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Article in *The European Physical Journal D* · April 2017

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# Electron impact ionization cross section studies of $C_2F_x$ ( $x = 1-6$ ) and $C_3F_x$ ( $x = 1-8$ ) fluorocarbon species<sup>\*</sup>

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Received 8 December 2016

Published online 13 April 2017 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2017

**Abstract.** The total ionization cross section for  $C_2F_x$  ( $x = 1-6$ ) and  $C_3F_x$  ( $x = 1-8$ ) fluorocarbon species are studied with the Binary-Encounter Bethe (BEB) model using various orbital parameters calculated from restricted/unrestricted Hartree-Fock (RHF/UHF) and Density Functional Theory (DFT). All the targets were optimized for their minimal structures and energies with several ab-initio methods with the aug-cc-pVTZ basis set. Among them, the present results with RHF/UHF orbital energies showed good agreement with the experimental results for stable targets  $C_2F_6$ ,  $C_2F_4$ ,  $C_3F_6$  and  $C_3F_8$ . The results with the DFT ( $\omega B97X/\omega B97X-D$ ) showed a reasonable agreement with the recent calculation of Bull et al. [J.N. Bull, M. Bart, C. Vallance, P.W. Harland, Phys. Rev. A **88**, 062710 (2013)] for  $C_2F_6$ ,  $C_3F_6$  and  $C_3F_8$  targets. The ionization cross section for  $C_2F$ ,  $C_2F_2$ ,  $C_2F_3$ ,  $C_3F$ ,  $C_3F_2$ ,  $C_3F_3$ ,  $C_3F_4$ ,  $C_3F_5$  and  $C_3F_7$  were computed for the first time in the present study. We have also computed the vertical ionization potentials and polarizability for all the targets and compared them with other experimental and theoretical values. A good agreement is found between the present and the previous results. The calculated polarizability in turn is used to study the correlation with maximum ionization cross section and in general a good correlation is found among them, confirming the consistency and reliability of the present data. The cross section data reported in this article are very important for plasma modeling especially related to fluorocarbon plasmas.

## 1 Introduction

The interaction of electrons with matter leading to ionization is one of the fundamental processes in collision physics and has variety of applications in modeling plasma processes, atmospheric chemistry, and fusion technology [1]. The scattering cross section serves as an important input for the development of dynamic models of the plasma particle interaction as it directly depends on the relative velocity of the colliding particles in the plasma [2,3]. These plasma particle interaction models are then used for studying various plasma properties [4,5]. Apart from that, the reliability of various plasma chemistry models depends on the availability of the basic data on electron molecule collisions [6]. The fluorocarbon molecules have been widely used for plasma processing in the semiconductor industry for various applications. The electron-impact dissociation of the stable parent fluorocarbons such as  $CF_4$ ,  $C_2F_6$ ,  $C_3F_8$  and  $C_4F_8$  in the plasma leads to the formation of reactive radicals  $C_xF_y$  ( $x = 1-3$ ,  $y = 1-7$ ) which are

important for the chemical reactions in fluorocarbon-containing plasmas [7]. The ionization of parent molecules along with its daughter fragments and radicals is one of the important chemical reactions occurring in these plasmas. In plasma processing the semiconductor manufacturing requires ionization cross section ( $Q_{ion}$ ) of fluorocarbons as feed gas, their ions and fragments [8]. The reactive neutrals and ion fragments originating from family of fluorocarbons and particularly fluoromethanes are extensively used for plasma etching application [9,10]. The ionization reaction is also a primary source of ions and electron in plasma volume for sustaining plasmas [11]. Recently, Verma et al. [12] emphasizing the need of cross section data for plasma modeling did calculations of inelastic and ionization cross section for many tetrahalide molecules. Hence the measurement and/or calculation of  $Q_{ion}$  have been of the most importance. There are number of studies of electron impact ionization, partial ionization and neutral dissociation done to understand the elementary processes in plasma etching for stable fluorocarbons [13], however there is still a dearth of cross section data for fluorocarbon radicals.

Nishimura et al. [13] have measured and calculated the  $Q_{ion}$  for  $C_2F_6$  and  $C_3F_8$ . The theoretical calculations are done using the binary-encounter Bethe (BEB) [14,15]

<sup>\*</sup> Contribution to the Topical Issue “Atomic and Molecular Data and their Applications”, edited by Gordon W.F. Drake, Jung-Sik Yoon, Daiji Kato, Grzegorz Karwasz.

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method using the Restricted Hartree-Fock (RHF) and complete active space (CAS) self-consistent field (SCF) wave-function for the orbital parameters. Bart et al. [16] have measured the  $Q_{ion}$  from threshold to 220 eV for several perfluorocarbons. i.e.  $C_2F_4$ ,  $C_2F_6$ ,  $C_3F_6$  and  $C_3F_8$  studied presently and have compared their values with the maximum  $Q_{ion}$  estimated by BEB method using Hartree-Fock (HF) orbitals and Deutsch-Märk (DM) [17] model.

Recently, Harland's group has also measured the partial ionization cross sections for  $C_2F_6$ ,  $C_3F_6$  and  $C_3F_8$  molecule (Bull et al. [18]). The sum of the partial ionization cross section for different fragments gives the total ionization cross section. To compare their measured  $Q_{ion}$  data they have also computed the BEB cross section from threshold to 210 eV using partial third order electron propagator theory (P3-EPT) [19] for the orbital energies with binding energies less than 20 eV and a linear extrapolation of P3 vs. self-consistent field (SCF) reference Koopmans data for ionization potential (IPs) greater than 20 eV. The BEB cross section was found to overestimate consistently the experimental values for fluorocarbons – by more than 40% for all the targets [18]. They have explained that the difference between their experimental and theoretical data may be due to the contribution from neutral dissociation cross section in the BEB data. However for many nonfluorinated species the BEB data is higher than experimental values on average by 7% only [20]. They have also suggested that the BEB cross section should be calculated using high level of theory for orbital parameters and not just by using the simple HF or correlated wave function for the same [18].

Beran and Kevan [21] have measured  $Q_{ion}$  of  $C_2F_6$  and  $C_3F_8$  at 20, 35 and 70 eV incident electron energy with a magnetic mass spectrometer. Basner et al. [22] measured the absolute partial and total ionization cross section of  $C_2F_6$  from threshold to 900 eV using the time-of-flight mass spectrometer. Kurepa [23] measured  $Q_{ion}$  for  $C_2F_6$ ,  $C_3F_6$  and  $C_4F_8$  from threshold to 100 eV. Using the quadrupole mass spectrometer Poll and Meichsner [24] measured  $Q_{ion}$  for  $C_2F_6$  and  $C_3F_8$  from 5 eV to 125 eV. The dissociative ionization and total ionization cross section of  $C_3F_8$  was also measured by Jiao et al. [25]. Tarnovsky et al. [7] have measured the absolute cross section for the electron impact ionization and dissociative ionization of  $C_2F_5$  radical from threshold to 200 eV using the fast-neutral-beam technique. They have compared their measured value with the calculated cross section by the same authors using the modified additivity rule of Deutsch et al. [26]. The spherical complex optical potential (SCOP) [27] and complex scattering potential-ionization contribution CSP-ic [28] method has been successfully employed by Antony et al. [29] to compute  $Q_{ion}$  for many fluorocarbons studied here, such as  $C_2F_4$ ,  $C_2F_6$  and  $C_3F_8$ , yielding a good agreement with the experiments [13,16]. Christophorou and Olthoff have given the recommended data for  $C_2F_6$  [30] and  $C_3F_8$  [31].

However, there are very few studies of  $Q_{ion}$  for the  $C_xF_y$  radicals. Moreover, there are no studies of ionization for the fluorocarbon molecules/radicals such as  $C_2F$ ,

$C_2F_2$ ,  $C_2F_3$ ,  $C_3F$ ,  $C_3F_2$ ,  $C_3F_3$ ,  $C_3F_4$ ,  $C_3F_5$ ,  $C_3F_7$  in the literature. The experimental study of electron ionization with  $C_xF_y$  radicals is rather difficult [32] and there is no rigorous method of calculation for  $Q_{ion}$ . Hence there is a need for more investigation of ionization processes in these systems.

In this work we have investigated in detail the influence of various computational levels for the calculation of orbital parameters and subsequently to the BEB cross section for the  $C_2F_x$  ( $x = 1-6$ ) and  $C_3F_x$  ( $x = 1-8$ ) species. The present study is motivated by the fact that there is no comprehensive report or data for these  $C_2F_x$  ( $x = 1-6$ ) and  $C_3F_x$  ( $x = 1-8$ ) fluorocarbons. Moreover, there exist clear discrepancies among previous results for targets for which theoretical or experimental investigations are available. The present study is intended to give  $Q_{ion}$  for all the targets with various levels of computational theory for the orbital parameters.

We have used the well-known BEB method to calculate and study the  $Q_{ion}$  for various fluorocarbon molecules/radicals. The main input to the BEB cross section are the binding energy ( $B$ ), kinetic energy ( $U$ ) and the electron occupation number ( $N$ ). We have also computed the target properties such as ionization potential and polarizability for these targets to study the correlation between the maximum  $Q_{ion}$  and polarizability. The details of these calculations are provided in subsequent sections. In the next section we give a brief account of the BEB method used for the present study and subsequently the details of the computational methods used for the calculation of orbital parameters, polarizability and ionization potential.

## 2 Theoretical methodology

This section is devoted to a brief description of the BEB method employed in this work. The binary-encounter Bethe (BEB) method of Kim and co-workers is one of the most successful methods for predicting the  $Q_{ion}$  for atoms, molecules and radicals and ions (Kim and Rudd [14], and Hwang et al. [15]). The BEB model combines Mott's [33] approximation at low energies and Bethe's [34] approximation for high energy collisions and the approximation for the  $Q_{ion}$  is given as,

$$\sigma_{BEB} = \frac{S}{t + u + 1} \left[ \frac{\ln t}{2} \left( 1 - \frac{1}{t^2} \right) + 1 - \frac{1}{t} - \frac{\ln t}{t + 1} \right] \quad (1)$$

where

$$t = \frac{T}{B}; \quad u = \frac{U}{B}; \quad S = 4\pi a_0^2 N \left( \frac{R}{B} \right)^2. \quad (2)$$

Here,  $T$  is the incident electron energy;  $B$  is the binding energy of an electron on a given molecular orbital and  $U$  is its kinetic energy;  $N$  is the number of electrons on the orbital,  $R$  is a Rydberg energy and  $a_0$  is the Bohr radius.

The first logarithmic term in equation (1) represents the dipole interaction from the Born approximation,  $1-1/t$

**Table 1.** Target properties obtained in present calculations, as compared to other experimental and theoretical results.

| Targets                       | VIP (eV) |               | Polarizability ( $\text{\AA}^3$ ) |                    | Present HOMO energy (eV) |               |                 |
|-------------------------------|----------|---------------|-----------------------------------|--------------------|--------------------------|---------------|-----------------|
|                               | Present  | Others (Exp.) | Present                           | Others (Theo.)     | RHF/UHF                  | $\omega$ B97X | $\omega$ B97X-D |
| C <sub>2</sub> F              | 11.353   | –             | 4.451                             | 4.649 [54]         | 12.04                    | 11.34         | 10.75           |
| C <sub>2</sub> F <sub>2</sub> | 11.145   | 11.60 [45]    | 3.553                             | 3.542 <sup>1</sup> | 11.62                    | 10.74         | 10.15           |
| C <sub>2</sub> F <sub>3</sub> | 10.743   | 10.20 [46]    | 4.127                             | –                  | 11.57                    | 10.45         | 9.89            |
| C <sub>2</sub> F <sub>4</sub> | 10.276   | 10.69 [47]    | 4.35                              | 4.352 <sup>2</sup> | 10.86                    | 10.06         | 9.50            |
| C <sub>2</sub> F <sub>5</sub> | 10.586   | 9.98 [48]     | 4.552                             | –                  | 12.53                    | 10.34         | 9.71            |
| C <sub>2</sub> F <sub>6</sub> | 13.924   | 14.4 [49]     | 4.797                             | 4.838 <sup>2</sup> | 16.00                    | 13.90         | 13.28           |
| C <sub>3</sub> F              | 10.458   | –             | 5.700                             | 5.999 [54]         | 11.43                    | 10.25         | 9.69            |
| C <sub>3</sub> F <sub>2</sub> | 10.077   | –             | 4.887                             | –                  | 11.01                    | 10.00         | 9.45            |
| C <sub>3</sub> F <sub>3</sub> | 9.226    | –             | 6.253                             | –                  | 10.23                    | 8.43          | 7.93            |
| C <sub>3</sub> F <sub>4</sub> | 10.854   | 11.24 [50]    | 6.324                             | 6.50 <sup>3</sup>  | 11.67                    | 10.92         | 10.40           |
| C <sub>3</sub> F <sub>5</sub> | 8.084    | 8.44 [51]     | 6.488                             | –                  | 9.87                     | 8.10          | 7.60            |
| C <sub>3</sub> F <sub>6</sub> | 10.819   | 10.60 [52]    | 6.397                             | 6.346 [55]         | 11.67                    | 10.74         | 10.23           |
| C <sub>3</sub> F <sub>7</sub> | 10.751   | 10.06 [48]    | 6.456                             | –                  | 12.90                    | 10.73         | 10.12           |
| C <sub>3</sub> F <sub>8</sub> | 13.194   | 13.38 [53]    | 6.719                             | 6.812 <sup>2</sup> | 15.32                    | 13.37         | 12.75           |

originates from the direct and exchange collision terms in the Mott cross section, and the last logarithmic term stands for the interference between the direct and exchange collision terms. The BEB formula for  $Q_{ion}$  has been shown to give good agreement with the experimental data at the peak (approx. 15% or better) with the use of HF molecular wave functions for binding and kinetic energy calculations. It has been shown by Kim and co-workers that it works quite well from threshold to 5 keV for a wide range of molecules/radicals from H<sub>2</sub> to SF<sub>6</sub> (Kim and Rudd [14], Hwang et al. [15], Kim et al. [35], Ali et al. [36], Kim et al. [37,38]). However, several other electronic structure methods have been used to compute binding and kinetic energies parameters for small molecules as the BEB cross section is most sensitive to the parameter  $u$  which is the ratio of  $U$  to  $B$ . It is found that the energy of the highest occupied molecular orbital (HOMO) is quite important and plays a dominant role in the computation of  $Q_{ion}$  in the BEB model [15,35]. Hence the orbital parameters are sometimes combined with experimental ionization potential replacing the HOMO energy when available and have been routinely used for BEB cross section as it is found to give a slightly better agreement with experimental data for small molecules.

### 3 Calculations of molecular parameters

The geometrical and orbital parameters of the present targets were fully optimized by using Density Functional Theory (DFT) methods with the  $\omega$ B97X-D [39],  $\omega$ B97X [40], B3LYP [41] and PBE0 [42] hybrid functional. The polarizabilities of the targets were determined from static frequency calculations. The vertical ionization potentials (VIPs) were computed as the energy difference between the neutral and the cation, at the

neutral's optimized geometry. The restricted/unrestricted Hartree-Fock (RHF/UHF) methods were also applied for the calculations of orbital binding and kinetic energies. The Dunning's basis set, aug-cc-pVTZ (here abbreviated aVTZ), was used in all of the calculations in the present work, based on the fact that not only a set of polarization functions but also at least one set of diffuse functions has to be added to split valence-shell type basis sets for the correct determination of the geometries and stabilities of 1,2-dihaloethylene (C<sub>2</sub>H<sub>2</sub>X<sub>2</sub>; X = F, Cl) in the previous theoretical study by Kanakaraju et al. [43]. All of the ab-initio calculations in this work were carried out by using the Gaussian 09 suite of programs [44]. In our calculations for BEB cross section we have used the experimental VIPs for the outermost valence orbital for the targets for which it is available. We have used the present calculated VIPs for other targets such as C<sub>2</sub>F, C<sub>3</sub>F, C<sub>3</sub>F<sub>2</sub>, C<sub>3</sub>F<sub>3</sub>, C<sub>3</sub>F<sub>4</sub>, C<sub>3</sub>F<sub>5</sub> for which there are no experimental values. The present data for VIP and polarizability are presented in Table 1 along with available experimental and theoretical comparison. We have also presented in Table 1 the binding energy of the HOMO calculated using RHF/UHF wave function and with DFT ( $\omega$ B97X-D/ $\omega$ B97X) [39,40] as the BEB cross section is quite sensitive to the lower values of the binding energies.

It is worth noting here that the binding energy of the HOMO computed with DFT ( $\omega$ B97X) is in a good agreement with experimental VIPs as presented in Table 1. Such good comparison gives us confidence to use this DFT functional for binding and kinetic energies for other higher orbitals and suitably employ it to the BEB model. However the HOMO energy with B3LYP and PBE0 functional are quite low compared to experimental VIPs and hence are not included in Table 1. The present results for VIPs are also compared with the experimental VIPs as given in the references [45–53] and a good agreement is found. Most of these experimental values are also there in the NIST chemistry website<sup>1</sup>, taken from different sources [45–53].

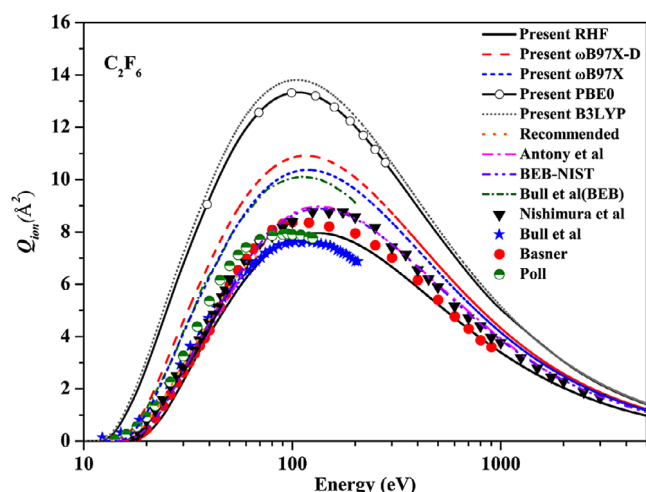
The present polarizability are compared with other calculated values as there are no experimental data for these systems. For C<sub>2</sub>F and C<sub>3</sub>F, the present data

<sup>1</sup> <http://physics.nist.gov/RhysRefData/Ionization/MolTable.html>

<sup>2</sup> <http://cccbdb.nist.gov/>

<sup>3</sup> <http://www.chemspider.com/>





**Fig. 1.** Total ionization cross section for  $C_2F_6$  in  $\text{\AA}^2$  along with available comparisons: solid line: present RHF; dash line: present  $\omega B97X-D$ ; short dash line: present  $\omega B97X$ ; line symbol: present PBE0; short dot line: present B3LYP; dot line: recommended [30]; dash dot line: Antony et al. [29]; dash dot dot line: BEB-NIST<sup>1</sup>; short dash dot line: Bull et al. (BEB) [18]; triangle: Nishimura et al. [13]; stars: Bull et al. [18]; solid circle: Basner et al. [22]; half circle: Poll and Meichsner [24].

is compared with the recently calculated data of Wang et al. [54] and the comparison is good. The results for  $C_2F_2$ ,  $C_2F_4$ ,  $C_2F_6$  and  $C_3F_8$  are compared with the DFT (B3LYP/aug-cc-pVDZ) calculated data as given in the CCCBDB<sup>2</sup> database and the results compare quite well among each other. The polarizability for  $C_3F_4$  and  $C_3F_6$  are compared with the data as given in the references<sup>3</sup> [55] and it compares well with the present computations. For  $C_2F_3$ ,  $C_2F_5$ ,  $C_3F_2$ ,  $C_3F_3$ ,  $C_3F_5$  and  $C_3F_7$  there are no available theoretical or experimental data for comparison, to the best of our knowledge. All the results are presented in Table 1.

## 4 Results and discussions

The BEB ionization cross section obtained within the approximation of RHF/UHF and DFT ( $\omega B97X/\omega B97X-D$ ) for orbital energies are plotted in Figures 1–5 for  $C_2F_x$  ( $x = 1-6$ ) and  $C_3F_x$  ( $x = 1-8$ ). The results obtained within these approximations are plotted together for each molecule along with the available comparisons in the literature. For  $C_2F_6$  we have plotted in Figure 2, for an overall comparison, the BEB cross section obtained from all orbital parameters in different models studied presently. Except for some stable molecules like  $C_2F_4$ ,  $C_2F_6$ ,  $C_3F_6$  and  $C_3F_8$  there is scarcity of data for other molecules/radicals which are investigated for the first time in the present study. The interesting study of correlation between the maximum of  $Q_{ion}$  and the polarizability is plotted in Figure 6. The cross section data is reported for a wide energy for all the species studied – from ionization threshold to 5 keV. The data for polarizability and maximum  $Q_{ion}$  are presented in Table 2.

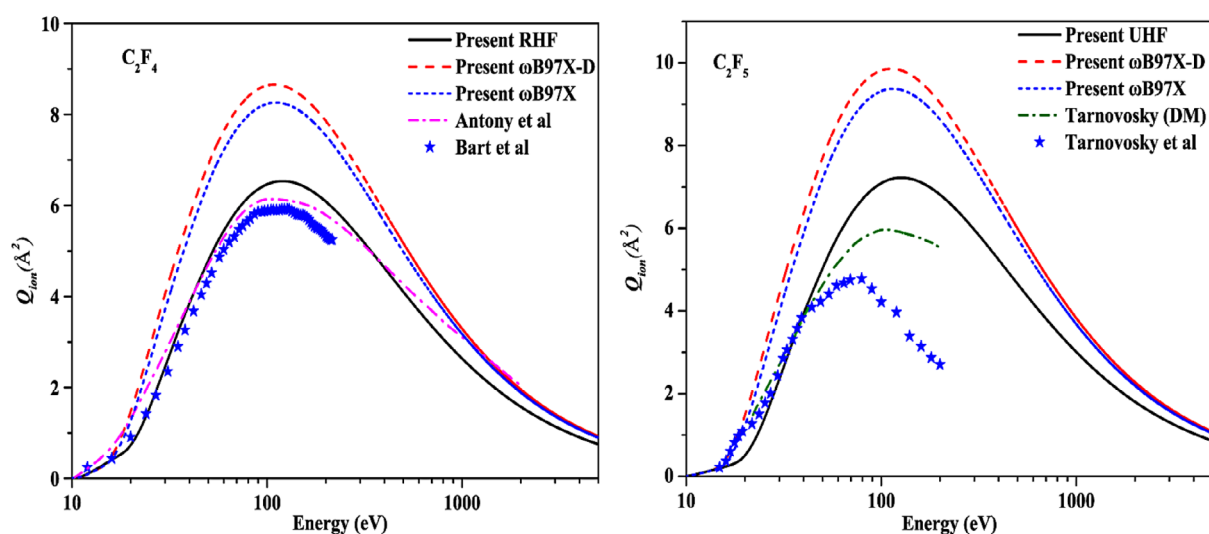
### 4.1 $C_2F_x$ ( $x = 1-6$ )

The ionization of  $C_2F_6$  is well studied both experimentally and theoretically in the literature. We have compared the present BEB data with the experimental results of Nishimura et al. [13], Bull et al. [18], Basner et al. [22] and Poll and Meichsner [24] and with theoretical data of Antony et al. [29], Bull et al. [18] and the recommended value of Chirstophorou and Olthoff [30]. The BEB<sup>1</sup> data from NIST are also included for comparison. In the case of  $C_2F_6$  we have plotted all the results with RHF wave functions and DFT functionals. The present RHF result shows an excellent agreement with all the experimental results from threshold to the peak, after which the present results compare quite well with the experimental values of Basner et al. [22] at high energies. The RHF result also compare well with all the theoretical data at low energies till 80 eV after which it is lower than other results. The cross section data of Antony et al. [29] and the BEB data from NIST<sup>1</sup> show excellent agreement with the experimental data of Nishimura et al. [13].

Recently, Bull et al. [18] suggested that the orbital parameters used in BEB cross section should be computed using a high level of theory. The results due to such orbital energies are found to overestimate consistently the experimental values for fluorocarbons studied here. Anyhow, the present result for  $C_2F_6$  using the DFT ( $\omega B97X$ ) functional for orbital energies shows a good agreement with the P3-EPT calculations of Bull et al. [18]. The slight variations in cross section at the peak are due to difference of model used for the calculations of the orbital energies. The DFT ( $\omega B97X-D$ ) which includes dispersion is slightly higher than the DFT ( $\omega B97X$ ). The other two functionals DFT (B3LYP) and DFT (PBE0) are found to give large cross sections as compared to all other results, what is due to the low binding energy prediction with these models. The BEB cross section is very much sensitive to this binding energy. The results due to B3LYP and PBE0 functional are dropped from the other figures as they predicted very low binding energies for the valence orbitals as compared to experiment, and the BEB cross section were found to overestimate consistently all other data.

The  $Q_{ion}$  results for  $C_2F_4$  and  $C_2F_5$  are plotted in Figure 2 along with available comparison. It is quite surprising to see that  $C_2F_4$  being a very important molecule for plasma applications, it has less studies of ionization cross section – only by Bart et al. [16] experimentally and by Antony et al. [29] theoretically. Bart et al. [16] have given the maximum value for  $C_2F_4$  using BEB and DM method, of  $6.38 \text{ \AA}^2$  and  $7.19 \text{ \AA}^2$ , respectively. The present RHF result for  $C_2F_4$  is in a good agreement with the data of Bart et al. [16] and Antony et al. [29] from ionization threshold to 40 eV after which the present result is little higher at the peak. However, the peak value reported by Bart et al. [16] using HF wave function for orbital parameters in the BEB method coincides with the present BEB data. This may be due to the same level of theory used for the calculation of orbital energies in both cases.

For  $C_2F_5$ , there is only one measurement and calculation of Tarnovsky et al. [7]. They compare their measured



**Fig. 2.** Total ionization cross section for  $C_2F_4$  and  $C_2F_5$  in  $\text{\AA}^2$  along with available comparisons. Solid line: present RHF/UHF; dash line: present  $\omega B97X-D$ ; short dash line: present  $\omega B97X$ ; dash dot line: Antony et al. ( $C_2F_4$ ) [29] and Tarnovsky et al. ( $C_2F_5$ ) [7]; stars: Bart et al. ( $C_2F_4$ ) [16] and Tarnovsky et al. ( $C_2F_5$ ) [7].

value with the calculations done using DM model. A reasonable agreement is found from threshold till around 40 eV after which the calculated values are higher than the experimental one. The present BEB data using UHF model shows a good agreement from threshold to 40 eV after which it overestimates both the experimental and DM values. We have plotted the results due to DFT ( $\omega B97X/\omega B97X-D$ ) orbital energies for both the molecules, and they are found to be consistently higher than the HF results.

In Figure 3 we have plotted the  $Q_{ion}$  for  $C_2F$ ,  $C_2F_2$ , and  $C_2F_3$  for which there is no data available in the literature for comparison. The present RHF/UHF and DFT ( $\omega B97X/\omega B97X-D$ ) based results are plotted together for each molecule and a similar kind of dependence is seen for these targets where the DFT based cross section is consistently higher than the HF results. It is also worth noting here that with the increase in the size of the target the cross section also increases. We need more investigations into these systems experimentally and theoretically to validate our results.

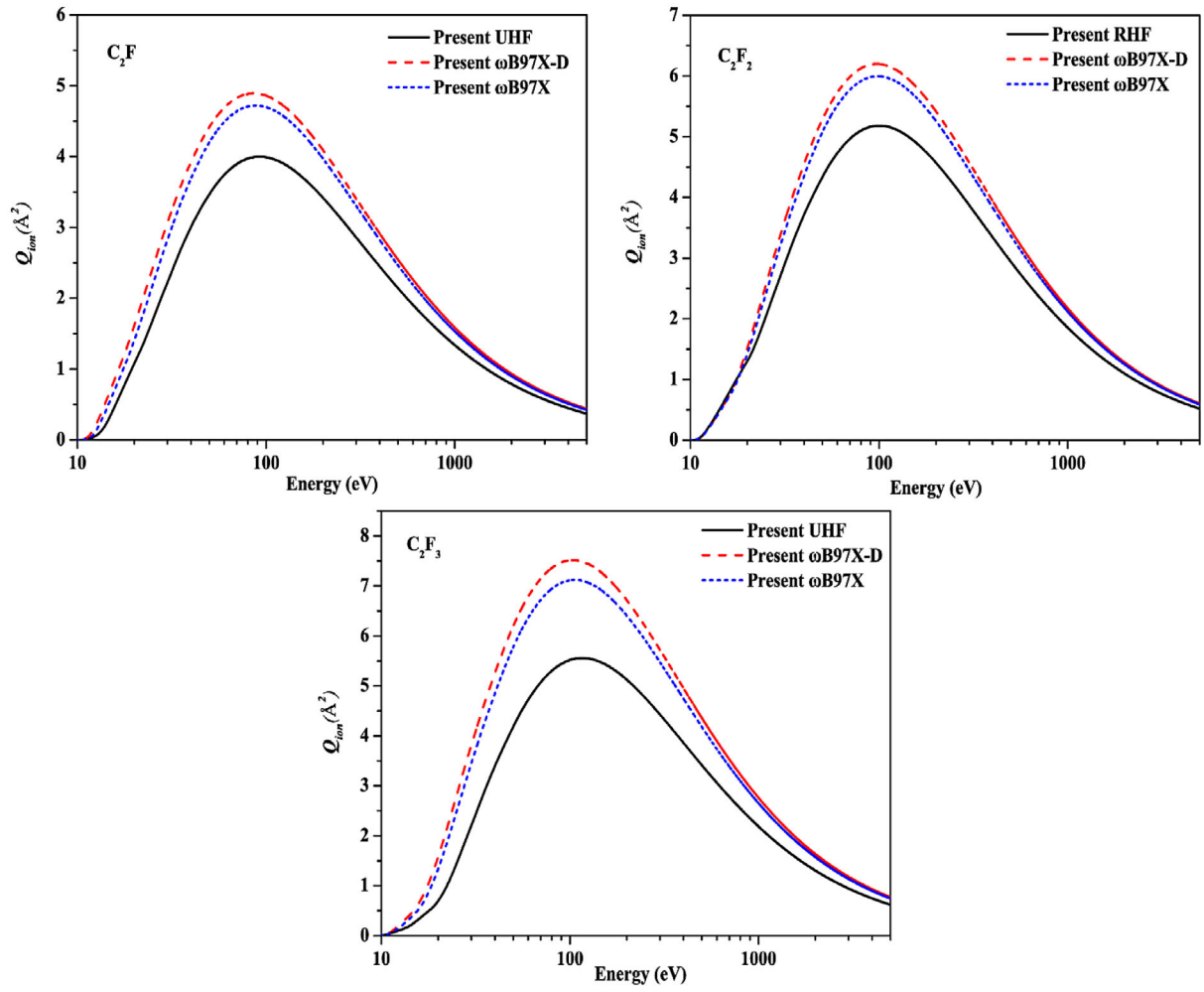
## 4.2 $C_3F_x$ ( $x = 1-8$ )

The present BEB cross section calculated using RHF and DFT orbital energies for  $C_3F_8$  and  $C_3F_6$  are plotted in Figure 4 along with the available comparisons.  $C_3F_8$  is a very well-studied target – experimentally and theoretically for ionization. We have compared the present BEB data with the experimental results of Nishimura et al. [13], Bull et al. [18], Poll and Meichsner [24] and Jiao et al. [25] and with the theoretical data of Antony et al. [29], Bull et al. [18] and the recommended value of Chirstophorou and Olthoff [31]. The NIST<sup>1</sup> BEB data is also included for comparison. The present RHF calculated BEB cross

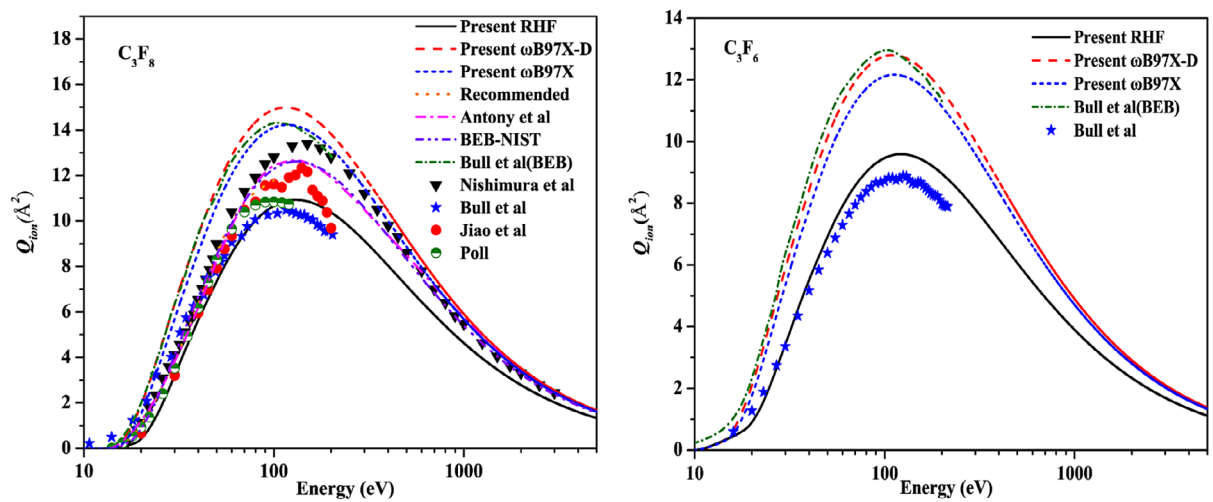
section shows an excellent agreement at low energies with all the experimental data till 70 eV and then it is lower than that of experimental values of Jiao et al. [25] and Nishimura et al. [13] at the peak. However it shows a good agreement at the peak with the experimental values of Bull et al. [18] and Poll and Meichsner [24]. The present results for  $C_3F_8$  using DFT functionals are higher than other values from threshold to peak, however it shows a good agreement with the experimental data of Nishimura et al. [13] at higher energies. The present result with DFT ( $\omega B97X$ ) agrees with a recent calculation of Bull et al. [18] who also used BEB method.

For  $C_3F_6$ , the present BEB data computed using RHF and DFT orbitals are compared with the only experimental data of Bull et al. [18]. They have also computed the BEB data for  $C_3F_6$  for comparing their experimental value using the P3-EPT model for orbital energies. The agreement is poor among the two data and their BEB result is seen to overestimate the experimental values by more than 40%. In turn, the present RHF results shows an excellent agreement with the experimental data of Bull et al. [18] till 70 eV after which it is little higher than the experiment. On the other hand, present DFT ( $\omega B97X-D$ ) results for  $C_3F_6$  agree very well with the BEB data of Bull et al. [18]. It is generally observed that the BEB cross section with HF orbital energies agrees well with the experimental data within 15–20%.

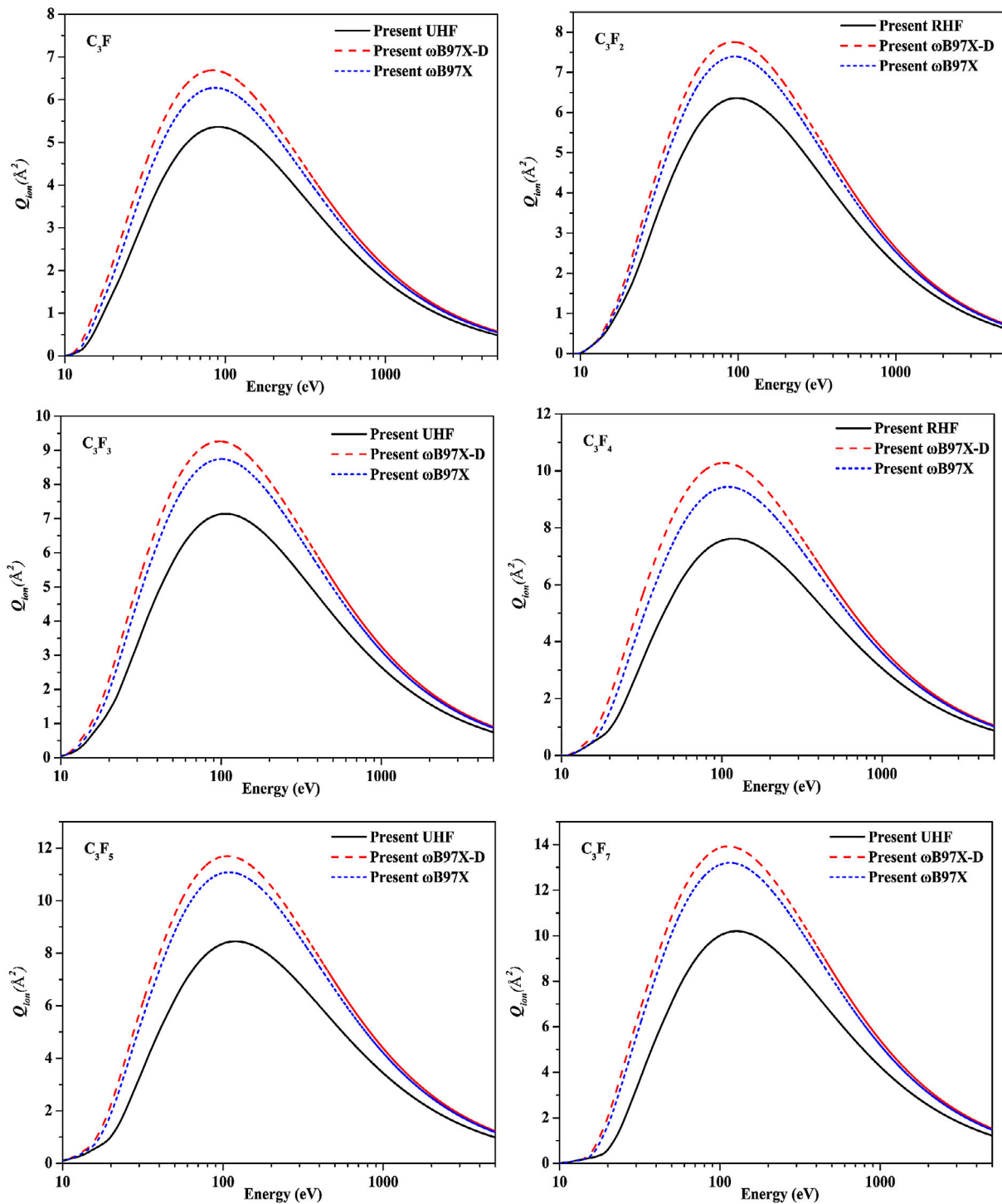
In Figure 5 the  $Q_{ion}$  for  $C_3F$ ,  $C_3F_2$ ,  $C_3F_3$ ,  $C_3F_4$ ,  $C_3F_5$  and  $C_3F_7$  is plotted, with orbital parameters calculated using RHF/UHF and DFT ( $\omega B97X/\omega B97X-D$ ) level of theory. Similar to Figure 3 there are no available comparison for these targets and the results show a general trend similar to other results. The DFT results are consistently higher than the corresponding HF results as the correlation effect in DFT theories significantly reduces the binding energies. However, the results are reported



**Fig. 3.** Total ionization cross section for  $C_2F$ ,  $C_2F_2$  and  $C_2F_3$  in  $\text{\AA}^2$ . Solid line: present RHF/UHF; dash line: present  $\omega B97X-D$ ; short dash line: present  $\omega B97X$ .



**Fig. 4.** Total ionization cross section for  $C_3F_8$  and  $C_3F_6$  in  $\text{\AA}^2$  along with available comparisons. Solid line: present RHF; dash line: present  $\omega B97X-D$ ; short dash line: present  $\omega B97X$ ; dot line: recommended [31]; dash dot line: Antony et al. [29]; dash dot dot line: BEB-NIST¹; short dash dot line: Bull et al. (BEB) [18]; triangle: Nishimura et al. [13]; stars: Bull et al. [18]; solid circle: Jiao et al. [25]; half circle: Poll and Meichsner [24].



**Fig. 5.** Total ionization cross section for  $C_3F$ ,  $C_3F_2$ ,  $C_3F_3$ ,  $C_3F_4$ ,  $C_3F_5$  and  $C_3F_7$  in  $\text{\AA}^2$ . Solid line: present RHF/UHF; dash line: present  $\omega B97X-D$ ; short dash line: present  $\omega B97X$ .

with both levels of theories as DFT ( $\omega B97X$ ) functional showed good agreement with the recent BEB cross section of Bull et al. [18] for some stable targets. Moreover, these data could be very useful for plasma modeling and could act as benchmark data for comparison in future. The experimental investigation is not easy for such radicals and hence the theoretical results are important.

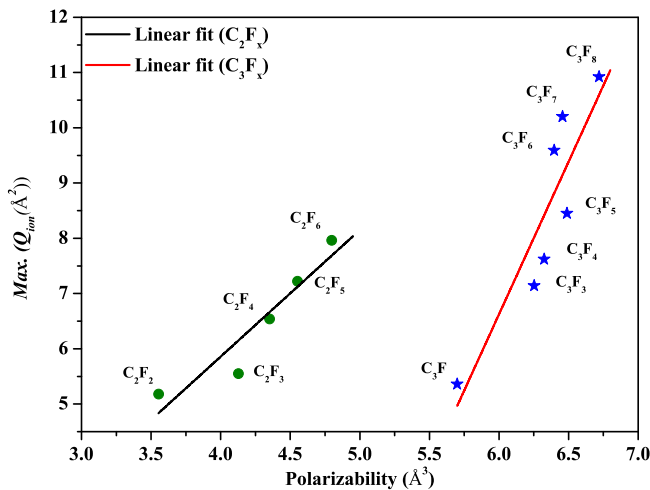
### 4.3 Correlation study

The study of correlation between maximum  $Q_{ion}$  and polarizability of atoms and molecules has been subject of great interest ever since the study of Franklin and co-workers in 1957 who confirmed such correlation between these quantities (Lampe et al. [56]). The polarizability



**Table 2.** Present polarizability and maximum  $Q_{ion}$  for the targets studied.

| Targets                       | Present polarizability ( $\text{\AA}^3$ ) | Present $Q_{ion}$ max ( $\text{\AA}^2$ ) |               |                 |
|-------------------------------|---|--|---------------|-----------------|
|                               |   | RHF/UHF                                  | $\omega$ B97X | $\omega$ B97X-D |
| C <sub>2</sub> F              | 4.451                                     | 4.00                                     | 4.72          | 4.89            |
| C <sub>2</sub> F <sub>2</sub> | 3.553                                     | 5.18                                     | 6.00          | 6.20            |
| C <sub>2</sub> F <sub>3</sub> | 4.127                                     | 5.55                                     | 7.12          | 7.51            |
| C <sub>2</sub> F <sub>4</sub> | 4.35                                      | 6.54                                     | 8.26          | 8.65            |
| C <sub>2</sub> F <sub>5</sub> | 4.552                                     | 7.22                                     | 9.37          | 9.86            |
| C <sub>2</sub> F <sub>6</sub> | 4.797                                     | 7.96                                     | 10.37         | 10.91           |
| C <sub>3</sub> F              | 5.700                                     | 5.36                                     | 6.28          | 6.89            |
| C <sub>3</sub> F <sub>2</sub> | 4.887                                     | 6.36                                     | 7.39          | 7.76            |
| C <sub>3</sub> F <sub>3</sub> | 6.253                                     | 7.14                                     | 8.75          | 9.26            |
| C <sub>3</sub> F <sub>4</sub> | 6.324                                     | 7.62                                     | 9.44          | 10.28           |
| C <sub>3</sub> F <sub>5</sub> | 6.488                                     | 8.45                                     | 11.08         | 11.70           |
| C <sub>3</sub> F <sub>6</sub> | 6.397                                     | 9.59                                     | 12.17         | 12.80           |
| C <sub>3</sub> F <sub>7</sub> | 6.456                                     | 10.20                                    | 13.20         | 13.92           |
| C <sub>3</sub> F <sub>8</sub> | 6.719                                     | 10.92                                    | 14.23         | 14.99           |

**Fig. 6.** Correlation plot between maximum  $Q_{ion}$  and polarizability of the targets. Circles: present maximum  $Q_{ion}$  for C<sub>2</sub>F<sub>x</sub>; stars: present maximum  $Q_{ion}$  for C<sub>3</sub>F<sub>x</sub>; solid line: linear fits.

volume can be related to the size of the molecule as seen by the incoming electron. The only size related quantity for the incident electron is its de Broglie wavelength suggesting that the peak in the  $Q_{ion}$  may be due to the resonance condition when the wavelength of the incoming electron matches with the effective diameter of the molecule implied by the polarizability volume [57]. The group of Harland and co-workers has done extensive study on such correlation for many atomic and molecular systems and has confirmed the existence of such correlation for many systems (Bart et al. [16], Harland and Vallance [57], and Hudson et al. [58]).

Recently the group of Antony and co-workers has also obtained such correlations for many atomic and molecular targets (Verma et al. [12], Gupta and Antony [28], Gupta et al. [59], Kaur et al. [60], and Gupta et al. [61]). The correlation is very useful to check the consistency and reliability of the cross section data when there is no comparison available. This correlation can also be used to roughly estimate either maximum  $Q_{ion}$  or polarizability if we know

either one of the quantities from them. Since most of the targets are investigated for the first time in the present study we also plotted the correlation between these quantities. As there was no result for polarizability for many targets, we also computed the same for studying the correlation with maximum  $Q_{ion}$ . We have plotted two sets of correlation for C<sub>2</sub>F<sub>x</sub> and C<sub>3</sub>F<sub>x</sub> and a good linear fit is obtained for C<sub>2</sub>F<sub>x</sub> and for C<sub>3</sub>F<sub>x</sub> the linear fit lies in between the maximum  $Q_{ion}$  values on either side of the fit. However it gives a good correlation overall showing the consistency of the data reported here.

In the correlation plot we have not included C<sub>2</sub>F and C<sub>3</sub>F<sub>2</sub> as it was going quite away from the linear fit. For C<sub>2</sub>F the polarizability calculated presently seems to be somewhat too high and for C<sub>3</sub>F<sub>2</sub> it is on the lower side, thus taking it away from the linear fit. The correlation is shown only for HF calculated maximum  $Q_{ion}$  and polarizability here, but the correlation of maximum  $Q_{ion}$  with DFT ( $\omega$ B97X/ $\omega$ B97X-D) functionals is also found to be of similar nature.

The linear correlation between  $Q_{ion}$  and the polarizability found presently is of the same kind as indicated recently [62] for a tetragonal-like series of fluoromethanes, CH<sub>4</sub>, CH<sub>3</sub>F, CH<sub>2</sub>F<sub>2</sub>, CHF<sub>3</sub> and CF<sub>4</sub>. For those molecules the ratio between the maximum of the cross section (expressed in  $10^{-16}$  cm<sup>2</sup>) and the polarizability (expressed in  $\text{\AA}^3$ ) was found 1.33. For molecules and radicals studied presently such ratios are different – 1.5 for C<sub>2</sub>F<sub>4</sub> and 1.63 for C<sub>3</sub>F<sub>8</sub>. Note that polarizability of the molecule depends not only on type of constituent atoms but mainly on the type of molecular bonds and the geometry. This prompts further studies of possible correlations, that would facilitate rough estimates of  $Q_{ion}$  for species difficult to study experimentally but important for practical applications, like semiconductor etching and/or thermonuclear plasmas.

## 5 Conclusions

The BEB model, previously applied widely for atoms and small molecules, is presently employed to calculate the  $Q_{ion}$  for C<sub>2</sub>F<sub>x</sub> ( $x = 1-6$ ) and C<sub>3</sub>F<sub>x</sub> ( $x = 1-8$ )

fluorocarbon species using different levels of approximation for the orbital energies. We found that the BEB cross section with RHF/UHF approximation for orbital energies gave good agreement with the experimental results for  $C_2F_4$ ,  $C_2F_6$ ,  $C_3F_6$  and  $C_3F_8$ . The present results due to DFT ( $\omega B97X$ ) functional for orbital parameters gave good agreement with the recent calculations of Bull et al. [18] for  $C_2F_6$ ,  $C_3F_6$  and  $C_3F_8$ . The present DFT ( $\omega B97X$ ) result and that of Bull et al. [18] are both higher than the experimental values by more than 30%, however the orbital parameters with such calculation are more accurate. It is evident from Table 1 where the present binding energy (HOMO) with DFT ( $\omega B97X$ ) is in a good agreement with the vertical experimental ionization energy. The BEB cross section is sensitive to the valence orbital binding energies and hence its accurate determination is important. We have presented our result both with RHF/UHF and DFT ( $\omega B97X/\omega B97X-D$ ) for all the targets. The  $Q_{ion}$  for many targets such as  $C_2F$ ,  $C_2F_2$ ,  $C_2F_3$ ,  $C_3F$ ,  $C_3F_2$ ,  $C_3F_4$ ,  $C_3F_5$  and  $C_3F_7$  are calculated for the first time and hence there is a need for investigation into these systems experimentally and theoretically to validate the present results. However, a good agreement with experiments for stable targets gives us confidence that the present result for other targets is reliable.

The ionization potential and polarizability were also computed in the present study for all the targets to check the consistency of the  $Q_{ion}$  data by studying the correlation effect between maximum  $Q_{ion}$  and polarizability of the targets. We have obtained a good correlation for both sets ( $C_2F_x$  and  $C_3F_x$ ) of targets confirming the consistency of the present data. The ionization potential and polarizability is also compared with other results and a good agreement is found between present and previous values, as shown in Table 1. The present study will be continued with the  $Q_{ion}$  studies for  $C_4F_x$  and  $C_5F_x$  species.

D.G. is pleased to acknowledge the support of this research to the National Fusion Research Institute (NFRI), South Korea for the research grant and scholarship. G.K. kindly acknowledges the financial support from NFRI and a warm welcome.

## Author contribution statement

M.Y.S and D.G. conceived of the presented idea. D.G. and H.C. performed the calculations and wrote the manuscript with support from G.P.K., J.S.Y., M.Y.S. All the authors provided critical feedback and helped shape the research, analysis and manuscript.

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