ATOMIC AND MOLECULAR PHYSICS

Fragment Appearance Energies in Dissociative Ionization of a Sulfur Hexafluoride Molecule by Electron Impact

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Abstract—Theoretical analysis of the fragment appearance energies corresponding to possible channels of formation of SF_k^+ fragments in dissociative ionization of the SF_6 molecule by an electron impact is carried out. The total energies of neutral and ion molecular and atomic fragments are calculated using the theoretical methods of the GAMESS program complex. It is concluded that apart from dissociative ionization via autoionizing repulsive electronic states of the SF_6 molecule, the excitation channels for SF_k^+ fragments and F_2 molecules play a significant role, which leads to higher values of the observed fragment appearance energy as compared to theoretical values. The dependence of the energy corresponding to the formation of SF_k^+ c fragments on the number k of fluorine atoms is considered.

INTRODUCTION

The physical meaning of the appearance energy of an ion fragment (appearance energy AE, denoted further by E_{AP}) in dissociative ionization (DI) of a molecule by an electron impact is the energy spent for the escape of the corresponding ion from the molecule. In the case of a polyatomic molecule, the value of E_{AP} depends on the atomic and molecular products formed in the final state. For a given configuration of the products, the energy E_{AP} for which these products are in the ground state and have zero kinetic energy has the lowest value. In other words, DI is a "chemical reaction" stimulated by an impinging electron, which occurs at the threshold between two processes, viz., autoionization and dissociation. Since the energy of the impinging electron exceeds the ionization potential of the corresponding molecular fragment, DI occurs via the electronic states in the continuous spectrum (i.e., in the autoionizing region of the initial molecule). In accordance with the Frank–Condon principle, the most probable transitions under electron excitation are those occurring between the peaks of the wavefunctions of vibrational states of the initial and excited (final) molecule with the same configuration (geometry) of atoms. Thus, the energies of vertical transitions under electron excitation are higher than the energies of transitions between the ground states.

Processes of autoionization and dissociation can effectively occur simultaneously if the electronic and atomic types of motion of an excited molecule are strongly coupled (in other words, as a result of the interaction of excited electronic vibrational states). Experiments like those in [1] with the SF_6 molecule provide information on highly excited electronic and vibrational states of the molecule and on the DI mechanisms. This mainly concerns the cases when a small number k of fluorine atoms in an ion fragment are left as a result of the reaction (i.e., when a large number $(6 - k)$ of fluorine atoms are detached as a result of interaction with an impinging electron).

To determine the appearance energy reliably, it is necessary to measure and analyze the states of all reaction products. If, however, only a molecular ion fragment is detected in experiment, it is possible to determine the energy which is generally determined by the state of final products obtained in the most probable processes. For example, the atomic and molecular reaction products can be in excited states and can also be bound with one another. In analysis of the measured AE, it should be borne in mind that the molecular ion fragments, as well as atoms and molecules, can be excited and negative ions can be formed. The formation of such ions is a threshold process that can be especially effective when atoms forming a molecule have a high electron affinity energy.

During DI of the SF_6 molecule by an electron impact, the AE of the $SF_{k=0-6}^+$ ion in the ground state is equal to the energy spent on its detachment from the molecule via the channel associated with the formation of the corresponding number of fluorine atoms or molecules in the ground states and an electron. This

means that the AE of the SF_k^+ ion in this case is determined by the presence of fluorine atoms and molecules in the final reaction products for the given channel.

The absolute values of E_{AP} of ion fragments SF_k^+ ($k = 0–5$) were determined in [1] in mass-spectroscopic studies of DI of a sulfur hexafluoride (SF_6) molecule by an electron impact. The nonmonotonic behavior of the $E_{AP}(k)$ dependence was also considered. In [2], this dependence on the number of fluorine atoms (or, in other words, mass of SF_k^+ fragments) was also studied qualitatively using information on reaction products.

The results of earlier measurements of the yield of ion fragments SF_k^+ in various processes of dissociation of the SF_6 molecule were reported in [3–12]. In [3], the F^+ and F_2^+ ions with AEs of 37.5 ± 1.0 eV and 18.0 ± 1.0 eV were also observed. In [4], the measured values of AEs of the F^+, SF_2^{2+}, and SF_4^{2+} ions were 35.8 ± 1.0, 46.5 ± 0.5, and 40.6 ± 0.5 eV, respectively. In [13], the yields of SF_k^+ ions ($k = 5–1$) and S^+, F^+, SF_4^{2+}, SF_3^{2+}, SF_2^{2+}, S_2^+, F_2^+, SF_3^{3+}, and S^{3+} ions under DI of SF_6 molecules by high-energy electrons (10–20 keV) were investigated. It was shown in [14] that along with direct DI process, the decomposition of the SF_4^{2+} ion also contributes to the formation of the SF_3^+ and F^+ ions for high energies of electrons (>45 eV):

$$e + SF_6 \longrightarrow SF_4^{2+} + 2F + 3e \longrightarrow SF_3^+ + F^+ + 2F + 3e.$$
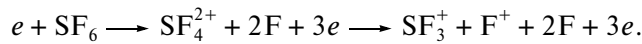
In review [15], the advances in the study of the structure of the SF_6 molecule and various processes of interaction of an electron with this molecule are considered. It is pointed out that beginning with energies exceeding 15 eV, the molecule dissociates into neutral fragments SF_k ($k = 1, 2, 3$) and F atoms. The dissociative ionization by an electron impact becomes significant beginning with energies of ~16 eV, leading to the formation of ion fragments SF_k^+ ($k = 1, 3, 4, 5$) and F^+ ions. However, information on the AE of ion fragments SF_k^+ is not given or analyzed in [15], where the behavior of partial ionization cross sections is mainly considered.

In this study, we report on the results of our ab initio calculations of the AE of ion fragments formed during DI of the SF_6 molecule by an electron impact. We analyze the experimental data on the AE and compare them with the data calculated for possible channels of this process.

1. APPEARANCE ENERGY

The energy corresponding to the appearance of fragment SF_k^+ from the SF_6 molecule in accordance with the reaction

$$e + SF_6 \longrightarrow SF_k^+ + 2e + nF, \quad n = 6 - k, \qquad (1)$$
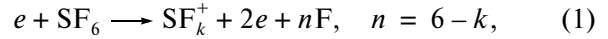
is defined as

$$E_{AP}[(SF_k^+ - nF)/SF_6] = E_t(SF_k^+) + nE_t(F) - E_t(SF_6)$$
$$= D[(SF_k - nF)/SF_6] + I(SF_k). \qquad (2)$$

Quantities E_t, D, and I in relation (2) are the total energy corresponding to the minimum of the electronic state with the vibrational energy of the molecule, and the energies of dissociation and ionization, respectively. Thus, the appearance energy of fragment SF_k^+ under DI of the SF_6 molecule is the sum of the binding energy of n fluorine atoms in the molecule and the ionization potential of fragment SF_k. Here, we have two limiting cases: direct ionization of the SF_6 molecule, $k = 6$, i.e., when fluorine atoms are not detached ($n = 0$) and conversely, the ionization of the sulfur atom ($k = 0$) during DI, when all fluorine atoms are detached ($n = 6$).

The allowance for vibrational energy $G_v > 0$ of the ground state of SF_k molecules (in calculations, the energies for neutral SF_k molecules and their ions SF_k^+ and SF_k^- are different) affects the energy characteristics of the molecules. For example, the AEs disregarding and taking into account G_v differ by $\Delta G_v = G_v(SF_6) - G_v(SF_k^+)$. With increasing k, the value of ΔG_v decreases (at 0 K) from 0.495 eV (SF) to 0.084 eV (SF_5) and 0.114 eV (SF_6).

The fragment appearance energy $E_{AP}[(SF_k^+ - nF)/SF_6]$ (2) is the energy spent for detaching n fluorine atoms and ionization of the fragment (particles are in the ground state and have zero kinetic energies). If the F_2 molecule is formed in the course of DI, the appearance energy decreases by the binding energy of fluorine atoms; e.g.,

$$E_{AP}[(SF_3^+ - F - F_2)/SF_6]$$
$$= E_{AP}[(SF_3^+ - 3F)/SF_6] - D(2F/F_2). \qquad (3)$$

The formation of the F_2^- and F^- ions also reduces the AE by the electron affinity energy of F_2 and F:

$$E_{AP}[(SF_3^+ - F^- - F_2)/SF_6]$$
$$= E_{AP}[(SF_3^+ - F - F_2)/SF_6] - E_a(F) \qquad (4)$$
$$= E_{AP}[(SF_3^+ - 3F)/SF_6] - D(2F/F_2) - E_a(F).$$

Thus, the AE energy of a fragment from the initial molecule is determined for the specific reaction. Since each reaction channel is characterized by its own

probability of occurrence, the main contribution to the total yield of the ion fragment is determined by the most probable channel (or channels) of the relevant process.

2. CALCULATION OF CHARACTERISTICS

To determine the total energies of the ground states of molecules, atoms, and ions, we used the programs of the GAMESS complex [16], which are based on the density functional theory [17]. In our calculations, we used the Linux cluster from the Institute of Electron Physics, National Academy of Sciences of Ukraine, with a high parallelization level. Computations were performed with two types of hybrid exchange-correlation functionals (B3LYP [18] and B3PW91 [19]) in the generalized gradient approximation. Both functionals include the Hartree−Fock-type exchange (by 20%) together with the Slater-type exchange (by 80%), while the correlation interaction is described by the Lee−Yang−Parr (LYP) functional in B3LYP [20] and the Perdew−Wang (PW) functional in B3PW91 [21].

The initial electron density matrix was determined by the unrestricted Hartree−Fock method (see literature cited in [16]). The convergence boundary of the iterative procedure in the total energy in this case was 5×10^{-3} a.u. The further refinement of the total energy of the system was performed using the approximations of the density functional theory. The total energy of all molecules under investigation was determined in two multiplet states from which the state with the lowest energy was selected. We used the standard Dunning−Hay Gaussian "double zeta" basis set consisting of ($9s$, $5p$)/[$3s$, $2p$] functions for fluorine and ($11s$, $7p$)/[$6s$, $4p$] functions for sulfur with additional Dunning-type polarization functions ($1d$, $1f$) and diffusion functions for the s and p shells [22].

The structure of the SF_6 molecule was optimized in the algorithm of quadratic approximation [23] disregarding the effect of symmetry. For the initial geometry, the minimal atomic spacing was specified. After the obtaining of the equilibrium optimized geometry of the SF_6 molecule, two types of calculations were carried out: the vertical and adiabatic energy characteristics of the SF_k fragments were determined.

The vertical energy characteristics were calculated as follows. Proceeding from the equilibrium geometry of the SF_6 molecule, the geometry of all its fragments was determined. In the case of SF_4, SF_3, and SF_2, the fluorine atoms were detached from the SF_6 molecule in such a way that each fragment was three-dimensional and not planar. Preliminary calculations of various variations of the geometries of such objects revealed that it is the system with such a 3D configuration that possesses the lowest energy. It should be noted that the spatial arrangement of atoms in the ion fragments was the same as in neutral atoms. For example, the geometries of the SF_4, SF_4^+, and SF_4^- mole-

cules and ions were identical. Using this algorithm, the vertical energy characteristics of the SF_k fragments ($k = 1-6$) and F_2 molecules, such as the ionization potentials and the electron affinity energies E_a, and dissociation energies D were determined (Table 1).

In calculations of the adiabatic characteristics, the equilibrium geometry of SF_k and F_2 molecules was also determined in the course of geometrical optimization in accordance with the algorithm of quadratic approximation. The above characteristics were determined as the difference between the total energies of relaxed states of neutral and ionized systems (see Table 1).

In Table 1, the experimental and calculated (with allowance for the energy of vibrations) adiabatic values of some constants for atoms and molecules are compared. The experimental value [24] for $G_v(F_2)$ is $\omega_e/2$, where ω_e is the vibrational energy. The values are generally in good agreement. The electron affinity energy $E_a(SF_6)$ for the molecule is compared with the value recommended in [15], where several measured and calculated values strongly differing from one another are compared. These data will subsequently be used for corresponding estimates.

3. RESULTS AND DISCUSSION

Table 2 contains the experimental AEs of ion fragments SF_k^+ from [1] in comparison with the results of earlier measurements borrowed from [3−12]. The appearance energy of the SF_6^+ ion in experiments [1, 3, 4, 9, 14] has not been measured. According to estimates (see [15]), the intensity of this ion in the mass spectrum is approximately four orders of magnitude lower than the intensity of the SF_5^+ ion. It is well known that both the ground state and the excited state of the SF_6^+ ion are unstable and rapidly (during a few picoseconds) dissociate via the channel $SF_6^+ \longrightarrow SF_5^+ + F$ (see [3−5, 14]) with nonzero kinetic energies of the SF_5^+ and F fragments. In other words, the formations of SF_6^+ and SF_5^+ ions are interrelated. For this reason, the AE $E_{AP}(SF_6^+/SF_6)$ measured in [1] is close to energy $I(SF_6)$ and to the results obtained in [5−8], although it is found to be slightly smaller than the values from [3, 4], but higher than the data from [11, 12]. In Table 2, we used ionization potential $I(SF_6)$ for $E_{AP}(SF_6^+/SF_6)$. It can be seen that the values of AE for the remaining ions from [1] are close to other results or is slightly smaller in value.

Six singularities (at energies of 14.3, 15.9, 17.5, 18.7, 20.3, and 22.2 eV) were obtained in [33] by direct measurement of the total ionization potential of the

Table 1. Theoretical adiabatic and experimental energy characteristics of atoms and molecules. Vibrational energy $G_v(SF_k)$ at 0 K (zero-point energy). GAMESS: B3LYP (1) and B3PW91 (2)

Energies	Theoretical data, eV		Experimental data, eV
	1	2	
F			
E_a	3.355	3.317	3.4 [24]
E_{exc}	–	–	$F(2p^{52}P^0_{3/2})$: 0.05 [24]
			$F(2p^4 3s^4 P, {}^2P)$: 12.70–13.03 [24]
I	17.65	17.61	17.423 [24]
F$_2$			
E_a	3.609	3.498	2.96 [24]
E_{exc}	–	–	≈2 (as for the Cl_2, Br_2, I_2) [24]
I	15.62	15.59	15.686 [24]
$D(2F/F_2)$	1.51	1.52	1.38 [24]; 1.63 [25]
G_v, 0 K	0.067		~0.055 [24]; 0.0565 [26]
S			
E_a	2.129	2.157	2.077 [24]
$E_{exc}(S^+)$	–	–	$S^+(3p3, {}^2D^0, {}^2P^0)$: 1.84–3.05 [24]
			$S^+(3s3p^{44}P)$: ≈9.9 [24]
I	10.49	10.51	10.36 [24]
SF$_k$			
$I(SF_6)$	14.78	14.84	15.7 [15, 24]
$E_a(SF_6)$	2.52	2.23	1.06 [15, 27]; 0.65 [24]
$G_v(SF_6)$	0.558		–
$I(SF_5)$	10.41	10.32	10.5 ± 0.1 [28]; 9.6 [29]
$D(SF_5–F/SF_6)$	3.69	3.84	3.38 [8]; 3.9 ± 0.15 [30]; 4.1 ± 0.13 [12]
$G_v(SF_5)$	0.400		–
$I(SF_4)$	11.94	11.88	12.03 ± 0.05 [28]; 11.69 [29]
$D(SF_4–2F/SF_6)$	5.08	5.37	–
$G_v(SF_4)$	0.310		–
$I(SF_3)$	8.88	8.01	11.0 ± 1.0 [31]; 8.18 [29]
$D(SF_3–3F/SF_6)$	8.58	9.79	–
$G_v(SF_3)$	0.162		–
$I(SF_2)$	10.16	10.17	10.08 [28]; 11.8 [32]
$D(SF_2–4F/SF_6)$	10.95	11.38	–
$G_v(SF_2)$	0.124		–
$I(SF)$	10.23	10.26	10.09 [28]
$D(SF–5F/SF_6)$	14.51	15.00	–
$G_v(SF)$	0.052		0.052 [26]
$D(S–6F/SF_6)$	18.00	18.49	–
$D(S–F/SF)$	3.49	3.49	3.5 [24]

SF_6 molecule. Three of them (at 15.9, 18.7, and 20.3 eV) are attributed to the AE of the SF_5^+, SF_4^+, and SF_3^+ ions, respectively (see also [15]). These AEs coincide with the results obtained in [4] to within ±0.2 eV and exceed the values from [1] in which the AEs of the SF_4^+ and SF_3^+ ions are almost identical. It should also be noted that the value of 14.3 eV is close to the AE of the SF_5^+ ion from [11, 12] (see Table 2). The allowance

Table 2. Experimental energies E_{AP} of appearance of SF_k^+ fragments (the channel of formation of a fragment is given in parentheses)

Ion fragments	[1]	[3]	[4]	Other results
SF_6^+	–	–	–	15.7 [24] ($I(SF_6)$)
SF_5^+	15.5 ± 0.5	16.2 ± 0.2	15.9 ± 0.2	15.29 [5]
				15.3 ± 0.2 [6]
				15.32 ± 0.04 [7]
				15.50 ± 0.10 [8]
				15.75 ± 0.05 [9]
				15.85 ± 0.15 [10]
				13.97 ± 0.04 [11]
				14.62 ± 0.09 [12]
SF_4^+	18.4 ± 0.5	19.6 ± 1.0 (2F)	18.9	18.44 ± 0.10 (2F) [8]
				18.50 ± 0.10 (2F) [9]
				19.1 ± 0.5 (2F) [6]
SF_3^+	18.7 ± 0.5	19.8 ± 0.5 (?)	20.1	18.79 ± 0.14 (?) [7]
				19.4 ± 0.5 (?) [6]
				19.80 ± 0.10 ($F_2 \pm$ F?) [9]
				20.0 ± 0.50 (?) [8]
				21.5 (3F) [9]
SF_2^+	27.0 ± 0.5	27.0 ± 0.3 (?)	26.8 ± 0.3	27.5 ± 0.5 (?) [8]
SF^+	30.4 ± 0.5	37.6 ± 3.0 (?)	31.3 ± 0.3	30.5 ± 0.5 (?) [8]
S^+	36.4 ± 0.5	–	37.3 ± 1.0	–

for other reaction channels makes it possible to explain the remaining features from [33]. For example, the singularity at 17.5 eV can be due to the channel $SF_4^+ + F_2 + 2e$, for which we obtain from the AE of 18.7 eV the AE of 17.32 eV in view of dissociation energy $D(2F/F_2) = 1.38$ eV. Probably, the $SF_3^+ + F^- + 2F + e$ channel gives $E_{AP} = 16.9$ eV (because $E_a = 3.4$ eV). Analogously, the singularities at 15.9, 18.7, and 22.2 eV can be associated with the channels $SF_4^+ + F^- + F$ ($E_{AP} = 15.3$ eV) and $SF_3^+ + F + F_2 + 2e$ ($E_{AP} = 18.92$ eV) and with the reaction $SF_3^+ + F + F_2^*$ (~2 eV) $+ 2e$ ($E_{AP} = 20.7$ eV), respectively. The efficiency of the reactions is obviously determined by the channel cross sections.

For the SF_k^+ fragment, the AE from the SF_6 molecule can be obtained from the expression

$$
E_{AP}[(SF_k^+ - (6-k)F)SF_6]
$$
$$
= E_{AP}[(SF_k^+ - (m-k)F)SF_m] \quad (5)
$$
$$
+ D[(SF_m - (6-m)F/SF_6)].
$$

Here, $6 > m \geq k$. In this case, we can use the AE of this ion fragment from a simpler molecule and the corresponding dissociation energy. For example, using the experimental values of $E_{AP}[(SF_k^+ - (5-k)F)/SF_5]$ ($m = 5$, $k = 1-5$) from [15] (see the literature cited therein) and the measured dissociation energy from Table 1, we obtain for $E_{AP}^{exp}(SF_k^+/SF_6)$ the following intervals of possible values (in electronvolts) for k from 5 to 1: 13.88–15.3, 17.88–18.6, 20.38–21.1, 25.18–25.9, and 31.18–31.9. It can be seen that these values are in conformity with the data from Table 2.

It should be noted that the method for determining the AEs of ion fragments from the total ionization cross section of the molecule is problematic in many cases. Their values can be determined more exactly by

measuring the partial cross sections of the yield of SF_k^+ fragments or atomic ions F^+ and S^+ as it was done in [1, 34, 35]. If a given ion appears due to effective operation of several channels, each of them leads to more clearly manifested singularities in the energy dependence of the corresponding cross section [36] (e.g., in DI of methane). Therefore, we must consider the AE of an ion via a specific reaction channel.

Table 3 contains the theoretical values of AE E_{AP}^{th} for SF_k^+ ions for some reaction channels, taking into account vibrational energies $G_v(SF_6)$ and $G_v(SF_k^+)$. It can be seen that experimental values E_{AP}^{exp} [1] systematically exceed theoretical values E_{AP}^{th}, the excess being larger for small values of k (detachment of a large number of fluorine atoms) and smaller for large k. The maximal AE corresponds to the reaction of type (1) (i.e., detachment of unbound fluorine atoms in the ground states). However, even these maximal values of the AE are smaller than experimental values obtained in [1] (by 11.86 and 11.51 eV for $k = 0$ and by 2.39 and 2.35 eV at $k = 5$ depending on computational method 1 or 2). The vertical values of AE slightly exceed the adiabatic values. These excess increases with k: from 0.07 eV ($k = 1$) to 0.64 eV ($k = 3$) and to values of 0.82 eV ($k = 4$) and 1.75 eV ($k = 5$) (see the figure).

The formation of fluorine molecules and negative atomic and molecular ions reduces the value of E_{AP} still further, and the excitation of final products leads to its increase. It should be noted that the semi-empirical estimates of the AE obtained using experimental constants I, E_a, and D (see Table 1) generally coincide with calculated values.

The figure shows the experimental and theoretical adiabatic AEs E_{AP} for SF_k^+ fragments as functions of number k of fluorine atoms. The calculated values correspond to the reaction of type (1), for which the AE has the maximal value, and the reaction products are in the ground state. It can be seen that the behaviors of these AEs coincide qualitatively, but experimental values systematically exceed theoretical values. It can also be seen that for values $k \leq 3$ and $k \geq 3$, the AEs $E_{AP}^{exp}(SF_k^+/SF_6)$ and $E_{AP}^{th}(SF_k^+ - (6-k)F/SF_6)$ exhibit different behaviors upon an increase in k.

A possible reason for the excess of experimental values of AEs over theoretical values can be the peculiarity of excitation of the repulsive (without a minimum) autoionizing electronic state of the SF_6 molecule as compared to the excitation of the term with a minimum. The effective formation of the ion fragment occurs via the regions of the dissociable electron term of the electron-excited SF_6 molecule, which correspond to a higher energy. The spatial width of such a region is determined by the analogous width of the

Table 3. Energies of appearance of SF_k^+ fragments via various reaction channels. GAMESS: B3LYP (1) and B3PW91 (2)

Ion fragments	ΔG_v, eV	E_{AP}^{exp}, eV [1]	E_{AP}^{th}, eV		
			channel	1	2
SF_6^+	0.114	15.7 [24]	–	14.78	14.84
SF_5^+	0.084	15.50 ± 0.5	F	14.10	14.16
			F^-	10.75	10.84
SF_4^+	0.232	18.44 ± 0.5	2F	17.02	17.27
			F_2^*	17.51	17.75
			F_2	15.51	15.75
			$F-F^-$	13.67	13.95
SF_3^+	0.300	18.70 ± 0.5	3F	17.47	17.80
			$F-F_2^*$	17.96	18.28
			$F-F_2$	15.96	16.28
			$F^--F_2^*$	14.61	14.96
SF_2^+	0.411	27.0 ± 0.5	4F	21.11	21.55
			$2F_2^*$	22.09	22.51
			$2F-F_2^*$	21.60	22.03
			$2F-F_2$	19.60	20.03
SF^+	0.495	30.44 ± 0.5	5F	24.74	25.26
			$F-2F_2^*$	25.72	26.22
			$3F-F_2^*$	25.23	25.74
			$3F-F_2$	23.23	23.74
			$F^--2F_2^*$	22.37	22.90
S^+	0.558	36.40 ± 0.5	6F	28.49	29.00
			$3F_2^*$	29.96	30.44
			$2F-2F_2^*$	29.47	29.96
			$4F-F_2^*$	28.98	29.48
			$4F-F_2$	26.98	27.48
			$F-F-2F_2^*$	26.12	26.64

vibrational state of the initial SF_6 molecule, while the energy difference in this region is determined by the steepness of the term (rate of decrease). The steeper term (and, hence, the larger energy difference) corresponds to a larger number of detached F atoms during DI. This leads to an increase in the excess of the observed AE over the theoretical value (see Table 3). This energy excess is spent for excitation of the reaction products and for an increase in their kinetic energy.

The excitation of the Rydberg states of F_2, F, and S during dissociation of SF_6 was pointed out in [15]. The effective excitation of the F_2 molecules, SF_k^+ ions, and
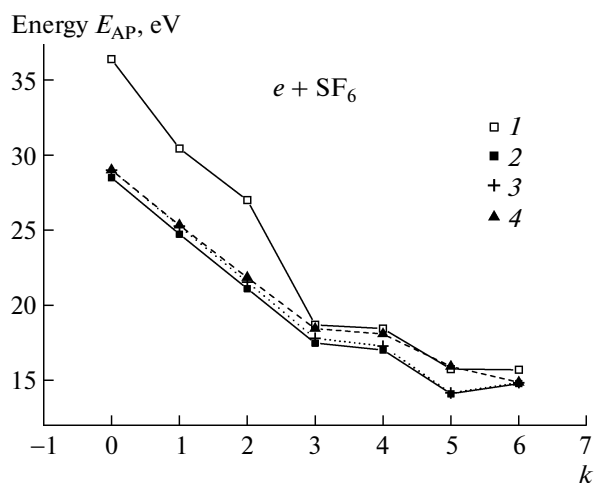
Energy E_{AP}, eV

Appearance energy E_{AP} of SF_k^+ fragments as a function of number k of fluorine atoms. Experimental values of E_{AP}^{exp} (SF_k^+/SF_6) obtained in [1] (*1*) and calculated adiabatic values of E_{AP}^{th} ($SF_k^+ - (6-k)F/SF_6$) with B3LYP (*2*), B3PW91 (*3*), and B3PW91 (vertical) (*4*). The experimental and calculated ionization potentials of SF_6 correspond to $k = 6$.

atomic particles F and S^+ during DI may strongly increase the value of the AE.

The excitation energy of metastable level $2p^5\,{}^2P_{3/2}^0$ of the fluorine atom is low and amounts to 0.05 eV. Conversely, the energy of excitation of levels $2p^43s\,{}^4P$ and ${}^2P$ are higher (12.70–13.03 eV) [25], and excitation of fluorine does not occur at the DI threshold (1).

The excitation energies of the lower electron levels $A^3\Pi_u(1_u)$ and $B^3\Pi_u(0_u^+)$ of the Cl_2, Br_2, and I_2 molecules chemically close to the F_2 molecule are 2.21, 1.96, and 1.96 eV [24]. Thus, we can assume that the electron excitation energy for the F_2 molecule amounts approximately to 2 eV (the vibrational energy in this case is only ~0.055 eV). These values were used in Table 3 for obtaining estimates (denoted by F_2^*). In the case of detachment of three molecules, the vibrational energy is ~0.165 eV, which affects the value of AE insignificantly.

SF_6^+ and SF_5^+ ions. The figure shows the ionization potentials for the SF_6 molecule calculated in our study (see Table 1). The ionization potential for SF_6 corresponds to the appearance energy of the SF_6^+ ion ($k = 6$) in the course of direct ionization.

In both computational methods 1 and 2, the ground state of the electron term of the SF_6^+ ion lies above the ground electron term of the SF_5^+ ion. Ener-

gies $E_{AP}(SF_5^+)$ are lower than ionization potential $I(SF_6)$ and amount to 14.10 and 14.16 eV. It can be seen that these values of the AE are close to the results obtained in [11] (13.97 ± 0.04 eV) and [12] (14.62 ± 0.09 eV) (see Table 2). Using the extreme experimental values [15] of $D[(SF_5 - F)/SF_6] = 3.38$ or 4.1 eV and $I(SF_5) = 10.5$ eV [28] (see Table 1), we obtain $E_{AP}[(SF_5^+ - F)/SF_6] = 13.88$ or 14.60 eV. These values are in good agreement with the results obtained in [11, 12] (see Table 2).

The high probability of occurrence of the reaction via the direct ionization channel for SF_6 followed by dissociation into SF_5^+ exceeds the probability of the DI channel. This apparently gives the experimental value of AE for the SF_5^+ ion, which is approximately equal to the ionization potential of the SF_6 molecule.

SF_4^+ ion. The difference between the measured values of AE attains 0.5 and 1.2 eV (see Table 2). The values of $E_{AP}[(SF_4^+ - 2F)/SF_6]$ calculated by methods 1 and 2 are smaller by 1.42 and 1.17 eV, respectively, than the experimental value from [1]. The formation of an excited F_2 molecule increases these values of AE by approximately 0.5 eV, and the difference from the measured value of AE decreases. The energies of electron excitation of this ion are quite high and amount to 3.17 eV (A and B levels) and 3.90 eV (C and D levels) [37].

SF_3^+ ion. The AE of this ion measured in [7] is in good agreement with the results obtained in [1] (see Table 2). The values of AE measured in [3, 4, 6, 8, 9] exceed the values of AE given in [1] from 0.7 to 2.8 eV. The values of $E_{AP}[(SF_3^+ - 3F)/SF_6]$ calculated by methods 1 and 2 are smaller by 1.23 and 0.9 eV, respectively, than the experimental value from [1], which resembles the difference in the case of the SF_4^+ ion. The formation of the F_2^* molecule also increases the AE by ~0.5 eV.

SF_2^+ ion. The values of AE for this ion measured in [1, 3, 4, 8] are in good agreement with one another (see Table 2). The detachment of four fluorine atoms leads to an increase in the excess of experimental values of AE over the theoretical values by 5.89 eV (method 1) and by 5.45 eV (method 2). The electron excitation energies for this ion amount to (in electron-volts) 5.32 (A level), 6.12 (B, C), 8.22 (D), and 9.22 (E) [37]. The values of AE for the channel of formation of $2F_2^*$ calculated using methods 1 and 2 are only higher by ~1 eV and are 22.09 and 22.51 eV, respectively. Thus, either the A level of the SF_2^+ ion or two fluorine molecules can be excited.

SF$^+$ ion. The value of E_{AP}(SF$^+$) for this ion from [1] is in good agreement with the results obtained in [8], but is smaller than the results obtained in [3, 4] (see Table 2). The excess of the measured values of AE [1] over the values calculated by methods 1 and 2 for the channel SF$^+$−5F are 5.7 and 5.18 eV, which resembles the difference for the SF$_2^+$ ion. The energies of excitation of electron levels for ions exceed the energies for neutral fragments SF$_k$. For example, the energies of the levels of the SF$^+$ ion apparently slightly exceed the values 3.07 and 3.14 eV for the $A^2\Pi_{3/2}$ and $A^2\Pi_{1/2}$ levels of the SF molecule [24]. The formation of two F$_2$ molecules excited via the SF$^+$−F−2F$_2^*$ channel increases the AE to values of 25.72 and 26.22 eV.

S$^+$ ion. The AE of this ion measured in [1], which is associated with the detachment of all 6 fluorine atoms, is lower by 0.9 eV than the energy borrowed from [4]. The excess of the values of AE measured in [1] over the values calculated using methods 1 and 2 for this channel is 7.91 and 7.4 eV. The formation of three F$_2$ molecules excited via the channel S$^+$−3F$_2^*$ reduces this difference to 6.44 and 5.96 eV. These values are lower than the excitation energy (9.9 eV) of the subvalent $3s$ subshell of the S$^+$ ion, but are higher than the energies (from 1.84 to 3.05 eV) of metastable terms $2D^0$ and $2P^0$ of the $3p^3$ configuration of the ground state of S$^+$ [24] (see Table 1).

It should be noted that the energies of ionization of valence orbitals in the configuration of the ground state of SF$_6$,

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

which are given in [15], are close to the thresholds of the processes leading to the formation of the corresponding fragments SF$_k^+$. For example, the ionization of the outer orbital $1t_{1g}$ (energies from 15.29 to 16.0 eV) leads to the emergence of SF$_5^+$; the ionization of the $2e_g$, $3e_g$, and t_{2u} orbitals (18.0−19.1 eV) leads to the formation of the SF$_4^+$ ion; the ionization of the $1t_{2g}$ orbital (19.0−20.3 eV) leads to the formation of the SF$_3^+$ ion, and the ionization of the a_1 orbital (26.0−26.8 eV) leads to the formation of the SF$_2^+$ ion, while for energies 31.0 and 31.3 eV, this leads to the formation of SF$^+$, and for 37.0 and 37.3 eV, the S$^+$ ion appears. The ionization of the $2e_g$ orbital (energies from 39.3 to 40.6 eV) leads to the emergence of double ion fragments, while the ionization of the $3t_u$ orbital (above 41.2 eV) leads to the appearance of a pair of positive ions SF$_k^+$ and F$^+$ or F$_2^+$. The ionization of these orbitals by an electron impact can apparently be

also an effective mechanism of DI of the SF$_6$ molecule.

CONCLUSIONS

We have analyzed theoretically the appearance energies of positive ion fragments under dissociative ionization of the sulfur hexafluoride molecule by electron impact on the basis of computations using GAMESS program complex.

The behavior of the theoretical and experimental appearance energies for SF$_k^+$ ion fragments as functions of the number of remaining fluorine atoms is qualitatively the same. The excess of experimental appearance energies over theoretical values can be explained by effective excitation of high-energy regions of repulsive autoionizing electronic states of the electron-excited SF$_6$ molecule. Such a mechanism of dissociative ionization may lead to excited states of the final atomic and molecular reaction products that may have substantial kinetic energies.

A more accurate interpretation of the ion fragment appearance energy necessitates the determination of the characteristics of final products, corresponding to various channels of the process (kinetic energy as well as excited and charge states).

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