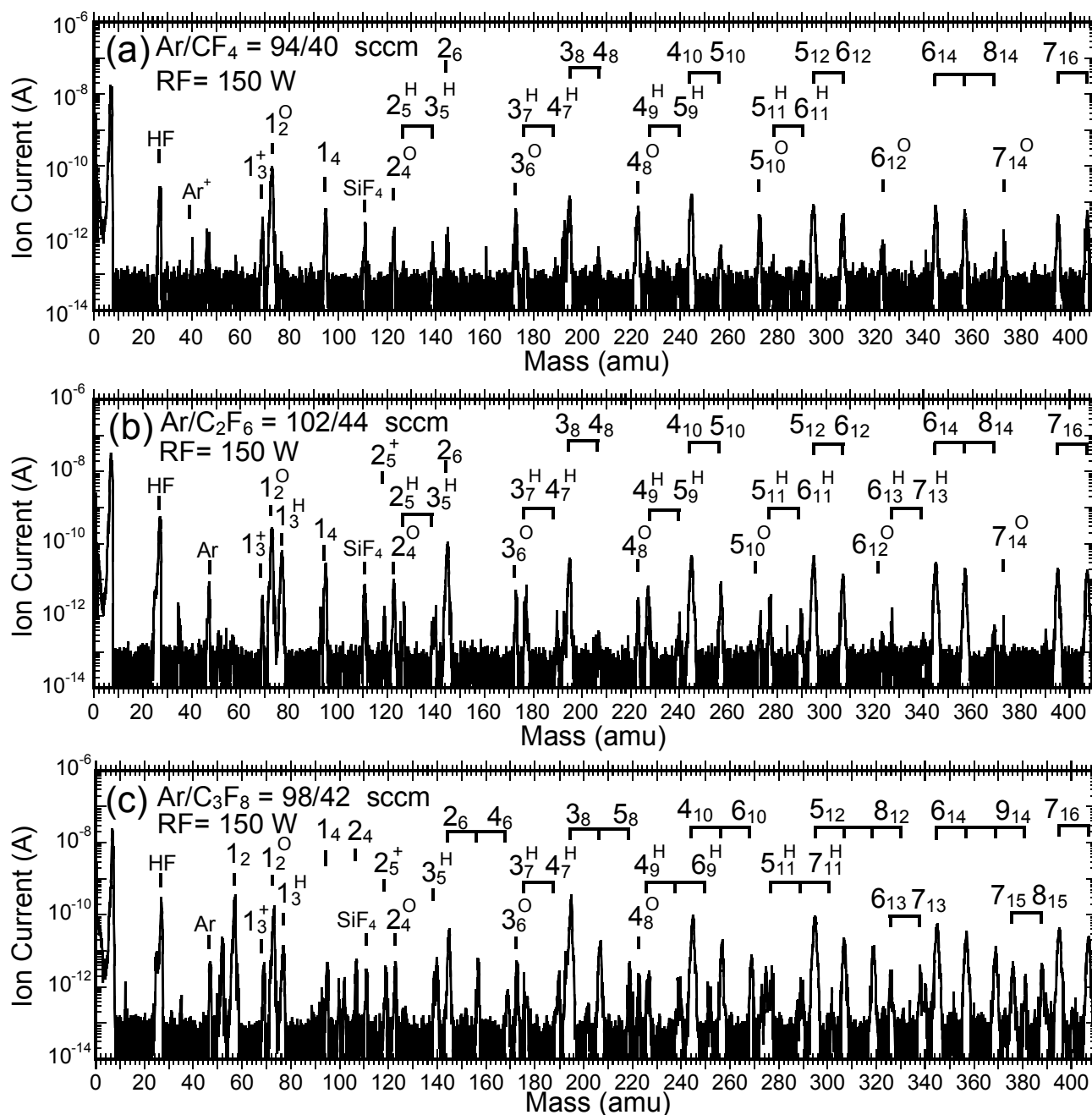


Fig. 2. Mass spectra of neutral molecules observed in the downstream region of (a) Ar/CF_4 , (b) $\text{Ar}/\text{C}_2\text{F}_6$ and (c) $\text{Ar}/\text{C}_3\text{F}_8$ plasmas.

SANSO) or C_3F_8 (Octafluoropropane, 99.9%, NIPPON SANSO) and Ar (99.999%, NIPPON SANSO) were supplied into the chamber using mass flow controllers (KOFLOC, 3660). The pressure was measured with a ceramic capacitance gauge (PFEIFFER, CCR264) and a cold cathode gauge (BALZERS, KR260) in the chamber, and with an ionization gauge (CANON ANELVA, MG-2F) in the mass spectrometer. The base pressure was 6×10^{-5} Pa in the chamber and 1×10^{-7} Pa in the mass spectrometer.

The DC voltages of 0, -71 and +79 V were applied to each of three grids in order of those close to the plasma. These grids prevent excessive electrons and ions produced in the plasma from flowing into the Li^+ ion attachment mass spectrometer.

3. Results and discussion

3.1 Product analysis

Typical mass spectra of the neutral species observed in the downstream region of the Ar/ CF_4 , C_2F_6 and C_3F_8 plasmas are shown in Fig. 2. The plasmas were generated at a pressure of 1.0 Pa and at flow rates of 94 and 40 sccm for Ar and CF_4 , respectively, in the Ar/ CF_4 plasma; 102 and 44 sccm for Ar and C_2F_6 , respectively, in the Ar/ C_2F_6 plasma; and 98 and 42 sccm for Ar and C_3F_8 , respectively, in the Ar/ C_3F_8 plasma. The abbreviation N_M in the figure means $C_NF_MLi^+$. The superscript "O" or "H" means the presence of the O or H atom in the molecules, for example, $2_4^O = C_2F_4OLi^+$, and the superscript "+" means the positive ion without Li^+ , for example, $1_3^+ = CF_3^+$. The Si and O atoms arise from the etching of SiO_2 used at the plasma-generating area, and the H and O atoms are due to the presence of a trace amount of water as a contaminant in the chamber.

All the detected C_NF_M products are summarized in Table 1, where the numbers in parentheses mean the mass number of the Li^+ adduct ion. Many kinds of neutral molecules containing only single bonds as C_nF_{2n+2} ($n = 1-7$), a double bond or cyclic structure as C_nF_{2n} ($n = 4-8$), and two double bonds or a combination of a double bond and cyclic structure as C_nF_{2n-2} ($n = 8$) were commonly observed in all of the plasmas. In contrast, C_nF_{2n} ($n = 2$ and 3), C_nF_{2n-2} ($n = 4-7$) and C_nF_{2n-4} ($n = 8$ and 9) were observed only in the Ar/ C_3F_8 plasma.

Neutral radicals which have odd-numbered fluorine atoms and less than six carbon atoms were not observed

in the present experiment. Sablier *et al.* [13] have identified several low-mass PFC products, such as CF_2 , CF_4 , C_2F_6 , C_2F_2 , C_4F_2 and CF_3 in the upstream region of the He/ CF_4 plasma using a high-pressure type Li^+ ion mass spectrometer. In their experiment, the plasma was generated under the conditions of a total pressure range of 213–2133 Pa and the CF_4 ratio in a range of 10–100%. In addition, the neutral products were derived into the mass spectrometer without preventing excessive electrons and ions. The peak at 69 amu observed by them should then be assigned not to $C_2F_2Li^+$ but to CF_3^+ , because there are a large quantity of CF_3^+ in the plasma. They have assigned the peak at $m/e = 35$ to N_2Li^+ , which has been observed without generating the plasma. They have discussed that N_2 might be attributable to a small unavoidable leak in the flow tube. However, this assignment seems strange: The sensitivity of N_2 in the Li^+ attachment mass spectrometry at a total pressure of 100 Pa is ten times less than that of CF_4 [14]. This fact would result in 50% of CF_4 as the N_2 partial pressure in the chamber.

In general, intensity observed in Li^+ -IAMS depends strongly on the attaching probability of the Li^+ ion to the target molecules. The attaching probability is reported to be critically dependent on the Li^+ affinity of the target molecules in the case of high-pressure (100 Pa) type IAMS [14]. Therefore, it is important to investigate whether the Li^+ affinities of PFCs concerned are large enough to suggest the possible experimental detection by the Li^+ ion attachment mass spectrometry. Table 2 summarizes the Li^+ ion affinities to some PFCs obtained through the B3LYP/6-311+G(3df) level calculations. At a pressure of 100 Pa in the chamber [14], where third-body collisions play a crucial role in the stabilization of the adducts, the sensitivity in Li^+ -IAMS increases 6.3 times per 0.1 eV with the Li^+ affinity in the range of 0.3–1 eV and becomes constant above 1 eV. In the Ar/ C_3F_8 plasma, the peaks of 57 and 107 amu to be assigned to CF_2 and C_2F_4 , respectively, appeared. The Li^+ affinity estimated for CF_2 was 1.03 eV, significantly larger than those to CF_3 and CF_4 , 0.60 and 0.53 eV, respectively. There are two isomers in C_2F_4 : one is CF_2CF_2 and the other is CF_3CF . The Li^+ affinity to

Table 1. Products observed in the downstream region of Ar/ CF_4 , Ar/ C_2F_6 and Ar/ C_3F_8 plasmas.

Type	Common products	Products observed only in the C_3F_8 plasma
C_nF_{2n+2}	C_2F_6 (145), C_3F_8 (195), C_4F_{10} (245), C_5F_{12} (295), C_6F_{14} (345), C_7F_{16} (395)	
C_nF_{2n}	C_4F_8 (207), C_5F_{10} (257), C_6F_{12} (307), C_7F_{14} (357), C_8F_{16} (407)	C_2F_4 (107), C_3F_6 (157)
C_nF_{2n-2}	C_8F_{14} (369)	C_3F_4 (119), C_4F_6 (169), C_5F_8 (219), C_6F_{10} (269), C_7F_{12} (319), C_8F_{14} (369)
C_nF_{2n-4}		C_8F_{12} (331), C_9F_{14} (381)
C_nF_{2n+1}		C_6F_{13} (325), C_7F_{15} (376)
C_nF_{2n-1}		C_7F_{13} (338), C_8F_{15} (388)

CF_3CF was estimated to be 1.12 eV, significantly larger than those of CF_2CF_2 and C_2F_5 , 0.74 and 0.64 eV, respectively. These findings suggest that the peak at 57 amu should be assigned to CF_2 and the peak at 107 amu should be assigned to CF_3CF and/or CF_2CF_2 .

3.2 Mixing ratio dependence

Figures 3a and 3b show the dependence of the intensity in C_7F_{16} and C_7F_{14} on the mixing ratio of CF_4 and C_2F_6 . Similar tendency was also observed about the other $\text{C}_n\text{F}_{2n+2}$ and C_nF_{2n} species. The intensity in C_7F_{16} and C_7F_{14} was slightly increased with the mixing ratio of CF_4 and C_2F_6 in a range of 0.2–0.3. Figure 3c shows that in the C_3F_8 case. Their intensity was slightly decreased with increasing the mixing ratio of C_3F_8 from 0.2 to 0.3. The intensity decrease was remarkable for C_7F_{12} and C_7F_{10} , as shown in Fig. 3d. C_7F_{15} and C_7F_{13} were also slightly decreased in intensity. In contrast, the C_2F_4 intensity was increased with the C_3F_8 mixing ratio. C_2F_4 can be produced by the direct decomposition of C_3F_8 in the generating area of the C_3F_8 plasma [15]. In general, C_2F_6 decomposes dominantly into fragments having only single bond. In contrast, C_3F_8 can

decompose into fragments containing double or triple bond. Various reactions concerning species with

Table 2. Li^+ ion affinities estimated through B3LYP/6-311+G(3df) level calculations.

Species	Li^+ affinity (eV)
Ar	0.33
CF	0.89
CF_2	1.03
CF_3	0.60
CF_4	0.53
C_2F_4 ($\text{CF}_2\text{--CF}_2$)	0.78
C_2F_4 ($\text{CF}_3\text{--CF}$)	1.12
C_2F_5	0.75
C_2F_6	0.74
$\text{C}_2\text{F}_5\text{CF}$	1.03
C_3F_6 ($\text{CF}_3\text{--CF--CF}_2$)	1.03
C_3F_7 ($\text{CF}_2\text{--CF}_2\text{--CF}_3$)	0.93
C_3F_7 ($\text{CF}_3\text{--CF--CF}_3$)	1.02
C_3F_8	0.89
C_4F_8 ($\text{CF}_2\text{=CF}(\text{CF}_3)_2$)	1.22
C_4F_{10} ($\text{CF}_3\text{--CF}_2\text{--CF}_2\text{--CF}_3$)	1.01
C_4F_{10} ($\text{CF}_3\text{--CF}(\text{CF}_3)_2$)	0.96

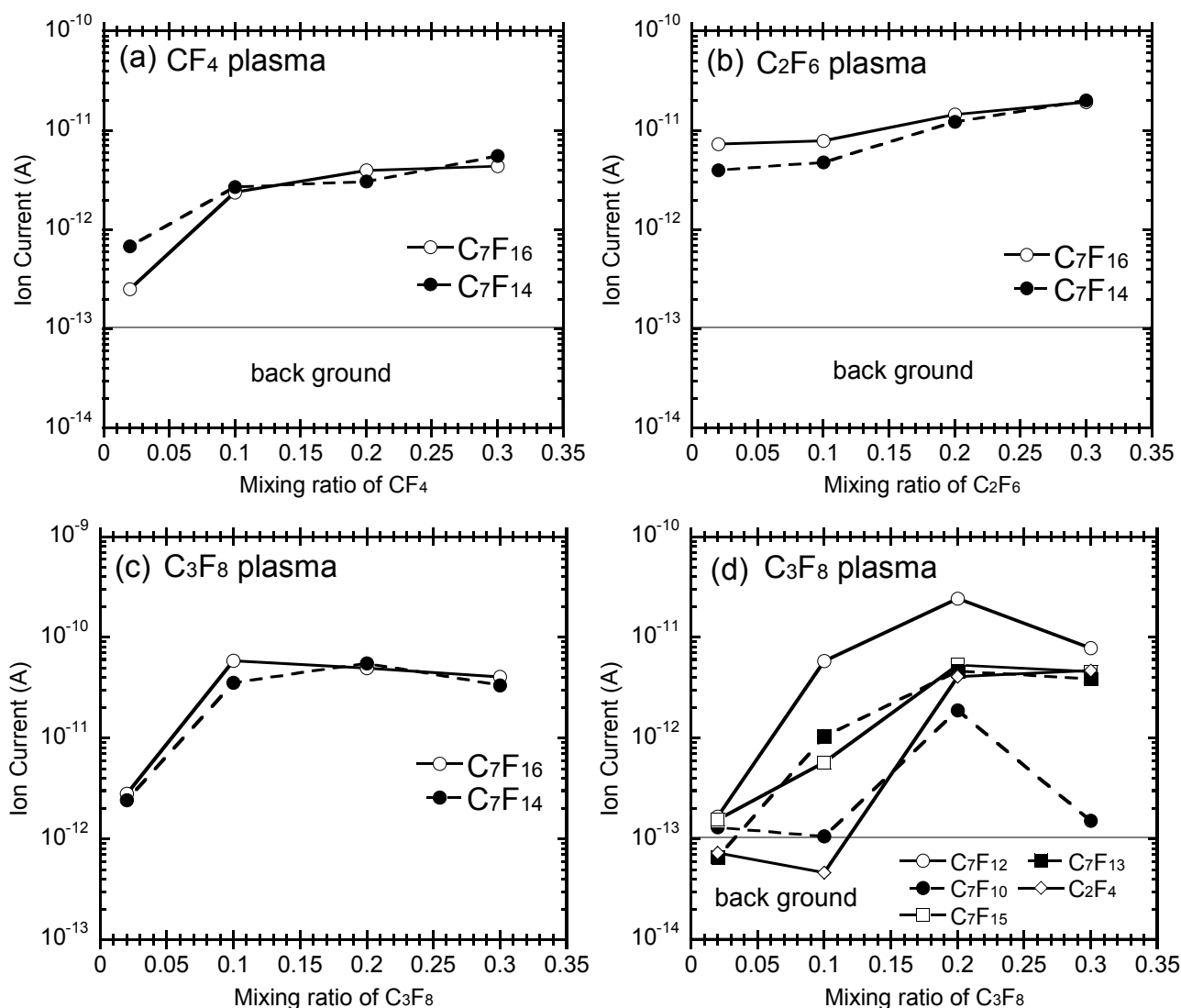


Fig. 3. Intensity dependence of C_7F_{16} ($\text{C}_n\text{F}_{2n+2}$), C_7F_{14} and C_2F_4 (C_nF_{2n}), C_7F_{12} ($\text{C}_n\text{F}_{2n-2}$), C_7F_{15} ($\text{C}_n\text{F}_{2n+1}$) and C_7F_{13} ($\text{C}_n\text{F}_{2n-1}$) on the mixing ratio of parent gas, (a) CF_4 , (b) C_2F_6 and (c) and (d) C_3F_8 . The total pressure was kept at 1.0 Pa.

unsaturated chemical bond would lead to the formation of C_nF_{2n} ($n = 2$ and 3), C_nF_{2n-2} ($n = 4-8$) and C_nF_{2n-4} ($n = 8$ and 9) which were observed only in the C_3F_8 plasma.

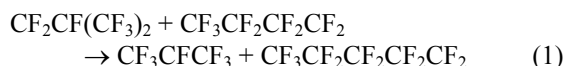
3.3 Formation mechanisms of high-mass species

The gas temperature measured using a thermocouple at a position 30 cm downstream from the center of the plasma-generating area was within 300–320 K in the case of Ar/ CF_4 plasma [6]. Thus, reactions accompanied by a significant potential barrier do not take place in the downstream region of the plasmas, even if the reactions are exothermic. In many cases, there is not a significant barrier in radical-radical reactions. We then estimated the enthalpy change ($\Delta_r H^\circ$) in radical-radical reactions of PFC radicals by the B3LYP/6-311+G(3df) level calculations. The results are summarized in Table 3.

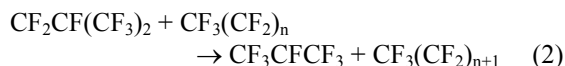
The reaction represented by $A + B \rightarrow C + D$ takes place preferentially in comparison to the association reaction $A + B \rightarrow AB$ if the former reaction is exothermic and does not have a significant barrier. This is because the excess energy in the former reaction can be partitioned not only into the internal energy of the products, C and D, but also into their translational energy. However, it should be noted that the dependence of the association cross-section on pressure is clearly visible even far below 1 Pa in the association between Li^+ and dimethoxyethane [16]. The association reactions can take place substantially provided that the adducts have many vibrational modes allowing the storage of the excess energy in the reactions and that all of the other reaction paths which produce two species or more are blocked.

Only C_nF_{2n+2} and C_nF_{2n} were observed at 0.02 Pa of partial pressure of the parent gas even in the Ar/ C_3F_8 plasma. The growth mechanisms of these species would be common among all the plasmas we used in the present experiments.

The following reaction can promote the growth of high-mass species:



This reaction is exothermic, as indicated in Table 3, and the $A + B \rightarrow C + D$ type reaction. The production of the CF_3CFCF_3 radical, which is relatively stable due to hyperconjugation, makes this reaction exothermic. Similarly, the following reactions,



are likely to promote the growth of high-mass species.

The termination reactions of the C_nF_{2n+1} radicals to form the C_nF_{2n+2} molecules can advance by the exothermic reactions of C_nF_{2n+1} with small radicals like CF_3 and C_2F_5 as follows:

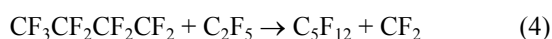
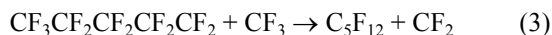
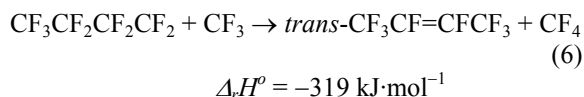
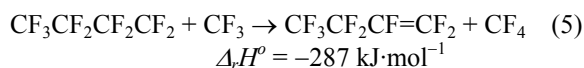


Table 3. Reaction enthalpies in some radical–radical reactions estimated through the B3LYP/6-311+G(3df) level calculations

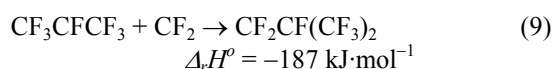
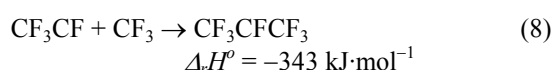
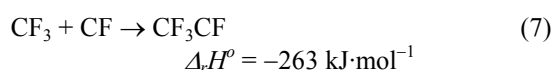
Reaction	$\Delta_r H^\circ$ (kJ·mol ⁻¹)
$CF_3 + CF_3 \rightarrow C_2F_5 + F$	136
$CF_3 + CF_3 \rightarrow C_2F_6$	-364
$C_2F_5 + F \rightarrow 2CF_3$	-136
$C_2F_5 + F \rightarrow C_2F_6$	-499
$C_2F_5 + CF_3 \rightarrow CF_3CF_2CF_2 + F$	154
$C_2F_5 + CF_3 \rightarrow CF_3CFCF_3 + F$	125
$C_2F_5 + CF_3 \rightarrow C_3F_8$	-339
$C_2F_5 + C_2F_5 \rightarrow CF_3CF_2CF_2 + CF_3$	18.5
$C_2F_5 + C_2F_5 \rightarrow C_3F_8 + CF_2$	-115
$C_2F_5 + C_2F_5 \rightarrow CF_3CF_2CF_2CF_2 + F$	179
$C_2F_5 + C_2F_5 \rightarrow CF_3CF_2CFCF_3 + F$	143
$C_2F_5 + C_2F_5 \rightarrow C_4F_{10}$	-313
$CF_3CF_2CF_2 + F \rightarrow C_2F_5 + CF_3$	-154
$CF_3CF_2CF_2 + F \rightarrow C_3F_8$	-493
$CF_3CF_2CF_2 + CF_2 \rightarrow CF_3CF_2CF_2CF_2$	-200
$CF_3CF_2CF_2 + CF_3 \rightarrow CF_3CF_2CF_2CF_2 + F$	160
$CF_3CF_2CF_2 + CF_3 \rightarrow CF_3CF_2CFCF_3 + F$	124
$CF_3CF_2CF_2 + CF_3 \rightarrow C_4F_{10}$	-331
$CF_3CF_2CF_2 + C_2F_5 \rightarrow CF_3CF_2CF_2CF_2 + CF_3$	24.8
$CF_3CF_2CF_2 + C_2F_5 \rightarrow CF_2CF(CF_3)_2 + CF_3$	8.1
$CF_3CF_2CF_2 + C_2F_5 \rightarrow C_4F_{10} + CF_2$	-107
$CF_3CF_2CF_2 + C_2F_5 \rightarrow C_5F_{12}$	-305
$CF_3CFCF_3 + F \rightarrow C_2F_5 + CF_3$	-125
$CF_3CFCF_3 + F \rightarrow C_3F_8$	-464
$CF_3CFCF_3 + CF_2 \rightarrow CF_2CF(CF_3)_2$	-187
$CF_3CFCF_3 + CF_3 \rightarrow CF_2CF(CF_3)_2 + F$	173
$CF_3CFCF_3 + CF_3 \rightarrow CF_3C(CF_3)_2 + F$	106
$CF_3CFCF_3 + CF_3 \rightarrow CF_3CF(CF_3)_2$	-315
$CF_3CFCF_3 + C_2F_5 \rightarrow CF_3CF_2CFCF_3 + CF_3$	17.9
$CF_3CFCF_3 + C_2F_5 \rightarrow CF_2CF(CF_3)_2 + CF_3$	37.6
$CF_3CFCF_3 + C_2F_5 \rightarrow CF_3CF(CF_3)_2 + CF_2$	-90.6
$CF_3CF_2CF_2CF_2 + C_2F_5 \rightarrow C_5F_{12} + CF_2$	-105
$CF_3CF_2CF_2CF_2 + CF_3CF_2CF_2CF_2 \rightarrow CF_3CF_2CF_2 + CF_3CF_2CF_2CF_2CF_2$	1.3
$CF_2CF(CF_3)_2 + CF_3CF_2CF_2 \rightarrow CF_3CFCF_3 + CF_3CF_2CF_2CF_2$	-12.8
$CF_2CF(CF_3)_2 + CF_3CF_2CF_2CF_2 \rightarrow CF_3CFCF_3 + CF_3CF_2CF_2CF_2CF_2$	-11.5
$CF_3CF_2CF_2CF_2CF_2 + F \rightarrow C_4F_{10} + CF_2$	-293
$CF_3CF_2CF_2CF_2CF_2 + F \rightarrow CF_3CF_2CF_2CF_2 + CF_3$	-162
$CF_3CF_2CF_2CF_2CF_2 + CF_3 \rightarrow C_5F_{12} + CF_2$	-131

The termination reactions of C_nF_{2n+1} to form C_nF_{2n} can also take place as follows:

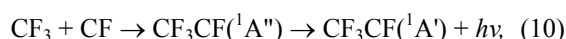


$\Delta_r H^\circ$ for the *cis*- $CF_3CF=CFCF_3$ formation in reaction (6) was estimated to be $-309 \text{ kJ}\cdot\text{mol}^{-1}$

$CF_3CF(CF_3)_2$ can be produced by the successive association reactions as follows:

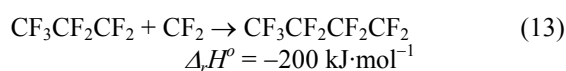
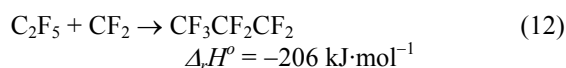
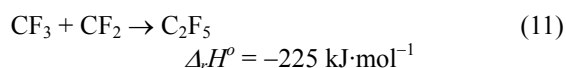


These reactions may have potential barriers on the way to the reactions. Hynes *et al.* have reported that the barrier heights in reaction (7) and (8) are 14.7 and 0.2 $\text{kJ}\cdot\text{mol}^{-1}$, respectively, based on G2-MP2 calculations [17, 18]. Bacskay [19] have estimated the barrier height in reaction (7) to be 8.7 $\text{kJ}\cdot\text{mol}^{-1}$ in more accurate calculation. Both of the reactants in reaction (7) are produced through the direct decomposition of the parent gas in the plasma-generating area where RF power is being supplied. Therefore, reaction (7) can take place even if it has a significant potential barrier. CF_3CF can stabilize through a radiation process as follows:



judging from the electronic states of CF_3CF [19, 20]. The potential barrier in reaction (8) is negligible under the present experimental conditions. Therefore, reaction (8) can take place easily.

$CF_3CF_2CF_2CF_2$ can be produced by the successive association reactions as follows:



The values of the barrier height in reaction (11) and (12) are estimated to be 20.9 and 8.4 $\text{kJ}\cdot\text{mol}^{-1}$ [17].

Reactions (9) and (13) should take place dominantly in the downstream region, especially of the Ar/CF_4 plasma, because one of the reactants should be produced

through the successive reactions from relatively small species. Detailed calculations for the barrier heights in reactions (9) and (13) are in progress.

4. Conclusion

We have demonstrated the existence of a few kinds of high-mass PFC radicals in the downstream region of the Ar/C_3F_8 plasma by Li^+ ion attachment mass spectrometry. The quantitative measurement of PFC radicals with two or more carbon atoms in the plasma is essential for better understanding of the growth mechanisms of high-mass neutral PFCs.

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