

VUV dissociative photoionization of CHF<sub>2</sub>ClZhenya Wang<sup>a,\*</sup>, Liqing Hao<sup>a</sup>, Shikang Zhou<sup>a</sup>, Bin Yang<sup>b</sup>, Chaoqun Huang<sup>b</sup>,  
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## Abstract

VUV dissociative photoionization of CHF<sub>2</sub>Cl in an energy region ~12–22 eV was investigated with photoionization mass spectroscopy (PIMS) using synchrotron radiation (SR). The ionization energy of CHF<sub>2</sub>Cl and appearance energies for its fragment ions, CHF<sub>2</sub><sup>+</sup>, CF<sup>+</sup>, CHF<sup>+</sup>, CHFCl<sup>+</sup>, CF<sub>2</sub><sup>+</sup>, Cl<sup>+</sup>, CFCI<sup>+</sup>, CCI<sup>+</sup>, HCl<sup>+</sup>, CF<sub>2</sub>Cl<sup>+</sup>, H<sup>+</sup> and CHCl<sup>+</sup>, were determined with photoionization efficiency spectroscopy (PIES). The dissociation energies of some possible dissociation channels to produce those fragment ions were also determined experimentally. The total energies of CHF<sub>2</sub>Cl and its main photofragments were calculated using Gaussian 98 program and Gaussian – 2 calculations. And then, the ionization energy of CHF<sub>2</sub>Cl, appearance potentials for its fragment ions, and the dissociation energies to produce them were predicted using high accuracy energy model. The mechanism of photoionization and photodissociation of CHF<sub>2</sub>Cl was discussed deeply based on comparison of our experimental results with those predicted theoretically. According to our research results, the experimental dissociation energies were in reasonable agreement with either the calculated dissociation energies (*E<sub>d</sub>*) or the reaction barriers *V*(G2) of possible photodissociation channels of CHF<sub>2</sub>Cl.

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**Keywords:** CHF<sub>2</sub>Cl; Photoionization; Photodissociation; Synchrotron radiation

## 1. Introduction

The chlorofluorocarbons (CFCs) can release chlorine atoms which could initiate the ozone depletion in stratosphere, and they are ozone depletion substances. According to the international regulations (Montreal Protocol and amendments), they should be phased out at last [1–4]. The hydrochlorofluorocarbons (HCFCs) are used as interim replacements for the CFCs and their molecules contain one or more hydrogen atoms, which are susceptible to attack by the OH radical in the troposphere, they do not reach the upper atmosphere in significant abundance. However, they possess the possibility for ozone attack if they arrive at the stratosphere, because they still contain

chlorine atoms. CHF<sub>2</sub>Cl is one of the key molecules in atmosphere environment and the alternatives for CFC1<sub>3</sub> (CFC-11) and CF<sub>2</sub>Cl<sub>2</sub> (CFC-12). CHF<sub>2</sub>Cl has been studied widely with various kind of spectroscopic technologies, such as IR and millimeter-wave spectra [5,6], IR multiple-photon dissociation [7], photodissociation and molecular dynamics [8], monitoring measurements using infrared spectroscopy [9], VUV and photoelectron spectra [10], VUV absorption spectra [11], angle-resolved electron energy loss spectroscopy [12,13], electron impact mass spectroscopy (EIMS) [14], molecular beam electron impact mass spectroscopy (MBEIMS) [15], and VUV photoionization mass spectroscopy [16,17]. Even so, the mechanism of VUV dissociative photoionization of CHF<sub>2</sub>Cl above its ionization energy is still less understood in detail experimentally and theoretically. In order to determine Ionization energy (IE) of CHF<sub>2</sub>Cl and appearance potentials (APs) for its fragmental ion, and to explore the mechanism

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for its dissociative ionization, we present a study of VUV dissociative photoionization of  $\text{CHF}_2\text{Cl}$  in the energy range  $\sim 12$ – $22$  eV. The quantum chemistry calculation is also performed using Gaussian 98 program and G2 method to obtain some photochemical parameters, and then, the mechanisms of dissociative photoionization of  $\text{CHF}_2\text{Cl}$  will be discussed.

## 2. Experimental set-up

Our experimental was described previously elsewhere [18]. In brief, synchrotron radiation from the Hefei 800 MeV storage ring is focused by a toroidal mirror onto the entrance slit of a 1 m Seya-Namioka monochromator. The monochromator disperses the radiation in the range of 350–3000 Å with resolution of greater than 500 with 220  $\mu\text{m}$  entrance and exit slits. The monochromatized radiation is focused by another toroidal mirror into the photoionization chamber and the photon flux was monitored by a silicon photodiode (SXUV-100, International Radiation Detectors, Inc.). In general, the photon flux at the excitation region of sample is about  $\sim 10^{10}$  photons/s. A lithium cutoff filter of 1 mm in thickness can be inserted into the light beam path to eliminate second- and higher-order radiation in the wavelength region longer than 1050 Å.

The sample of  $\text{CHF}_2\text{Cl}$  (purity 99%) was introduced by supersonic expansion through a continuous beam nozzle with an orifice of 70  $\mu\text{m}$  diameter from the molecular beam chamber into the ionization chamber through a  $\phi 1$  mm skimmer. The  $\text{CHF}_2\text{Cl}$  molecular beam intersected the monochromatized synchrotron radiation beam at 70 mm from the nozzle. A reflectron time-of-flight mass spectrometer (RTOFMS) was employed for the VUV photoionization/fragmentation studies. Photoions produced by the VUV light were drawn out of the photoionization region by a pulse extraction field triggered with a pulse generator (DG 535 SRS) and detected by a microchannel plate (MCP) detector. The ion signal was recorded by a multiscaler P7888 (FAST Comtec, Germany) after it was amplified with preamplifier VT120C (EG & G, ORTEC).

In this experiment, He (purity 99.99%) was used as the carrier gas and the stagnation pressure was in the range of 1–3 bars. The pressure of the ionization chamber was about  $4 \times 10^{-4}$  Pa when the molecular beam was introduced. The PIES curve was measured while the monochromator is scanned with a wavelength increment of 0.2–0.5 Å and the data acquisition time for each point is 10–20 s depending on ion abundance.

## 3. Quantum chemical calculations

The total energies of  $\text{CHF}_2\text{Cl}$  and its fragment products were calculated with GAUSSIAN 98 program [19] and G2 method [20,21]. Briefly, the equilibrium structure of a molecule was optimized and its harmonic vibrational

frequencies were calculated at first by HF/6-31G(d), its zero point energy was timed by a factor of 0.8929. Then, the equilibrium structure of each species was optimized again at MP2 (Full)/6-31G\* level. To calculate an  $E(\text{G2})$  energy, single-point energy calculations were carried out at the levels of MP4/6-311G(d,p), MP4/6-311 + G(d,p), MP4/6-311G(2df,p), MP2/6-311 + G(3df,2p), and QSCISD (T)/6-311G(d,p) with a higher-level correction and a zero-point vibrational energy correction. After the calculation of the energy  $E(\text{G2})$ , the high accuracy energy model was used to calculate the thermochemical parameters, such as, ionization energy of  $\text{CHF}_2\text{Cl}$ , appearance potentials for its fragment ions and dissociation energies to produce them. In this paper, some transition structure and intermediate structure were determined, and the dissociation channel was confirmed by the calculation of intrinsic reaction coordinate (IRC).

## 4. Results and discussion

### 4.1. Experimental result

The photoionization mass spectrum of  $\text{CHF}_2\text{Cl}$  at the wavelength of 55.0 nm is shown in Fig. 1. As can be seen from the figure, the number of the parent ion  $\text{CHF}_2\text{Cl}^+$  is less, the signal of fragment ion  $\text{CHF}_2^+$  is the strongest one among all fragment ions, the ions  $\text{CF}^+$ ,  $\text{CHF}^+$ ,  $\text{CHFCI}^+$ ,  $\text{CF}_2^+$ , and  $\text{Cl}^+$  are observed as the major fragment ones, the ions  $\text{CFCI}^+$ ,  $\text{CCl}^+$ ,  $\text{HCl}^+$ ,  $\text{CF}_2\text{Cl}^+$ ,  $\text{CHCl}^+$  and  $\text{H}^+$  are the minor fragment ones, and chlorine isotopic variants are also observed as pairs. As no signal at mass greater than that of  $\text{CHF}_2\text{Cl}$  is detected under our experimental conditions, all detected fragment ions were considered to originate from dissociation of parent ion.

The photoionization efficiency spectroscopy (PIE) curves of  $\text{CHF}_2\text{Cl}^+$  and all observed fragment ions from their respective appearance onsets to 22 eV are recorded at a scan step of 0.2–0.5 Å and normalized with respect to the photon flux. As an example, the PIE curves of parent

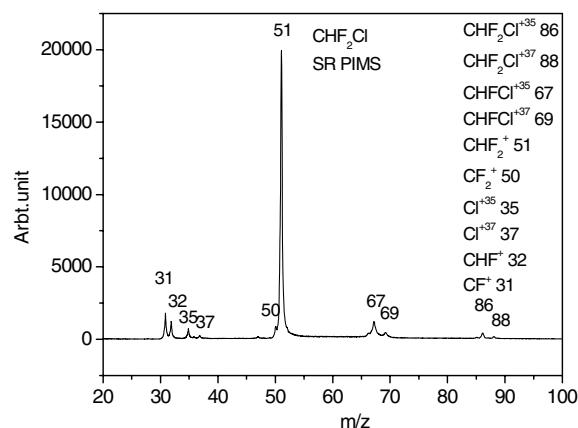


Fig. 1. Photoionization mass spectra of  $\text{CHF}_2\text{Cl}$  excited at zero order synchrotron radiation.

molecule ion  $\text{CHF}_2\text{Cl}^+$  and its daughter ion  $\text{CHF}_2^+$  are shown in Fig. 2a and b, respectively. In the study of VUV dissociative photoionization of  $\text{CHF}_2\text{Cl}$  in an energy region  $\sim 12\text{--}22\text{ eV}$ , the ionization energy of  $\text{CHF}_2\text{Cl}$  and the appearance energy for its fragment ions can reach directly by scanning the wavelength of the monochromatized synchrotron radiation. It should be pointed out that we ignored the thermal energy distribution of the parent molecule in our data processing, considering the present nozzle expansion condition mentioned above. In addition, no correction was made for possible kinetic shifts in determining the APs.

In the PIE curve of  $\text{CHF}_2\text{Cl}$ , the onset of ionization to  $\text{CHF}_2\text{Cl}^+$  is  $12.16 \pm 0.02\text{ eV}$ . The appearance potential (AP) of fragment ion was determined by the onset in each PIE curve, such as, the APs of  $\text{CHF}_2^+$  and  $\text{Cl}^+$  are determined as  $12.43\text{ eV}$  and  $18.51 \pm 0.02\text{ eV}$ , respectively. The dissociation channels producing fragment ions can be deduced and two possible cases should be considered during the calculation of dissociation energy: 1. The fragment ion is formed from a neutral fragment of parent molecule, the dissociation energy to produce it is calculated by subtracting ionization energy of neutral fragment from its appearance potential; 2. The fragment ion is formed by ionization of a parent molecule followed by spontaneous dissociation of the primary parent ion. The latter is generally referred to as dissociative ionization and the

emphasis of this paper is placed on it. The dissociation energy  $E_d$  to produce it is calculated empirically by subtracting ionization energy of parent molecule from its appearance potential,  $E_d = \text{AP} - \text{IE}$ , where  $E_d$  is the dissociation energy, AP is the appearance potential for fragment ion, IE is the ionization energy of parent molecule. As an example, the IE of  $\text{CHF}_2\text{Cl}$  is  $12.16 \pm 0.02\text{ eV}$ , the AP of  $\text{Cl}^+$  is  $18.51 \pm 0.05\text{ eV}$ , then the  $E_d(\text{Cl}^+ - \text{CHF}_2)$  is  $6.35 \pm 0.05\text{ eV}$ . The ionization energy of  $\text{CHF}_2\text{Cl}$  and appearance potentials for its fragment ions,  $\text{CHF}_2^+$ ,  $\text{CF}^+$ ,  $\text{CHF}^+$ ,  $\text{CHFCI}^+$ ,  $\text{CF}_2^+$ ,  $\text{Cl}^+$ ,  $\text{CFCI}^+$ ,  $\text{CCI}^+$ ,  $\text{HCl}^+$ ,  $\text{CF}_2\text{Cl}^+$  and,  $\text{H}^+ \text{CHCl}^+$ , are listed in Table 1 along with some dissociation energies.

#### 4.2. Results of quantum chemical calculations

In this study, total energy  $E_0$  (G2) of  $\text{CHF}_2\text{Cl}$  and fragment radicals should be calculated at first with Gaussian 98 program and G2 method. At the same time, we also optimized equilibrium structure of some transition structure and intermediate, calculated their total energies  $E_0$  (G2), and the possible dissociation channels were confirmed with IRC calculation. The total energy of the related species is given in Table 2.

In high accuracy energy model of Gaussian 98[19], ionization energy (I.E) of each molecule is taken as the amount of energy required to remove an electron from a molecule, computed as the energy difference between the cation and the neutral molecule, For example, the ionization energy of  $\text{CHF}_2\text{Cl}$  is calculated as follows:

$$\begin{aligned} \text{I.E}(\text{CHF}_2\text{Cl}) &= E_0(\text{G2})(\text{CHF}_2\text{Cl}^+) - E_0(\text{G2})(\text{CHF}_2\text{Cl}) \\ &= 12.07\text{ eV}. \end{aligned}$$

This theoretical value of adiabatic ionization energy of  $\text{CHF}_2\text{Cl}$  is close to our experimental one of  $12.16 \pm 0.02\text{ eV}$ .

For possible dissociation channel  $\text{CHF}_2\text{Cl} \rightarrow \text{CHF}_2^+ + \text{Cl}$ , the appearance potential (AP) of  $\text{CHF}_2^+$  is calculated as

$$\begin{aligned} \text{AP} &= E_0(\text{G2})(\text{CHF}_2^+) + E_0(\text{G2})(\text{Cl}) - E_0(\text{G2})(\text{CHF}_2\text{Cl}) \\ &= 12.41\text{ eV}. \end{aligned}$$

In the dissociation channel  $\text{CHF}_2\text{Cl}^+ \rightarrow \text{CHF}_2^+ + \text{Cl}$ , its dissociation energy is calculated as

$$\begin{aligned} E_d &= E_0(\text{G2})(\text{CHF}_2^+) + E_0(\text{G2})(\text{Cl}) - E_0(\text{G2})(\text{CHF}_2\text{Cl}^+) \\ &= 0.34\text{ eV}. \end{aligned}$$

The appearance potentials of other fragment ions and some dissociation energies of other possible dissociation channels can also be calculated in similar ways. IE of  $\text{CHF}_2\text{Cl}$ , APs for fragmental ions,  $\text{CHF}_2^+$ ,  $\text{CF}^+$ ,  $\text{CHF}^+$ ,  $\text{CHFCI}^+$ ,  $\text{CF}_2^+$ ,  $\text{Cl}^+$ ,  $\text{CFCI}^+$ ,  $\text{CCI}^+$ ,  $\text{HCl}^+$ ,  $\text{CF}_2\text{Cl}^+$  and,  $\text{H}^+ \text{CHCl}^+$ , and  $E_d$ s of some possible dissociation channels, predicted by G2 calculations, are given in Table 1.

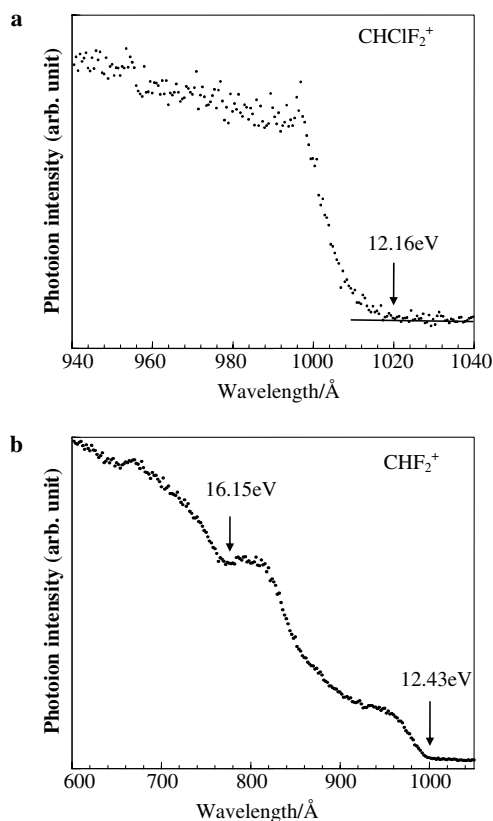


Fig. 2. (a) Photoionization efficiency curve of  $\text{CHClF}_2^+$  from  $\text{CHF}_2\text{Cl}$ . (b) Photoionization efficiency curve of  $\text{CHF}_2^+$  from  $\text{CHF}_2\text{Cl}$ .

Table 1

Theoretical and experimental results of Ionization energy, appearance potential and dissociation energy ( $E_d$ )

Ions	I.E. or A.P. [Theory (eV)]	I.E. or A.P. [Exp. (eV)]	Dissociation energy $E_d$ [Theory (eV)]	Dissociation energy $E_d$ [Exp. (eV)]	Possible dissociation channels
CHF <sub>2</sub> Cl <sup>+</sup>	12.07	12.16 ± 0.02	0.0		CHF <sub>2</sub> Cl <sup>+</sup>
CF <sub>2</sub> Cl <sup>+</sup>	13.06	14.16	0.99	2.00	CF <sub>2</sub> Cl <sup>+</sup> + H
CHFCI <sup>+</sup>	13.53	14.21	1.45	2.05	CHFCI <sup>+</sup> + F
CFCI <sup>+</sup>	12.60	12.47	0.54	0.31	CFCI <sup>+</sup> + HF
CHF <sub>2</sub> <sup>+</sup>	12.41	12.43	0.34	0.27	CHF <sub>2</sub> <sup>+</sup> + Cl
CF <sub>2</sub> <sup>+</sup>	13.42	13.57	1.35	1.41	CF <sub>2</sub> <sup>+</sup> + HCl
CF <sub>2</sub> <sup>+</sup>	17.86	18.30	5.80	6.14	CF <sub>2</sub> <sup>+</sup> + H + Cl
CHCl <sup>+</sup>	17.56	17.92	5.50	5.76	CHCl <sup>+</sup> + F <sub>2</sub>
CHF <sup>+</sup>	18.63	18.73	6.56	6.57	CHF <sup>+</sup> + F + Cl
CF <sup>+</sup>	16.41	16.25	4.34	4.09	CF <sup>+</sup> + F + HCl
HCl <sup>+</sup>	14.68	14.55	2.61	2.39	HCl <sup>+</sup> + CF <sub>2</sub>
CCl <sup>+</sup>	16.18	17.76	4.12	5.60	CCl <sup>+</sup> + HF + F
Cl <sup>+</sup>	18.77	18.51 ± 0.05	6.70	6.35 ± 0.05	Cl <sup>+</sup> + CF + HF
H <sup>+</sup>	20.02	19.72	7.95	7.56	H <sup>+</sup> + CF <sub>2</sub> + Cl

Table 2

The energies of molecules and radicals calculated using G2 method

Species	Energy $E_0$ (G2) (Hartrees)	Species	Energy $E_0$ (G2) (Hartrees)
CHF <sub>2</sub> Cl	−697.871530	CF	−137.627012
CHF <sub>2</sub> Cl <sup>+</sup>	−697.427860	CF <sup>+</sup>	−137.295314
CF <sub>2</sub> Cl	−697.209494	HCl	−460.340177
CF <sub>2</sub> Cl <sup>+</sup>	−696.899136	HCl <sup>+</sup>	−459.872907
CHF <sub>2</sub>	−238.056018	HF	−100.350008
CHF <sub>2</sub> <sup>+</sup>	−237.738777	HF <sup>+</sup>	−99.758889
CHFCI	−598.047741	CH	−38.412589
CHFCI <sup>+</sup>	−597.741415	CH <sup>+</sup>	−38.024467
CHF	−138.247081	F <sub>2</sub>	−199.323957
CHF <sup>+</sup>	−137.877099	F <sub>2</sub> <sup>+</sup>	−198.737486
CHCl	−498.239843	H	−0.500000
CHCl <sup>+</sup>	−497.901777	C	−37.784301
CFCI	−597.432256	C <sup>+</sup>	−37.373446
CFCI <sup>+</sup>	−597.058043	Cl	−459.676627
CF <sub>2</sub>	−237.458830	Cl <sup>+</sup>	−459.204535
CF <sub>2</sub> <sup>+</sup>	−237.038149	F	−99.632814
CCl	−497.613763	F <sup>+</sup>	−98.993867
CCl <sup>+</sup>	−497.293738		

### 4.3. Discussion

#### 4.3.1. Ionization energy and appearance energy

In our study of PIMS here, the experimental IE of CHF<sub>2</sub>Cl is 12.16 ± 0.02 eV, which is comparable with the theoretical one, 12.07 eV, predicted by G2 calculation. The value of 12.16 ± 0.02 eV is in reasonable agreement with an adiabatic ionization energy of 12.28 ± 0.02 eV determined using PIMS [16,22]. Our experimental appearance potentials of fragment ions from CHF<sub>2</sub>Cl<sup>+</sup> are also comparable with those ones predicted by G2 calculations. As an example, in the PIE curve of CHF<sub>2</sub><sup>+</sup> (Fig. 2b), its AP is 12.43 eV and in agreement with 12.41 eV predicted by G2 calculation (Table 1). At 16.15 eV, there is a further rise of the ion signal, whose energy difference between this energy and the IE of CHF<sub>2</sub>Cl is 3.99 eV. While in the PIE curve of CF<sub>2</sub><sup>+</sup> (not shown here), the AP of CF<sub>2</sub><sup>+</sup> is 13.57 eV, coming from the dissociation channel

CHF<sub>2</sub>Cl<sup>+</sup> → CF<sub>2</sub><sup>+</sup> + HCl, and this value close to 13.42 eV predicted by G2 calculation (Table 1). And then, there is also a further rise of the ion signal at 18.30 eV, which may originate from the dissociation channel CHF<sub>2</sub>Cl<sup>+</sup> → CF<sub>2</sub><sup>+</sup> + H + Cl. The energy value of 18.30 eV is comparable with 17.86 eV predicted by G2 calculations (Table 1).

In the studies of EIMS [14] and MBEIMS [15], the IEs of CHF<sub>2</sub>Cl are 12.69 ± 0.15 and 12.50 ± 0.05 eV respectively that are vertical ionization ones and greater than ours. In these studies, the appearance potentials of fragment ions from CHF<sub>2</sub>Cl<sup>+</sup> are greater than ours in general, for example, the APs of CF<sub>2</sub><sup>+</sup> are 16.10 ± 0.3 [14] and 15.36 ± 0.10 eV [15], respectively, while our value of CF<sub>2</sub><sup>+</sup> is 13.57 eV; the APs of CHClF<sup>+</sup> are 15.11 ± 0.15 [14] and 14.79 ± 0.10 eV [15] respectively, while our value of CF<sup>+</sup> is 14.21 eV. The poor agreement of our experimental values of ionization energy of CHF<sub>2</sub>Cl and appearance potential for its fragment ions with those ones in EIMS [14] and MBEIMS [15] can be explained as follows: A fundamental and important difference exists between photon impact ionization and electron impact ionization. A photon is annihilated in such an event whereas an electron is not; it is scattered with a lower energy than it had before its impact. Since a photon must be annihilated in the process of single photon excitation, the ionization by photon impact is a resonance process which occurs when  $h\nu = \text{IE}$ , unlike the electron impact situation where the primary electron energy  $E_p > \text{IE}$ . The ionization by electron impact and ionization by photon impact are also rather different phenomena, and they go by different threshold ionization laws. An obvious practical consequence of the differences in the threshold law is that accurate ionization and appearance potentials (for positive ions) are more easily obtainable from photon impact ionization efficiency curves than from the corresponding electron impact curves [23]. Another reason for these differences is due to the inherent lack of resolution in most electron impact apparatus, such as, about 0.3 eV in 1960s and 14 meV for MBEIMS [15].

#### 4.3.2. The mechanism of the dissociative photoionization of $\text{CHF}_2\text{Cl}$

In the process of the dissociative photoionization of  $\text{CHF}_2\text{Cl}$ , the possible dissociation channels can be divided into three different types:

The first type is the direct dissociation channel, its experimental dissociation energy is nearly the same as that one predicted from G2 method. For example,  $\text{CHF}_2\text{Cl}^+ \rightarrow \text{CHF}_2^+ + \text{Cl}$  (Fig. 3).

Theoretically, the bond lengths of C–Cl in neutral  $\text{CHF}_2\text{Cl}$  and  $\text{CHF}_2\text{Cl}^+$  ions are 1.759 and 2.796 Å, respectively, the theoretical dissociation energy is 0.34 eV for  $\text{CHF}_2\text{Cl}^+ \rightarrow \text{CHF}_2^+ + \text{Cl}$ . It means that the bond of C–Cl in  $\text{CHF}_2\text{Cl}^+$  will be broken down easily and the dissociation channel  $\text{CHF}_2\text{Cl}^+ \rightarrow \text{CHF}_2^+ + \text{Cl}$  may involve direct cleavage of the C–Cl bond due to that its dissociation energy is very small. In fact, the ion signal of  $\text{CHF}_2^+$  is the biggest one in the photoionization mass spectroscopy of  $\text{CHF}_2\text{Cl}$ . The experimental dissociation energy is 0.27 eV and nearly the same as that of theoretical one.

The second type of dissociation channels involves in the transition structure and intermediate. If the theoretical value of dissociation energy is smaller than that relative energy of transition structure, and then, the relative energy of transition structure is the reaction barrier of this dissociation channel, the experimental value of this dissociation energy might be nearly the same as the reaction barrier. For example, the dissociation channel,  $\text{CHF}_2\text{Cl}^+ \rightarrow \text{CCl}^+ + \text{HF} + \text{F}$ , belongs to this type. For the dissociation channel  $\text{CHF}_2\text{Cl}^+ \rightarrow \text{CCl}^+ + \text{HF} + \text{F}$ , its dissociation path includes five steps: formation of the parent molecule ions, formation of the fragment ion  $\text{CHFCl}^+$  from the dissociation channel  $\text{CHF}_2\text{Cl}^+ \rightarrow \text{CHFCl}^+ + \text{F}$ , the transition structure TS2 of the fragment ion  $\text{CHFCl}^+$ , the intermediate LM2 of the fragment ion  $\text{CHFCl}^+$  and formation of the reaction products  $\text{CCl}^+ + \text{HCl} + \text{F}$ . The optimized geometries of transition structure TS2, and intermediate structure LM2 of  $\text{CHFCl}^+$ , are shown in Fig. 4a and b.

In the view of the energy, under the conditions of larger photon energy, the dissociation channel,  $\text{CHF}_2\text{Cl}^+ \rightarrow \text{CCl}^+ + \text{HF} + \text{F}$ , may occur. The energies of the different process in this dissociation channel, and the relative energies to that one of parent ion, are calculated using Gaussian 98 and G2 method (Table 3). In Table 3, the energies of transition structure of  $\text{CHFCl}^+(\text{TS2})$  and intermediate

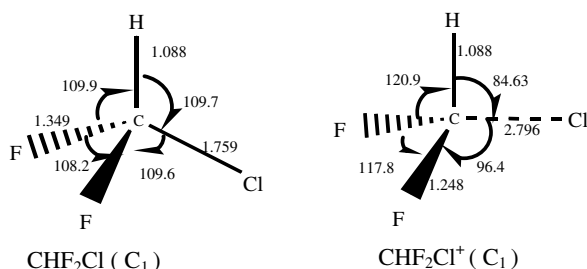


Fig. 3. Optimized structures of  $\text{CHF}_2\text{Cl}$  and  $\text{CHF}_2\text{Cl}^+$ .

Table 3  
Energies of various processes for the dissociation channel  $\text{CHF}_2\text{Cl}^+ \rightarrow \text{CCl}^+ + \text{HF} + \text{F}$

	$E_0(\text{G2})$ (Hartrees)	Relative energy $E_d(\text{G2})$ (eV)	Relative energy $E_d(\text{Exp})$ (eV)
$\text{CHF}_2\text{Cl}^+$	−697.42786	0.0	
$\text{CHFCl}^+ + \text{F}(3\text{-p})$	−697.374229	1.46	2
$\text{CHFCl}^+(\text{TS2}) + \text{F}$	−697.226412	5.48 V(G2)	
$\text{CHFCl}^+(\text{LM2}) + \text{F}$	−697.292237	3.69	
$\text{CCl}^+ + \text{HF} + \text{F}(\text{l})$	−697.27656	4.11	5.60
$\text{CHFCl}^+(\text{TS2})$	−597.5935982		
$\text{CHFCl}^+(\text{LM2})$	−597.659423		

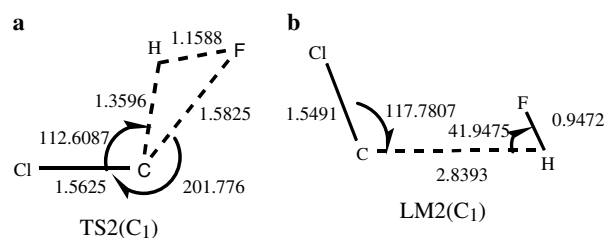


Fig. 4. (a)  $\text{CHFCl}^+$  transition structure TS2 (C1). (b)  $\text{CHFCl}^+$  intermediate LM2 (C1).

structure LM2 of  $\text{CHFCl}^+$  are also given. The relative energy for the various processes in the dissociation channel  $\text{CHF}_2\text{Cl}^+ \rightarrow \text{CCl}^+ + \text{HF} + \text{F}$  is shown in Fig. 5. The parent ion  $\text{CHF}_2\text{Cl}^+$  dissociates into fragment ion  $\text{CHFCl}^+$  and F at first by through direct cleavage of the C–F bond of  $\text{CHF}_2\text{Cl}^+$ , and requires 1.46 eV, then  $\text{CHFCl}^+$  subsequently proceeds through a transition structure TS2 and an intermediate structure LM2 of  $\text{CHFCl}^+$  to form  $\text{CCl}^+$  and HF. It is found from Fig. 5 that the relative energy of  $\text{CHFCl}^+(\text{TS2}) + \text{F}$  is 5.48 eV, and larger than theoretical value, 4.12 eV, of dissociation energy, so 5.48 eV is the reaction barrier of this dissociation channel. While the experimental value of dissociation energy for this dissociation channel is 5.60 eV, and nearly the same as this reaction barrier.

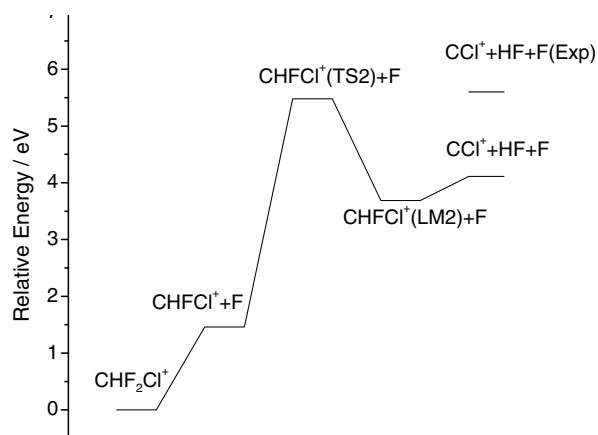


Fig. 5. the relative energies for the dissociation channel  $\text{CHF}_2\text{Cl}^+ \rightarrow \text{CCl}^+ + \text{HF} + \text{F}$ .



The third type of possible dissociation channels also involve in the transition structure and intermediate structure, however, the theoretical value of its dissociation energy is larger than the relative energy of its transition structure, and then, it is thought that there is no reaction barrier for this dissociation channel. Under this situation, the experimental value of the dissociation energy may be nearly the same as the theoretical one. Due to the complexity for the possible dissociation channel of a molecule, one should be careful while classifying on the possible dissociation channel.

## 5. Conclusion

Ionization energy of molecule, appearance potentials for its fragment ions, and dissociation energies to produce these fragment ions have been obtained from experimental studies of photoionization and fragmentation of  $\text{CHF}_2\text{Cl}$  using synchrotron radiation, photoionization mass spectroscopy, and photoionization efficiency spectroscopy. The total energies of  $\text{CHF}_2\text{Cl}$ , some related molecular ions, and radical ions have also been calculated using Gaussian 98 program and G2 method. And then, the ionization energy of  $\text{CHF}_2\text{Cl}$ , appearance potentials for its fragment ions, and dissociation energy of some possible dissociation channel to produce them are estimated using these total energies. On the basis of comparison between experimental results and those ones of theoretical calculation, the mechanism of photoionization and photodissociation of  $\text{CHF}_2\text{Cl}$  is discussed. Generally speaking, for a possible dissociative photoionization channel of  $\text{CHF}_2\text{Cl}$ , the experimental dissociation energy is in agreement with either the theoretical dissociation energies ( $E_d$ ) or the reaction barriers  $V(\text{G2})$  predicted from G2 calculation.

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