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S. Demes, Eugene Yu. Remeta. Ion appearance energies at electron-impact dissociative ionization of sulfur hexafluoride molecule and its fragments. *The European Physical Journal D: Atomic, molecular, optical and plasma physics*, 2015, 69 (7), pp.168. 10.1140/EPJD/E2015-50636-4 . hal-03038809

HAL Id: hal-03038809

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Eur. Phys. J. D (2015) 69: 168

DOI: [10.1140/epjd/e2015-50636-4](https://doi.org/10.1140/epjd/e2015-50636-4)

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Ion appearance energies at electron-impact dissociative ionization of sulfur hexafluoride molecule and its fragments^{*}

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Received 28 August 2014 / Received in final form 14 January 2015

Published online 7 July 2015 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2015

Abstract. Theoretical analysis of appearance energies for SF_k^+ ($k = 0-n$) ion fragments of SF_6 molecule as well as F^+ and F_2^+ ions at electron-impact dissociative ionization of SF_n ($n = 1-6$) molecules is presented. Theoretical methods of GAMESS software package were used to calculate the total energies of neutral and charged molecular and atomic fragments. The dissociative ionization process is concluded to occur via repulsive highly-excited electronic states of the SF_6 molecule and its fragments, due to which the observed appearance energies exceed the theoretical values. The electron binding energies on the molecular orbitals in the SF_6 molecule are compared with the ion fragment appearance energies.

1 Introduction

The appearance energy E_{AP} of an ionic fragment at the electron-impact dissociative ionization of a molecule is equal to the energy required for its formation in this process. The energy E_{AP} will be minimal if the final products (atoms, molecules, atomic and molecular ions) are in the ground state and have zero kinetic energies. Since the incident electron energy exceeds the ionization potential of the corresponding molecular fragment, the process of dissociative ionization proceeds via highly-excited electronic states of the initial molecule. Hence, this reaction takes place at the threshold of two complicated processes – ionization and dissociation.

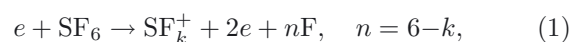
The effective simultaneous progress of high-excitation and dissociation processes is possible at a strong correlation of the electronic and atomic motion types for the excited molecule. In other words, the dissociative ionization is a result of interaction of the excited electronic and vibrational states. The difference between electronic and atomic types of motion would be very important, when the molecule achieves high energy from the collision, which leads to dissociation of atoms and to formation of ionic fragments. While measuring E_{AP} one should determine the states of all the reaction products. Registration of solely the molecular ion fragment enables one to find the energy which is in general determined by the states of the final products obtained in the most probable processes. Note that atomic and molecular reaction products can be in excited states, “couple” to each other as well as form

negative ions. Formation of such ions – i.e. the ion-pair formation process – is possible when the atoms and molecular fragments have large electron affinity. Excitation of the reaction products results in an increase of E_{AP} while any type of coupling of the particles in the finite states leads to its decrease.

Note here that all the excited electronic states of the SF_6 molecule are non-binding and repulsive while the ground and excited electronic states of the SF_6^+ ion are unstable and rapidly (within several picoseconds) dissociate in a channel: $\text{SF}_6^+ \rightarrow \text{SF}_5^+ + \text{F}$ (see Ref. [1]). Therefore, the process of dissociative ionization at the electron-impact excitation of the SF_6 molecule can possess specific features. Besides, this should also affect the appearance energies of the ion fragments of the molecule.

The importance of the SF_6 molecule studies from the fundamental and application point of view as well as the success achieved in the studies of its structure and various processes of interaction with an electron are well shown in reference [1]. It is shown there that the electron-impact dissociative ionization process becomes significant beginning from the energies of ~ 16 eV, resulting in an appearance of SF_k^+ ($k = 1, 3, 4, 5$) ion fragments and F^+ ions. However, neither the data, nor the analysis of the appearance energies for the SF_k^+ ion fragments as well as F^+ and F_2^+ ions are reported in reference [1].

The appearance energy of a SF_k^+ fragment of the SF_6 molecule according to the reaction



can be determined as follows:

$$\begin{aligned} E_{\text{AP}}[(\text{SF}_k^+ - n\text{F})/\text{SF}_6] &= E_t(\text{SF}_k^+) + nE_t(\text{F}) - E_t(\text{SF}_6) \\ &= D[(\text{SF}_k - n\text{F})/\text{SF}_6] + I(\text{SF}_k). \end{aligned} \quad (2)$$

^{*} Contribution to the Topical Issue “Elementary Processes with Atoms and Molecules in Isolated and Aggregated States”, edited by Friedrich Aumayr, Bratislav Marinkovic, Stefan Matejcek, John Tanis and Kurt H. Becker.

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Here the quantities E_t , D , and I in equation (2) are the total energy of the minimum of the electronic state with the molecular vibrational energy G_v as well as the energies of dissociation and ionization, respectively. Thus, the appearance energy of SF_k^+ fragments at the dissociative ionization of the SF_6 molecule equals the sum of the binding energies of n fluorine atoms within the molecule and the ionization potential of the SF_k fragment. In this case, at the ionization of the SF_6 molecule ($k = 6$) the fluorine atoms are not detached ($n = 0$) and the energy received by the molecule is minimal. The appearance of the sulfur ion ($k = 0$) corresponds to the detachment of all fluorine atoms ($n = 6$) which is possible when the SF_6 molecule receives the maximal energy value from the incident electron.

Here we report on the results of ab initio calculations of the appearance energy E_{AP} of the ions at the electron-impact dissociative ionization of the SF_6 molecule. The available experimental E_{AP} data are considered, some of them being compared with calculated values.

2 Model and method

In order to obtain the ground state total energies for the molecules, atoms, and ions, the GAMESS software [2] based on the density functional theory [3] was used, running on a Linux cluster with a high level of parallelization. The calculations were performed using two types of hybrid exchange-correlation functionals from the generalized gradient approximation (GGA) – B3LYP [4] and B3PW91 [5]. Both hybrid functionals include Hartree-Fock-type (20%) and Slater-type (80%) exchange, while the electron correlation in the case of B3LYP is described by the Lee-Yang-Parr (LYP) functional [6] and in the case of B3PW91 it is described by the Perdew-Wang (PW91) functional [7] (see also Ref. [8]).

The total energies of all the molecules under investigation were determined in two multiplicity states, among which the one with the lower energy was chosen. The SF_6 molecule structure was optimized using the quadratic approximation algorithm [9], without the account of the symmetry effect. For the initial geometry, the minimal interatomic distances were given. Once the optimized equilibrium geometry of the SF_6 molecule having been obtained, two types of calculations were performed: vertical and adiabatic energy characteristics of the SF_k fragments were determined.

To calculate the adiabatic characteristics, the equilibrium geometries of the SF_k and F_2 molecules were as well determined in the course of the geometry optimization using the quadratic approximation algorithm. The above characteristics were found as the differences between the total energies of the relaxed states of the neutral and the ionized systems. The vertical values are defined as an energy difference between the initial SF_6 molecule and those SF_k^+ ionic fragments, the structure of which (the bond distances, angles, etc.) was derived from the optimized structure of the SF_6 molecule, but without $(6-k)$ number of

fluorine atoms. Hence, we state that the structure of the ionic fragments is not relaxed.

The experimental and the calculated adiabatic values of the electron affinities E_a , ionization potentials I , and the dissociation energies D are compared in Table 1. For the molecules the total energy of vibrations G_v is taken into account. The ionization potential value $I(SF_6)$ is taken from reference [81] in [1], where the photoelectron spectroscopy method was applied for its determination (see also the discussion about the SF_6^+ ion measurements in Ref. [1]). In general, there is a fair agreement between the above data. The calculated vertical values are, in general, somewhat above the adiabatic data. The E_a , I , and D energy values are rather sensitive to the quality of account of the correlation interaction between the electrons in the atoms and ions. As one can see, this interaction is rather well taken into account by the GAMESS methods for F and S atoms and for F_2 and SF_k molecules, however the agreement of the values of $E_a(SF_6)$ and $I(SF_3)$ is very poor, compared with the experimental data. Thus, the GAMESS calculation data can be quite successfully used for the analysis of the fragment appearance energies. Hereinafter the data from Table 1 are used for the corresponding estimations.

3 Results and discussion

The E_{AP} of the ion fragments can be well determined by measuring the partial yield cross sections of the SF_k^+ fragments or F^+ and S^+ atomic ions, as it was made in references [23–25] (see also [1] and references therein).

3.1 Appearance energies of the SF_k^+ ion fragments

The values of the appearance energies E_{AP}^{th} of SF_k^+ ions calculated according to equation (1) with the account of the vibrational energies $G_v(SF_6)$ and $G_v(SF_k^+)$ are shown in Table 2. In this table the ionization potentials $I(SF_\ell)$ are used as appearance energies $E_{AP}(SF_\ell^+/SF_\ell)$. The average value of the binding energy E_b for a fluorine atom

$$E_b(F) = [E_{AP}(SF_k^+ - (n - k)F/SF_n) - I(SF_k)] / (n - k), \quad k < n, \quad (3)$$

is given in parentheses and is obtained using the experimental and theoretical values of E_{AP} and $I(SF_k)$. This energy slightly differs for different molecules. In the case of appearance of the SF_5^+/SF_6 ion, the binding energy $E_b(F)$, according to the experimental data, is within the interval 4.3–5.9 eV. These values are close to the experimental dissociation energies $D(SF_5-F/SF_6)$ 3.38 [17], 3.9 ± 0.15 [18], 4.1 ± 0.13 eV [19] and to our calculated data (see Tab. 1).

From Table 2 one can see that the experimental values E_{AP}^{exp} [23] systematically exceed the calculated E_{AP}^{th} values. With the decreasing number of the detached fluorine atoms (i.e. for large k and at a small value of the energy transferred to the SF_6 molecule) the difference between

Table 1. Calculated adiabatic and experimental energy characteristics of the F, S atoms and F₂, SF_k ($k = 1-6$) molecules.

Energy characteristics	Calculated values, eV		Experimental values, eV
	B3LYP	B3PW91	
F			
E_a	3.355	3.317	3.4 [10]
E_{exc}	–	–	F($2p^5 \ ^2P_{3/2}^o$): 0.05 [10] F($2p^4 3s \ ^4P, \ ^2P$): 12.70–13.03 [10]
I	17.65	17.61	17.423 [10]
F ₂			
E_a	3.609	3.498	2.96 [10]
E_{exc}	–	–	≈ 2 (for Cl ₂ , Br ₂ , I ₂) [10]
I	15.62	15.59	15.686 [10]
$D(2F/F_2)$	1.51	1.52	1.38 [10]; 1.63 [11]
$G_v, 0 \ ^\circ K$		0.067	~ 0.055 [10]; 0.0565 [12]
S			
E_a	2.129	2.157	2.077 [10]
$E_{exc}(S^+)$	–	–	S ⁺ ($3p^3 \ ^2D^o, \ ^2P^o$): 1.84–3.05 [10] S ⁺ ($3s3p^4 \ ^4P$): ≈ 9.9 [10]
I	10.49	10.51	10.36 [10]
SF _k			
$I(SF_6)$	14.78	14.84	15.69 ± 0.05 (see Ref. [81] in [1])
$E_a(SF_6)$	2.52	2.23	1.06 [1,13]; 0.65 [10]
$G_v(SF_6)$		0.558	–
$I(SF_5)$	10.41	10.32	10.5 ± 0.1 [14]; 9.6 [15]; 11.20 [16]
$D(SF_5-F/SF_6)$	3.69	3.84	3.38 [17]; 3.9 ± 0.15 [18]; 4.1 ± 0.13 [19]
$G_v(SF_5)$		0.400	–
$I(SF_4)$	11.94	11.88	12.03 ± 0.05 [14]; 11.69 [15]; 12.08 ± 0.10 [17]
$D(SF_4-2F/SF_6)$	5.08	5.37	–
$G_v(SF_4)$		0.310	–
$I(SF_3)$	8.88	8.01	11.0 ± 1.0 [16]; 8.18 ± 0.07 [20]
$D(SF_3-3F/SF_6)$	8.58	9.79	–
$G_v(SF_3)$		0.162	–
$I(SF_2)$	10.16	10.17	10.08 [14]; 11.8 [21]; 10.29 ± 0.10 [22]
$D(SF_2-4F/SF_6)$	10.95	11.38	–
$G_v(SF_2)$		0.124	–
$I(SF)$	10.23	10.26	10.09 [14]
$D(SF-5F/SF_6)$	14.51	15.00	–
$G_v(SF)$		0.052	0.052 [12]
$D(S-6F/SF_6)$	18.00	18.49	–
$D(S-F/SF)$	3.49	3.49	3.5 [10]

the experimental and the theoretical data rapidly decreases. Numerous experimental data in appearance E_{AP}^{exp} and binding energies E_b in general agree with each other fairly well; however, the channels of the dissociative ionization process often remain unknown. The existing differences in the measured energies of appearance of some SF_k⁺ ions are mostly related to the specific details of the experimental techniques.

Vertical values of the appearance energies are somewhat higher than the adiabatic values. For the appearance of SF_k⁺ fragments from the SF₆ molecule this increment increases with k : from 0.07 eV ($k = 1$) to 0.64 eV ($k = 3$) and further to the values of 0.82 eV ($k = 4$) and 1.75 eV ($k = 5$) (see Fig. 1 hereafter).

Figure 1 shows the experimental and calculated appearance energies E_{AP} for the SF_k⁺ fragments from the

Table 2. Appearance energies of SF_k^+ fragments from the SF_ℓ ($\ell = 0-6$) molecules.

SF_k^+ fragments	$E_{\text{AP}}^{\text{exp}}(E_b(F)), \text{eV}$	$E_{\text{AP}}^{\text{th}}(E_b(F)), \text{eV}$	
		B3LYP	B3PW91
$\text{SF}_k^+/\text{SF}_6$			
SF_6^+	15.69 ± 0.05 (see Ref. [81] in [1])	14.78	14.84
SF_5^+	15.50 ± 0.5 (4.3–5.9) [17,23]	14.10 (3.60)	14.16 (3.84)
	15.85 ± 0.15 (4.65–6.25) [26]		
	15.32 ± 0.04 (4.1–5.7) [27]		
	≤ 13.78 (2.58–4.18) [28]		
	13.97 ± 0.04 (2.8–5.4) [29]		
	≤ 14.4 (3.2–5.8) [30]		
	14.62 ± 0.09 (3.4–6.0) [19]		
	15.3 ± 0.2 (4.1–5.7) [31]		
	16.2 ± 0.2 (5.0–6.6) [32]		
	$\leq 14.53 \pm 0.05$ (3.33–5.93) [33]		
15.75 ± 0.05 (4.55–6.15) [34]			
15.29 (4.1–5.7) [35]			
SF_4^+	18.44 ± 0.5 (3.2; 3.38) [23]	17.02 (2.54)	17.27 (2.70)
	18.50 ± 0.10 (3.21–3.41) [34]		
	18.9 (3.41–3.61) [36]		
	19.1 ± 0.5 (3.51–3.71) [31]		
	19.6 ± 1.0 (3.76–3.96) [32]		
SF_3^+	18.70 ± 0.5 (2.57; 3.51) [23]	17.47 (2.86)	17.80 (3.26)
	20.1 (3.03; 3.97) [36]		
	21.5 (3.5; 4.4) [34]		
SF_2^+	27.00 ± 0.5 (4.23; 3.8) [23]	21.11 (2.74)	21.55 (2.85)
	27.0 ± 0.3 (4.23; 3.8) [32]		
	27.5 ± 0.5 (4.73; 4.3) [17]		
	26.8 ± 0.3 (3.75–4.18) [36]		
SF^+	30.44 ± 0.5 (4.07) [23]	24.74 (2.90)	25.26 (3.0)
	30.5 ± 0.5 (4.08) [17]		
	31.3 ± 0.3 (4.24) [36]		
	37.6 ± 3.0 (5.5) [32]		
S^+	36.40 ± 0.5 (4.34) [23]	28.49 (3.0)	29.00 (3.08)
	37.3 ± 1.0 (4.49) [36]		
$\text{SF}_k^+/\text{SF}_5$			
SF_5^+	10.5 ± 0.1 [14]; 9.6 [15];	10.41	10.32
	11.20 [16]		
SF_4^+	14.50 (2.47; 2.81) [16]	13.34 (1.40)	13.41 (1.53)
SF_3^+	17.00 (3.0; 4.41) [21]	13.78 (2.45)	13.96 (2.98)
SF_2^+	21.80 (3.91; 3.33) [21]	17.43 (2.42)	17.71 (2.77)
SF^+	27.80 (4.43) [21]	21.06 (2.71)	21.41 (2.79)
S^+	–	24.81 (2.86)	25.16 (2.93)
$\text{SF}_k^+/\text{SF}_4$			
SF_4^+	12.03 ± 0.05 [14]; 11.69 [15];	11.94	11.88
	12.08 ± 0.10 [17]		
SF_3^+	14.50 (3.5; 6.32) [21]	12.39 (3.51)	12.44 (4.43)
	12.63 ± 0.10 (1.63; 4.45) [17]		
SF_2^+	19.30 (4.61; 3.75) [21]	16.03 (2.94)	16.19 (3.01)
	17.4 ± 0.5 (2.8–3.66) [17]		
SF^+	25.30 (5.07) [21]	19.66 (3.14)	19.89 (3.21)
S^+	–	23.41 (3.23)	23.64 (3.28)
$\text{SF}_k^+/\text{SF}_3$			
SF_3^+	11.0 ± 1.0 [16];	8.88	8.01
	8.18 ± 0.07 [20]		
SF_2^+	15.40 (5.32; 3.6) [21]	12.53 (2.37)	11.76 (1.59)
SF^+	21.40 (5.66) [21]	16.16 (2.97)	15.47 (2.61)
S^+	–	19.91 (2.9)	19.22 (2.9)

Table 2. continued.

$\text{SF}_k^+/\text{SF}_2$			
SF_2^+	10.08 [14]; 11.8 [21]; 10.29 \pm 0.10 [22]	10.16	10.17
SF^+	18.80 (8.71) [21] 13.95 \pm 0.10 (3.86) [22]	13.80 (3.57)	13.88 (3.62)
S^+	–	17.55 (3.53)	17.63 (3.56)
SF_k^+/SF			
SF^+	10.09 [14]	10.23	10.26
S^+	–	13.98 (3.49)	14.01 (3.5)
S_k^+/S			
S^+	10.36 [10]	10.49	10.51

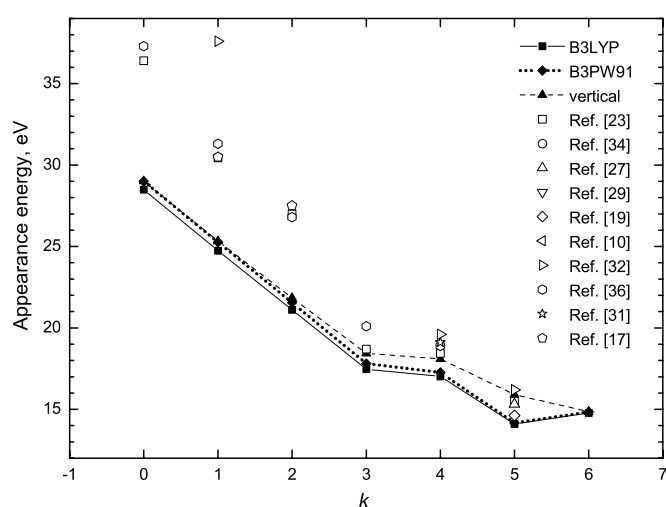


Fig. 1. Appearance energy $E_{\text{AP}}(\text{SF}_k^+/\text{SF}_6)$ as a function of the remaining fluorine atoms k ($k \leq 6$) in the final fragment SF_k^+ . For $k = 6$ the calculated and experimental values of the ionization potential of the SF_6 molecule are shown.

SF_6 molecule (see Tab. 2) as functions of the number of the remaining fluorine atoms k . The calculated values are given for the reaction of the type of equation (1), i.e. for the appearance energies in the case when the reaction products are in the ground state. As one can see, the behaviour of the experimental and the calculated appearance energies is qualitatively similar – they decrease with k . However, there is a systematic increment of the experimental data over the theoretical values. It can also be seen that for $k \leq 3$ the monotonous behaviour of the experimental $E_{\text{AP}}^{\text{exp}}(\text{SF}_k^+/\text{SF}_6)$ and the theoretical $E_{\text{AP}}^{\text{th}}(\text{SF}_k^+ - (6-k)\text{F}/\text{SF}_6)$ appearance energies is characterized by a rapid decrease with k . For $k \geq 3$ this energy decrease with k is less pronounced and the theoretical values are close to the experimental data.

Figures 2 and 3 show the behaviour of experimental and calculated adiabatic appearance energies for the SF^+ and SF_2^+ ion fragments depending on the number ℓ of fluorine atoms in the initial SF_ℓ fragment (see Tab. 2). It can also be seen that the behaviour of the above appearance energies is qualitatively similar as well; however, there is

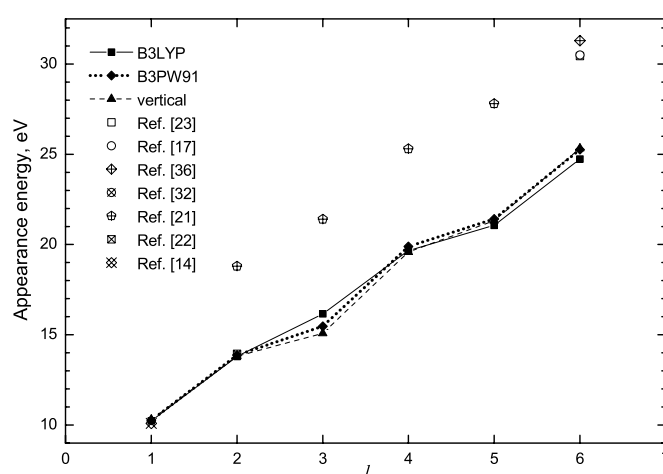


Fig. 2. Appearance energy $E_{\text{AP}}(\text{SF}^+/\text{SF}_\ell)$ as a function of the number ℓ of fluorine atoms in the initial SF_ℓ molecule. For $\ell = 1$ the calculated and experimental values of the ionization potential of the SF molecule are shown.

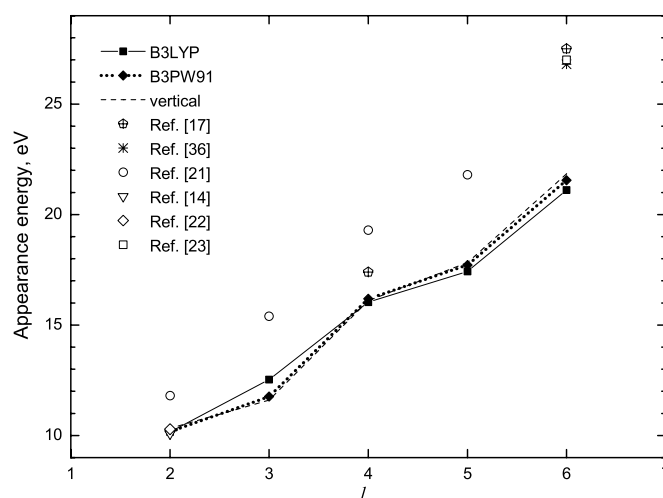


Fig. 3. Appearance energies $E_{\text{AP}}(\text{SF}_2^+/\text{SF}_\ell)$ versus the number of fluorine atoms ℓ in the initial SF_ℓ molecule. For $\ell = 2$ the calculated and experimental values of the ionization potential of the SF_2 molecule are shown.

Table 3. Appearance energies of F^+ and F_2^+ fragments from the SF_ℓ molecules.

SF_ℓ molecules	$E_{AP}^{exp}(E_b(F); E_b(F_2)), eV$	$E_{AP}^{th}(E_b(F); E_b(F_2)), eV$	
		B3LYP	B3PW91
F^+/SF_ℓ			
SF_6	–	21.49 (3.84)	21.61 (4.0)
SF_5	–	19.13 (1.48)	19.22 (1.61)
SF_4	–	21.30 (3.65)	22.18 (4.57)
SF_3	–	20.05 (2.4)	19.24 (1.63)
SF_2	–	21.29 (3.64)	21.30 (3.69)
SF	–	21.19 (3.54)	21.15 (3.54)
F_2^+/SF_ℓ			
SF_6	18.0 ± 1.0 (1.85, 1.97; 2.314) [32]	19.36 (2.63; 3.74)	19.61 (2.77; 4.02)
SF_5	–	19.17 (2.53; 3.55)	20.17 (3.05; 4.58)
SF_4	–	20.09 (2.99; 4.47)	20.19 (3.06; 4.6)
SF_3	–	20.07 (2.98; 4.45)	19.31 (2.62; 3.72)
SF_2	–	21.21 (3.55; 5.59)	21.23 (3.58; 5.64)

also a systematic increment of the experimental data over the theoretical E_{AP}^{th} values. The larger is the number of the fluorine atoms detached, the higher is the increment.

The appearance energies of other fragments are characterized by a similar behaviour. For example, the behaviour of the appearance energies of S^+ ions from the SF_ℓ molecules is a monotonously increasing function of ℓ : from ~ 10.5 eV ($\ell = 0$) and ~ 14 eV ($\ell = 1$) to ~ 28.5 – 29 eV ($\ell = 6$) (see Tab. 2).

All excited electronic states of the SF_6 molecule are antibonding [1]. A reason for the underestimated theoretical values of the appearance energies $E_{AP}(SF_k^+ - (\ell - k)F/SF_\ell)$ with respect to the corresponding experimental ones can be a specific feature of excitation of the repulsive (without a minimum) highly-excited electronic states of the SF_ℓ molecule in comparison with the excitation of a state possessing a minimum. An ion fragment is formed effectively via the repulsive electronic state of the electronically excited SF_ℓ molecules possessing higher energy. On an example of a diatomic molecule, the spatial width of the repulsive electronic state is determined by the similar width of a vibrational level in the initial molecule. The corresponding energy difference is determined by the slope of the electronic state. A higher number of the detached fluorine atoms at the dissociative ionization requires a higher excitation energy, which corresponds to a steeper electronic state and, consequently, to a higher energy difference. This results in an increasing increment of the observed appearance energy over the theoretical value. This excessive energy goes both to the excitation of the reaction products and the increase of their kinetic energy.

In order to excite the electronic state of the ions the following energy is required [37]: $SF_4^+ - 3.17$ eV (A and B states) and 3.90 eV (C and D states); $SF_2^+ - 5.32$ eV (A), 6.12 eV (B , C), 8.22 eV (D), 9.22 eV (C). The energy required to excite the SF^+ ion is not smaller than for the SF excitation: 3.07 eV ($A^2\Pi_{3/2}$) and 3.14 eV ($A^2\Pi_{1/2}$) [10]. About 0.5 eV is required for the formation of an excited F_2 molecule (see the energies $E_{exc}(F_2)$ and $D(2F/F_2)$ in Tab. 1).

One more mechanism of the ion fragment appearance can be understood analyzing the binding energies of molecular orbitals in the initial fragments. The ionization energies of an electron from the valence orbitals in the ground state configuration of SF_6

$$(core)^{22}(4a_{1g})^2(3t_{1u})^6(2e_g)^4(5a_{1g})^2(4t_{1u})^6(1t_{2g})^6(3e_g)^4 \\ [(1t_{2u})^6(5t_{1u})^6](1t_{1g})^6 A_{1g} \quad (4)$$

(given in Ref. [1]), are close to the threshold of the processes resulting in the formation of the corresponding SF_k^+ fragments. Ionization of an electron from the outer orbital $1t_{1g}$ (with the energy from 15.29 to 16.0 eV) can result in the formation of SF_5^+ , from the $2e_g$, $3e_g$, t_{2u} orbitals (18.0 to 19.1 eV) – in the formation of SF_4^+ , from the $1t_{2g}$ orbital (19.0 to 20.3 eV) – in the formation of SF_3^+ , and from the a_1 orbital (26.0 to 26.8 eV) – in the formation of SF_2^+ . At the energies 31.0 and 31.3 eV the ionization of the orbital can lead to the formation of SF^+ fragments while at 37.0 and 37.3 eV S^+ ions can be formed.

3.2 Appearance energies of F^+ and F_2^+ ions

The values of the calculated appearance energies E_{AP}^{th} of the F^+ ions (the reaction $e + SF_\ell \rightarrow F^+ + 2e + SF_{\ell-1}$, $\ell = 1$ – 6) and F_2^+ ions (the reaction $e + SF_\ell \rightarrow F_2^+ + 2e + SF_{\ell-2}$, $\ell = 2$ – 6) from the SF_ℓ fragments of the SF_6 molecule are listed in Table 3. Using the experimental and theoretical values of E_{AP} , I and D we evaluated the binding energy E_b for the F atom and F_2 molecule from the SF_6 molecule and its molecular fragments.

For the case of appearance of F^+ ions, the binding energy E_b of the fluorine atom

$$E_b(F) = E_{AP}(F^+ - SF_{n-1}/SF_n) - I(F) \quad (5)$$

is given in parentheses. The appearance energy $E_{AP}(F^+/SF) = 20.923$ eV estimated as an enthalpy

energy from the experimental values of $I(\text{F})$ and $D(\text{F-S}/\text{SF})$ [10] from Table 1. This value is close to the calculated one. The following values are presented for the appearance energy $E_{\text{AP}}(\text{F}^+/\text{SF}_6)$ (in Refs. [32,36]): 37.5 ± 1.0 eV and 35.8 ± 1.0 eV. As one can see, these values are much higher than our calculated ones. For example, in reference [32], the appearance energy was obtained by electron excitation with 45 eV energy, when the intensity of F^+ ions with ~ 7.5 eV kinetic energy is nearly equal to zero. The binding energy $E_{\text{b}}(\text{F})$, evaluated according to equation (5) and using the $E_{\text{AP}}(\text{F}^+/\text{SF}_6)$ of [32], is also too high: ~ 18.4 – 20 eV, which highly overestimates the mentioned dissociation energies in Table 1, where $D(\text{SF}_5\text{-F}/\text{SF}_6) \sim 3.4, 3.9, 4.1$ eV. According to this, ~ 17 eV energy goes to the excitation of the formed fragments and the F^+ ion.

For the case of formation of a F_2^+ ion from the SF_ℓ fragments, the average value of the binding energy E_{b} for the fluorine atom

$$E_{\text{b}}(\text{F}) = [E_{\text{AP}}(\text{F}_2^+ - \text{SF}_{n-2}/\text{SF}_n) - I(\text{F}_2) + D(2\text{F}/\text{F}_2)]/2 \quad (6)$$

and for the fluorine molecule

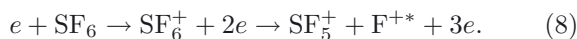
$$E_{\text{b}}(\text{F}_2) = E_{\text{AP}}(\text{F}_2^+ - \text{SF}_{n-2}/\text{SF}_n) - I(\text{F}_2) \quad (7)$$

is given in parentheses. We note here, that there is no such exceeding in case of appearance of a F_2^+ ion from the SF_6 molecule, as it was observed for the F^+ ion.

We can see, that the experimental values noticeably exceed the theoretical ones in the case of appearance of the F^+ ion from the SF_6 molecule. The appearance of the F^+ ion is most likely due to the excited repulsive electronic states of the SF_6^+ ion [32]. These experimental data for the appearance of the F^+ and F_2^+ ions correlated with the threshold excitation energies of neutral F and F_2 fragments which are formed at the dissociation of SF_6 by electron-impact (see Table 22 in Ref. [1]). There is a large number of channels leading to a partial or complete dissociation of SF_6 .

A possible reason for the experimental appearance energies $E_{\text{AP}}(\text{F}^+ - \text{SF}_5/\text{SF}_6)$ exceeding the theoretical values can be an effective excitation of the repulsive highly-excited electronic state of the SF_6 molecule. In this case the excessive energy goes to the excitation of F^+ and F_2^+ ions and the electronic states of neutral $\text{SF}_{\ell-1}$ and $\text{SF}_{\ell-2}$ molecules as well as to the increase of the kinetic energy of the reaction products. For example, the A , B' , and B electronic states of the SF_2 molecule have the following excitation energies (eV): 2.24 [38–41], 4.79 [42,43] and 6.75 [42,44]. The excitation energies of F^+ ions: ~ 2.5 eV for $2s^22p^4 \ ^1\text{D}_2$ and ~ 5 eV for $2s^22p^4 \ ^1\text{S}_0$ [10]; while the excitation energies of F_2^+ ions: 2.79 eV for the A state [45] and 5.33 eV for the B state [46].

It is also worth noting, that the appearance of an excited F^+ ion from SF_6 most likely occurs along with the SF_5^+ ion in reference [32], i.e. according to the process



Note that in this case the experimental value $E_{\text{AP}}(\text{F}^+/\text{SF}_6) \approx I(\text{SF}_6) + I(\text{F}) + E_{\text{exc}}(\text{F}^+)$ (see also [32]).

Similarly to the case of appearance of the SF_k^+ ion fragments (see above), ionization of an electron from the $1t_{2g}$ orbital (the energy from 19.0 to 20.3 eV) can also result in the formation of a F_2^+ molecular ion. Likewise, ionization of an electron from the $2e_g$ orbital (the energy from 39.3 to 40.6 eV [1]) can lead to the appearance of a F^+ ion, and from the $3t_u$ orbital (the energy above 41.2 eV) – to the formation of a pair of positive ions – SF_k^+ and F^+ or F_2^+ . Therefore, one more effective mechanism of dissociative ionization of the SF_6 molecule and its fragments by electron-impact can consist in a removal of electrons from the orbitals whose energies are close to the energies of appearance of the ions.

4 Summary

Theoretical analysis of appearance energies for various singly charged positive ion fragments at electron-impact dissociative ionization of sulfur hexafluoride molecule and its fragments was performed, based on the GAMESS software calculations.

The qualitative behaviour of the calculated and measured appearance energies of SF_k^+ ion fragments from the SF_6 molecule depending on the number k of the remaining fluorine atoms is the same. In a similar way, a good qualitative agreement is observed for the dependences of the calculated and experimental appearance energies of the SF_k^+ fragments from SF_ℓ molecule on the final number k and the initial number ℓ of fluorine atoms.

The fact that the theoretical values are underestimated with respect to the experimental appearance energies can be explained by a possible effective excitation of the repulsive highly-excited electronic states of the electronically excited SF_6 molecule and its molecular fragments. As a result, the final atomic and molecular products of reaction can exist in excited states and possess significant kinetic energies. Another possible mechanism of the molecular ion appearance can be removal of an electron from an energetically suitable molecular orbital in the initial SF_6 molecule or its molecular fragments. This mechanism also leads to highly-excited electronic states of these molecules.

A more detailed explanation of the specific features of the ion fragment appearance requires determination of characteristics of the reaction channel final products, namely the kinetic energy, the excited and charged states.

The authors are grateful to A.V. Snegursky, Yu.M. Azhniuk and V.V. Maslyuk for their support and fruitful discussions. One of the authors, Sh. Demesh, acknowledges the Collegium Talentum institution for the financial and professional support of his scientific work. This research was realized in the frames of TÁMOP 4.2.4. A/2-11-1-2012-0001, National Excellence Program “Elaborating and operating an inland student and researcher personal support system”. The project was subsidized by the European Union and cofinanced by the European Social Fund.

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