



## Synchrotron radiation VUV double photoionization of $\text{CHF}_2\text{Cl}$

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### ABSTRACT

VUV double photoionization of  $\text{CHF}_2\text{Cl}$  in an energy region 32–40 eV was investigated with photoionization mass spectroscopy by using synchrotron radiation. The double ionization energy of  $\text{CHF}_2\text{Cl}$  and appearance energies for its main fragment dications ( $\text{CHCl}^{2+}$ ,  $\text{CF}_2^{2+}$  and  $\text{CHFCl}^{2+}$ ), were determined with photoionization efficiency spectroscopy for the first time. The single point energies of  $\text{CHF}_2\text{Cl}$  and its parent dication ( $\text{CHF}_2\text{Cl}^{2+}$ ) were calculated using Gaussian 03 program and density functional theory (DFT and B3LYP functional). The vertical double ionization energy of  $\text{CHF}_2\text{Cl}$  was predicted by using B3LYP method and empirical equation. According to our research results, the experimental double ionization energy of  $\text{CHF}_2\text{Cl}$  is in good agreement with the theoretically calculated vertical double ionization energy. The mechanism of double photoionization of  $\text{CHF}_2\text{Cl}$  was discussed based on the comparison of our experimental results with those predicted theoretically.

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### 1. Introduction

Chlorofluorocarbons (CFCs), such as  $\text{CCl}_2\text{F}_2$  (Freon 12), are ozone depletion substances because they can release chlorine atoms which could initiate the ozone depletion in stratosphere. According to the international regulations (Montreal Protocol and amendments), they should be phased out eventually [1–4]. Hydrochlorofluorocarbons (HCFCs), such as  $\text{CHF}_2\text{Cl}$  (Freon 22), contain one or more hydrogen atoms and are easily attacked by the OH radical in the troposphere. Therefore, HCFCs do not reach the upper atmosphere in considerable abundance and are usually used as replacements for CFCs. However, HCFCs have the possibility for ozone attack if they arrive at the stratosphere, because they still contain chlorine atoms. In the future, HCFCs should be replaced by more environmentally friendly compounds which show null ozone-depleting potential, such as hydrofluorocarbons (HFCs), and the transfer from HCFCs to HFCs will be a good method. Thus, it is very important to have a detailed knowledge of the photochemical properties of HCFCs.

Chlorodifluoromethane ( $\text{CHF}_2\text{Cl}$ ) is one of the key molecules in atmospheric environment, and usually used as an alternative for  $\text{CCl}_2\text{F}_2$  [5].  $\text{CHF}_2\text{Cl}$  has been studied widely with various kinds of spectroscopic technologies, such as VUV absorption spectra

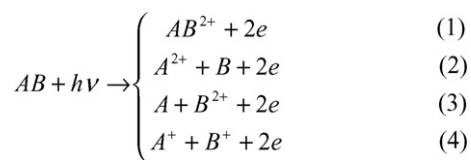
[6], VUV photoelectron spectra (PES) [7], molecular beam electron impact mass spectroscopy (MBEIMS) [8], electron impact mass spectroscopy (EIMS) [9], and VUV photoionization mass spectroscopy (PIMS) [10–12]. However, those studies have mainly focused on the ionization of  $\text{CHF}_2\text{Cl}$  in low energy range (10–32 eV). The ionization of  $\text{CHF}_2\text{Cl}$  in higher energy range, such as the double ionization energy (DIE), the appearance potentials (APs) for its fragment dications, has been very little investigated so far, either experimentally or theoretically, except that its vertical double ionization energy was calculated by Irikura et al. [13].

Doubly charged molecular ions or dications have been widely investigated over last decades, due to their unusual nature. Molecular ions with two positive charges or molecular dications, such as  $\text{CHF}_2\text{Cl}^{2+}$ , are usually intrinsically unstable and easy to dissociate into two singly charged fragment ions, because the coulombic repulsion between the positive charges dominates the long range interaction of two fragments from molecular dication. Stable and metastable molecular dications are still observed due to that at short range covalent bonding can overcome these repulsive coulombic forces within the molecule. The stability of these molecular dications is determined by the interaction between these forces. The forces are finally balanced in metastable states where molecular dications are stable for nanoseconds or longer and then become fragments [14].

Doubly charged dications can be formed in double photoionization via the simplified schemes depicted in the following for a

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diatomic molecule AB:



Of course, many more reaction pathways are possible for double photoionization of a polyatomic molecule, but the basic double ionization schemes still involve parent and fragment dication formation as well as the ion-pair process [8].

In order to determine DIE of CHF<sub>2</sub>Cl and APs for its main fragment dications, and to explore the mechanism for its dissociative double ionization, an experimental study of VUV dissociative double photoionization of CHF<sub>2</sub>Cl in the photon energy range 32–40 eV was performed by using synchrotron radiation (SR). The vertical DIE of CHF<sub>2</sub>Cl was predicted using density functional theory (DFT and B3LYP functional) and empirical equation [15]. The quantum chemistry calculation was carried out using Gaussian 03 program and B3LYP method to obtain some photochemical parameters. Then the mechanism of double photoionization of CHF<sub>2</sub>Cl was discussed.

## 2. Experiment

This experimental apparatus was described previously elsewhere [16–18]. In brief, the experiment was carried out at the Atomic and Molecular Physics Beamline U14-A station of the National Synchrotron Radiation Laboratory (NSRL), in Hefei, China. The synchrotron radiation beam from an Undulator of the 800 MeV electron storage ring of the NSRL is monochromatized with a 6-m length monochromator equipped with the three gratings (1250, 740 and 370) lines/mm. The 740 lines/mm grating covers the energy range from 15 to 45 eV, and its resolving power ( $E/\Delta E$ ) is about 1000–5000 depending on the widths of the entrance and exit slits. Usually these two slits are both adjusted to 80 μm width with a resolving power of 5000. The average photon flux was measured to be about  $5 \times 10^{12}$  photons/s. The monochromatized synchrotron radiation was focused by a toroidal mirror into the photoionization chamber. In this experiment, the wavelength of the monochromator was calibrated with the known ionization energies and special ionization spectra of the inert gases (He, Ne and Ar).

The sample of CHF<sub>2</sub>Cl (purity 99%) was introduced by supersonic expansion through a continuous beam nozzle with an orifice of 70-μm diameter from the molecular beam chamber into the ionization chamber through a Ø1 mm skimmer. The CHF<sub>2</sub>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 photoions signals from the detector were counted with a multiscaler P7888 counter (FAST Comtec, Germany) after they were amplified with preamplifier VT120C (EG&G, ORTEC) and transferred to a computer for further processing. The photoionization mass spectroscopy (PIMS) spectrum of CHF<sub>2</sub>Cl can be obtained when it is excited by using fixed photon energy above its ionization threshold.

In this experiment, the pressure of the ionization chamber was about  $2 \times 10^{-3}$  Pa when the molecular beam was introduced, while the stagnation pressure was about 0.2 MPa. The photoionization efficiency spectroscopy (PIES) curve was measured while the monochromator was scanned with an energy increment of 30 meV, and the data acquisition time for each point was 50 s depending

on the ion abundance. To normalize the ion signals, the photon intensity was monitored simultaneously with a silicon photodiode (SXUV-100, International Radiation Detectors, Inc.).

## 3. Quantum chemical calculations

According to the theory, the calculated value of vertical DIE refers to the energy difference ( $\Delta E$ ) of two potential hypersurfaces between the neutral molecule and its parent dication at the equilibrium geometry of the neutral molecule [19]. The single point energies of CHF<sub>2</sub>Cl and its parent dication were calculated with B3LYP method by using Gaussian 03 program [20]. Firstly, neutral molecular geometry was optimized using the B3LYP hybrid density functional [21,22] in conjunction with the 6-31G(d) basis sets as implemented in the Gaussian 03 program suite. Secondly, the single point energies of neutral molecule and its parent dication were calculated at the optimized geometry of the neutral molecule. Finally, the vertical DIE was the difference between these two single point energies.

## 4. Results and discussion

### 4.1. Results of experiment

The PIMS of CHF<sub>2</sub>Cl at the photon energy of 40 eV is shown in Fig. 1. The singly charged parent cation (CHF<sub>2</sub>Cl<sup>+</sup>) and all fragment cations (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>, CHCl<sup>+</sup>, F<sup>+</sup> and so on) are observed. Besides that, the doubly charged parent dication (CHF<sub>2</sub>Cl<sup>2+</sup> ( $m/z=43$ )) and fragment dications (CHCl<sup>2+</sup> ( $m/z=24$ ), CF<sub>2</sub><sup>2+</sup> ( $m/z=25$ ), CHF<sup>35</sup>Cl<sup>2+</sup> ( $m/z=33.5$ ), CHF<sup>37</sup>Cl<sup>2+</sup> ( $m/z=34.5$ )) are observed in this experiment for the first time. As no signal at mass greater than that of parent molecule CHF<sub>2</sub>Cl (CHF<sub>2</sub><sup>35</sup>Cl<sup>+</sup>,  $m/z=86$ ; CHF<sub>2</sub><sup>37</sup>Cl<sup>+</sup>,  $m/z=88$ ) is detected in Fig. 1, and no signal, whose ratio of mass to charge equals to those dications mentioned above, is detected in the PIMS of CHF<sub>2</sub>Cl at the photon energy of 22.5 eV, which is shown in Fig. 2, all detected fragment cations and dications (in Fig. 1) are considered as originating from dissociation of parent molecular cation or dication. From Fig. 1, we also find that the intensities of dications signal are quite weak, especially for parent dication (CHF<sub>2</sub>Cl<sup>2+</sup>), mainly because their lifetimes are very short due to the coulombic repulsion for dications with two positive charges. Both the intensities of ion signal CF<sub>2</sub><sup>35</sup>Cl<sup>+</sup> ( $m/z=85$ ) and its isotope (CF<sub>2</sub><sup>37</sup>Cl<sup>+</sup>  $m/z=87$ ) are stronger than that of CHF<sub>2</sub><sup>35</sup>Cl<sup>+</sup> ( $m/z=86$ ) in Fig. 1. It is mainly because the parent cation CHF<sub>2</sub>Cl<sup>+</sup> is very easily dissociated into fragment cations at the higher photon energy of 40 eV. As those singly charged par-

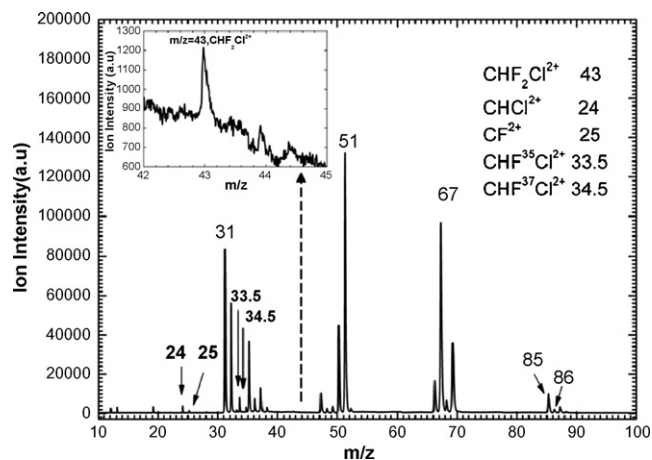


Fig. 1. Photoionization mass spectra of CHF<sub>2</sub>Cl at the photon energy of 40 eV.

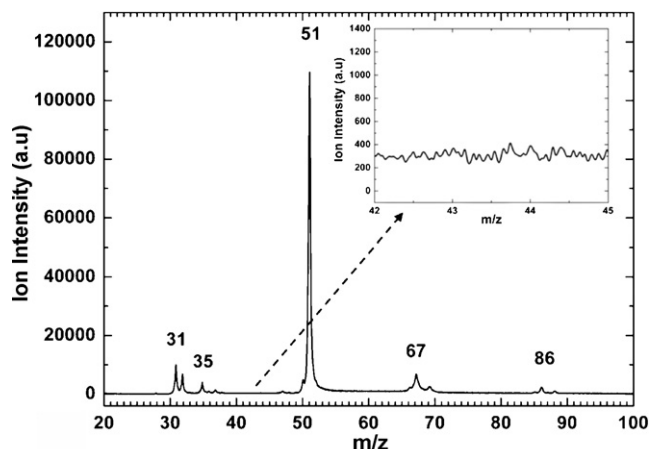


Fig. 2. Photoionization mass spectra of  $\text{CHF}_2\text{Cl}$  at the photon energy of 22.5 eV.

ent and fragment cations have been discussed in details previously [9–12], only discussed here are the doubly charged parent and its main fragment dications observed.

In order to study of SRVUV dissociative double photoionization of  $\text{CHF}_2\text{Cl}$ , the PIE curves of parent dication  $\text{CHF}_2\text{Cl}^{2+}$  and its fragment dications from 32 to 40 eV are recorded at a scan step of 30 meV, and normalized with respect to the photon flux. The DIE of  $\text{CHF}_2\text{Cl}$  and the APs for its fragment dications can be obtained directly by scanning the wavelength of the monochromatized synchrotron radiation. In the PIE curve of  $\text{CHF}_2\text{Cl}^{2+}$ , the onset of double ionization to  $\text{CHF}_2\text{Cl}^{2+}$  is  $33.80 \pm 0.03$  eV (Fig. 3). The APs of main fragment dications are determined by the onset in each PIE curve, such as the APs of  $\text{CHFCl}^{2+}$  (two isotopes,  $\text{CHF}^{35}\text{Cl}^{2+}$  (Fig. 4) and  $\text{CHF}^{37}\text{Cl}^{2+}$  (Fig. 5)),  $\text{CF}_2^{2+}$  (Fig. 6) and  $\text{CHCl}^{2+}$  (Fig. 7) are determined as  $34.34 \pm 0.06$ ,  $34.40 \pm 0.09$ ,  $36.59 \pm 0.15$  and  $37.22 \pm 0.03$  eV, respectively.

#### 4.2. Results of calculation

The vertical DIE of molecule is regarded as the amount of energy required to remove two electrons from neutral molecule with a negligible change of molecular geometry, and computed as described in Section 3. For example, the vertical DIE of  $\text{CHF}_2\text{Cl}$  is calculated as

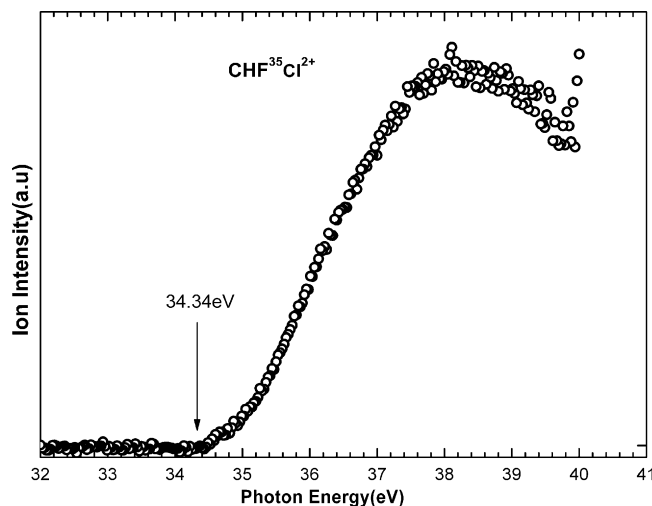


Fig. 4. Photoionization efficiency spectroscopy curve of  $\text{CHF}^{35}\text{Cl}^{2+}$ .

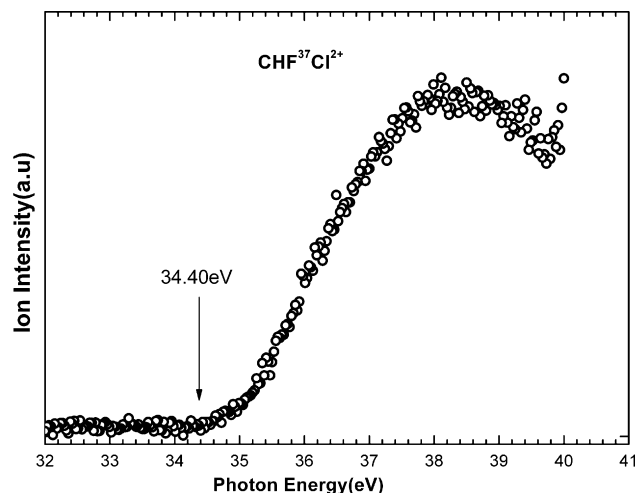


Fig. 5. Photoionization efficiency spectroscopy curve of  $\text{CHF}^{37}\text{Cl}^{2+}$ .

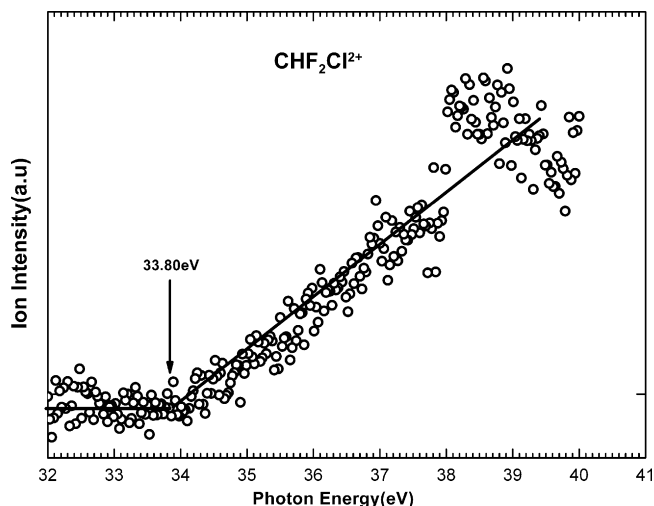


Fig. 3. Photoionization efficiency spectroscopy curve of  $\text{CHF}_2\text{Cl}^{2+}$ .

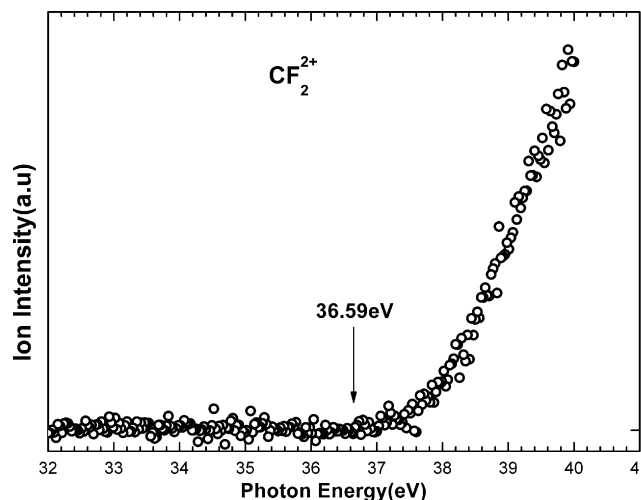


Fig. 6. Photoionization efficiency spectroscopy curve of  $\text{CF}_2^{2+}$ .

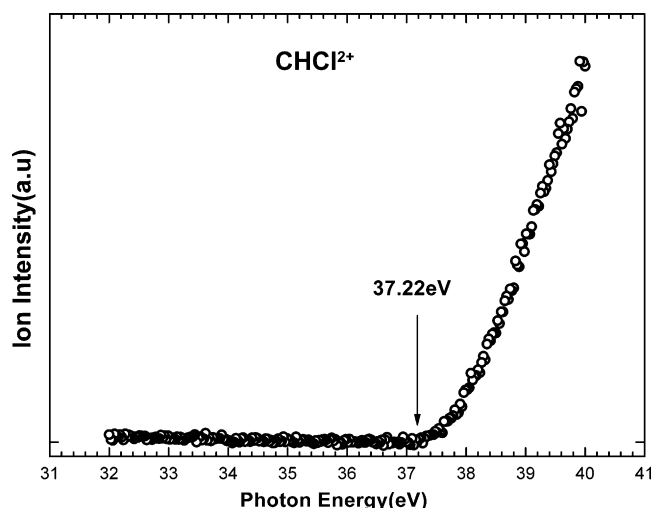


Fig. 7. Photoionization efficiency spectroscopy curve of  $\text{CHCl}_2^{2+}$ .

follows:

$$\begin{aligned} \text{DIE}(\text{CHF}_2\text{Cl}) &= E(\text{S})(\text{CHF}_2\text{Cl}^{2+}) - E(\text{S})(\text{CHF}_2\text{Cl}) \\ &= (-697.329931529) \\ &\quad - (-698.571994706) \text{ Hartree} = 33.798 \text{ eV}. \end{aligned}$$

Here,  $E(\text{S})$  refers to the single point energy at the optimized geometry of the neutral molecule. This theoretical value of vertical DIE of  $\text{CHF}_2\text{Cl}$  is very close to 33.5 eV calculated by Irikura et al. [13].

The DIE of small molecule can also be predicted by using empirical equation [15]:

$$\text{DIE} = (2.20 \pm 0.3) \times \text{IE} + \frac{11.50 \pm 1}{r_{12}}$$

Here, IE refers to single ionization energy of molecule;  $r_{12}$ , in Å units, refers to the distance between two charges in the molecular dications, its value can be obtained from molecular structure calculation.

By the quantum chemical calculation above, the two charges in dication  $\text{CHF}_2\text{Cl}^{2+}$  are mainly distributed at C and Cl atoms, the distance between these two atoms is 1.79726 Å, and the IE of  $\text{CHF}_2\text{Cl}$  is 12.16 eV [12]. By using the empirical equation above, the DIE of  $\text{CHF}_2\text{Cl}$  can be obtained about 33.707 eV.

#### 4.3. Discussion

The experimental DIE of  $\text{CHF}_2\text{Cl}$  is  $33.80 \pm 0.03$  eV, which is in good agreement with our theoretical value, 33.798, and 33.707 eV calculated above, also with the vertical DIE, 33.5 eV, calculated by Irikura et al. [13]. From discussion above, the experimental DIE of  $\text{CHF}_2\text{Cl}$  is reasonable and close to theoretical vertical one.

The dissociation channels producing fragment dications can be deduced from PIES curves of parent dication and its fragment dications. In the experimental study of dissociative ionization of molecule [12], the fragment dication may be formed by double ionization of a parent molecule followed by spontaneous dissociation of the primary parent dication, and the dissociation energy  $E_d$  to produce it can be calculated empirically by subtracting double ionization energy of parent molecule from its AP,  $E_d = \text{AP} - \text{DIE}$ , where  $E_d$  is the dissociation energy, AP is the appearance potential for fragment dication, and DIE is the double ionization energy of parent molecule.

Here, we only discuss the possible dissociative channels to produce some main fragment dications from parent dication  $\text{CHF}_2\text{Cl}^{2+}$ .

The dication  $\text{CHFCI}^{2+}$  comes from the dissociation channel:  $\text{CHF}_2\text{Cl}^{2+} \rightarrow \text{CHFCI}^{2+} + \text{F}$ , its experimental dissociation energy ( $E_d$ ) is calculated as

$$E_d(\text{CHFCI}^{2+} - \text{F}) = \text{AP}(\text{CHFCI}^{2+}) - \text{DIE}(\text{CHF}_2\text{Cl}) = 0.54 \text{ eV}.$$

Here  $\text{DIE}(\text{CHF}_2\text{Cl}) = 33.80$  eV and  $\text{AP}(\text{CHFCI}^{2+}) = 34.34$  eV.

The AP of dication  $\text{CF}_2^{2+}$  is  $36.59 \pm 0.15$  eV and the experimental dissociative energy  $E_d$  to produce it can be calculated in the same way as above:

$$E_d(\text{CF}_2^{2+} - \text{HCl}) = \text{AP}(\text{CF}_2^{2+}) - \text{DIE}(\text{CHF}_2\text{Cl})$$

In principle, the dication  $\text{CF}_2^{2+}$  comes from two possible dissociation channels:  $\text{CHF}_2\text{Cl}^{2+} \rightarrow \text{CF}_2^{2+} + \text{HCl}$  and  $\text{CHF}_2\text{Cl}^{2+} \rightarrow \text{CF}_2^{2+} + \text{H} + \text{Cl}$ . Generally speaking, the  $E_d$  of the former channel should be smaller than that of the latter channel. Because there is only one AP of  $\text{CF}_2^{2+}$  in its PIE curve, the most possible dissociation channel may be regarded as the former one and its  $E_d$  is 2.79 eV.

Similarly, the experimental dissociative energy  $E_d$  to produce  $\text{CHCl}^{2+}$  can also be calculated as:

$$E_d(\text{CHCl}^{2+} - \text{F}_2) = \text{AP}(\text{CHCl}^{2+}) - \text{DIE}(\text{CHF}_2\text{Cl})$$

Here the AP ( $\text{CHCl}^{2+}$ ) is  $37.22 \pm 0.03$  eV and the dissociative channel to produce  $\text{CHCl}^{2+}$  might be  $\text{CHF}_2\text{Cl}^{2+} \rightarrow \text{CHCl}^{2+} + \text{F}_2$  rather than  $\text{CHF}_2\text{Cl}^{2+} \rightarrow \text{CHCl}^{2+} + \text{F} + \text{F}$ , and its  $E_d$  is 3.42 eV.

## 5. Conclusions

The parent dication  $\text{CHF}_2\text{Cl}^{2+}$  and the main fragment dications ( $\text{CHCl}^{2+}$ ,  $\text{CF}_2^{2+}$  and  $\text{CHFCI}^{2+}$ ) are observed for the first time. Double ionization energy of molecule, appearance potentials for its main fragment dications and dissociation energies to produce these fragment dications, have been obtained from experimental studies of double photoionization of  $\text{CHF}_2\text{Cl}$  by using synchrotron radiation, photoionization mass spectroscopy, and photoionization efficiency spectroscopy. The single point energies of  $\text{CHF}_2\text{Cl}$  and its parent dication, which are both at the optimized geometry optimized of the neutral molecule, have been calculated using Gaussian 03 program and B3LYP method, then the vertical double ionization energy of  $\text{CHF}_2\text{Cl}$  is calculated. According to the comparison between experimental results and those of theoretical calculation, the experimental double photoionization energy is in reasonable agreement with either the theoretical vertical double ionization energy or the calculated result by using empirical equation. At the same time, the dissociative channel and energy  $E_d$  to produce main fragment dications from parent dication  $\text{CHF}_2\text{Cl}^{2+}$  are also discussed.

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