

# Dissociation of SF<sub>6</sub>, CF<sub>4</sub>, and SiF<sub>4</sub> by Electron Impact

By Vernon H. Dibeler and Fred L. Mohler

The dissociation by electron-impact of SF<sub>6</sub>, CF<sub>4</sub>, and SiF<sub>4</sub> has been studied with a consolidated mass spectrometer. Data are also given on the appearance potentials of various ions in the mass spectra and measurements on the isotope abundance of sulfur, carbon, and silicon. The observed appearance potentials of the F<sup>+</sup> ion in SF<sub>6</sub> and CF<sub>4</sub>, and the C<sup>+</sup> ion in CF<sub>4</sub> were found to be lower than the calculated value assuming formation of a positive atom ion and a free electron, but nearly equal to the calculated value assuming the formation of a positive atom ion and a negative fluorine ion. The large relative abundance of the SF<sub>4</sub><sup>++</sup> ion in SF<sub>6</sub> and the CF<sub>2</sub><sup>++</sup> ion in CF<sub>4</sub> is taken to indicate the formation of these ions by removal of two F<sup>-</sup> ions in the former and possibly an F<sup>-</sup> ion and a free electron in the latter case.

## I. Introduction

The results reported in this paper are a part of a general study of the dissociation of volatile fluoro compounds by electron impact. Many of these compounds have been useful in isotope abundance studies of a number of the elements because of their relatively high vapor pressure and the mono-isotopic character of fluorine. Apparently very little has been published, however, concerning the dissociation of such molecules by electron impact except to note in the isotope studies that dissociation, rather than formation of the molecular ion, is the more probable process. Kusch, Hustrulid, and Tate, [1],<sup>1</sup> and Baker and Tate [2] have shown that this is a property shared with the chlorides of phosphorous, arsenic, and antimony, as well as some halogen derivatives of methane namely, CCl<sub>4</sub>, CHBrF<sub>2</sub>, and CCl<sub>2</sub>F<sub>2</sub>. More recently, White and Cameron [3] have reported the critical potentials of various ions in the mass spectrum of UF<sub>6</sub>. No value was listed for the UF<sub>6</sub><sup>+</sup> ion, presumably because of its very low intensity. No information was given as to the relative abundance of the various dissociated ions. In view of considerable interest in these compounds, therefore, we wish to report in detail the dissociation patterns for several fluorocompounds as well as the appearance potentials of various ions in the mass spectra. Data are also given on the isotope abundance of sulfur, carbon,

and silicon for purposes of comparison with value previously obtained for these elements using other types of mass spectrometers and other compounds.

## II. Experimental Procedure

Pertinent details of the Consolidated mass spectrometer and the methods used to obtain the reported data have been described in detail in previous reports [4, 5]. The voltage scale of the appearance potential measurements was corrected using the observed value of the argon A<sup>+</sup> ion compared to the spectroscopic value [6]. The mass spectra were obtained at ionizing electron energies of 50, 70, and 100 volts. The most abundant ion in each 50-volt spectrum is assigned a value of 100 percent. The other ions are evaluated according to their abundance relative to the most abundant ion. The isotope abundance measurements were made at several different values of ion accelerating voltage and of electron energy and current. Whenever possible, the ratios were checked using different ions in the same mass spectrum. The fact that no significant variation in the isotope abundance ratios was observed under these conditions was assumed to indicate minimum discrimination in the ion source.

The SF<sub>6</sub> was obtained from the high voltage laboratory of the Massachusetts Institute of Technology and was a portion of a sample submitted to the Temperature Measurements Section of the Bureau for test purposes. Mass spectro-

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

metric analysis indicated an approximate purity of 99 percent with small amounts of fluorocarbons as impurities. It was used without further purification. The  $\text{CF}_4$  was obtained from the Jackson laboratory, E. I. du Pont de Nemours Co., and used without further purification. Mass spectrometric analysis showed a total impurity of about 2 percent, principally  $\text{CClF}_3$ ,  $\text{N}_2$ , and  $\text{CO}_2$ . Several samples of  $\text{SiF}_4$  were prepared by Howard W. Bond<sup>2</sup> by reacting  $\text{H}_2\text{SO}_4$  and  $\text{CaF}_2$  in the presence of  $\text{SiO}_2$  from various sources. These samples were also used without further purification. The mass spectrometer indicated a purity  $>99$  percent. The principal impurity was  $\text{CO}_2$ .

### III. Results and Discussion

*Sulfur hexafluoride.*—Table 1 shows the mass spectrum of  $\text{SF}_6$  at three different ionizing voltages. No correction has been made in this or following mass spectrum tables for the contribution of the ion accelerating field to the electron energy. No  $\text{SF}_6^+$  ion was observed. Its abundance is estimated to be less than 2/10,000 of the abundance of the  $\text{SF}_5^+$  ion. The most probable dissociation process is loss of one fluorine atom from the molecular ion. In the formation of ions requiring further dissociation, however, the subsequent loss of three fluorine atoms from the molecular ion is more probable than the loss of 2 atoms. For example, the abundance of the  $\text{SF}_3^+$  ion is greater than that of the  $\text{SF}_4^+$  ion, and the  $\text{SF}^+$  ion is more abundant than the  $\text{SF}_2^+$  ion. The doubly charged ions  $\text{S}^{++}$ ,  $\text{SF}^{++}$ ,  $\text{SF}_2^{++}$ ,  $\text{SF}_3^{++}$ , and  $\text{SF}_4^{++}$  were observed. The ions  $\text{F}^{++}$ ,  $\text{SF}_5^{++}$ , and  $\text{SF}_6^{++}$  were not found and are estimated to be less than 0.02 percent of the  $\text{SF}_5^+$  peak. It is of interest that for 100-volt electrons, the abundance of the  $\text{SF}_2^{++}$  ion and  $\text{SF}_4^{++}$  ion is greater than the abundance of the corresponding singly charged ions. The peak at  $m/e=91.8$  is a metastable ion that has undergone dissociation after traversing the ion accelerating field [7]. It can be ascribed to the transition



If  $m_a$  is the apparent mass,  $m_i$  and  $m_f$ , the initial and final masses, respectively,  $m_a = (m_f)^2/m_i = (108)^2/127 = 91.8$ .

<sup>2</sup> Now at the National Institute of Health, Bethesda, Maryland.

TABLE 1. Mass spectrum of  $\text{SF}_6$  for 50, 70, and 100-volt electrons

$m/e$	Ion	Relative intensities		
		50 volts	70 volts	100 volts
16	$\text{S}^{++}$	0.03	0.06	0.09
19	$\text{F}^+$	3.37	5.63	9.11
25.5	$\text{SF}^{++}$	-----	0.76	1.97
32	$\text{S}^+$	5.60	9.96	13.5
33	$\text{S}^+$	0.06	0.09	0.11
34	$\text{S}^+$	.27	.47	.60
35	$\text{SF}_2^{++}$	1.36	6.80	13.3
35.5	$\text{SF}_3^{++}$	-----	0.10	0.10
36	$\text{SF}_2^{++}$	0.07	.33	.62
44.5	$\text{SF}_3^{++}$	0.38	1.26	2.17
45.5	$\text{SF}_3^{++}$	-----	0.07	0.11
51	$\text{SF}^+$	8.66	11.0	11.6
52	$\text{SF}^+$	0.07	0.09	0.11
53	$\text{SF}^+$	.40	.51	.64
54	$\text{SF}_2^{++}$	4.05	11.0	17.6
54.5	$\text{SF}_3^{++}$	-----	0.09	0.11
55	$\text{SF}_4^{++}$	0.23	.54	.78
70	$\text{SF}_2^+$	5.74	6.39	6.46
71	$\text{SF}_2^+$	0.04	0.07	0.09
72	$\text{SF}_2^+$	.27	.30	.27
89	$\text{SF}_3^+$	27.6	33.5	35.7
90	$\text{SF}_3^+$	0.20	0.26	0.24
91	$\text{SF}_3^+$	1.22	1.48	1.56
91.8	$\text{SF}_5^+ \rightarrow \text{SF}_4^+ + \text{F}$	0.21	0.26	0.24
108	$\text{SF}_4^+$	8.98	10.8	11.5
109	$\text{SF}_4^+$	0.07	0.11	0.10
110	$\text{SF}_4^+$	.41	.47	.51
127	$\text{SF}_5^+$	100.	113	117
128	$\text{SF}_5^+$	0.92	1.14	1.15
129	$\text{SF}_5^+$	4.30	4.89	4.87
131	$\text{SF}_5^+$	0.04	0.04	0.04

Table 2 lists the appearance potentials of various ions in the mass spectrum of  $\text{SF}_6$ . A complete analysis of the appearance potential data is not possible because of the lack of necessary spectroscopic or thermochemical data. However, from the relation

$$D(\text{SF}_6) = Q(\text{SF}_6) + 3D(\text{F}_2) + L(\text{S}),$$

where  $Q(\text{SF}_6)$  is the energy of formation of  $\text{SF}_6$ ,  $D(\text{F}_2)$  is the dissociation energy of molecular fluorine,  $L(\text{S})$  is the heat of sublimation of sulfur, and the thermochemical data of Bichowsky and Roscini [8] the energy of dissociation of the process  $\text{SF}_6 \rightarrow \text{S} + 6\text{F}$ , is calculated to be 516 kcal/mole or 22.4 electron volts. It follows that the minimum energy required to produce an  $\text{S}^+$  ion and a free electron will be  $D(\text{SF}_6)$  plus the ionization poten-

tial (10.3 volts) [6] of sulfur ( $22.4 + 10.3 = 32.7$  volts). The observed appearance potential of the  $S^+$  ion is 37.3 volts. This is 4.6 volts in excess of the calculated minimum energy required to produce an  $S^+$  ion and a free electron. It is concluded that the production of  $S^+$  gives considerable kinetic energy to the seven dissociation fragments; namely 4.6 volts if a free electron is removed. If it is assumed that one of the fluorine atoms combines with the electron to form an  $F^-$  ion in the ionization process, the excess energy is increased to 8.6 volts by the value of the electron affinity (4.0 volts) [9] of fluorine. One could also assume that one or two pairs of fluorine atoms combined in the ionization process to form molecular fluorine with an energy of 2.7 volts per molecule of  $F_2$ , but this seems to be an improbable process in spontaneous dissociation.

TABLE 2. Appearance potentials of various ions in the mass spectrum of  $SF_6$

<i>m/e</i>	Ion	Appearance potential
		<i>e</i>
19	F <sup>+</sup>	35.8±1
32	S <sup>+</sup>	37.3±1
35	SF <sub>2</sub> <sup>++</sup>	46.5±0.5
51	SF <sup>+</sup>	31.3±.3
54	SF <sub>2</sub> <sup>++</sup>	40.6±.5
70	SF <sub>2</sub> <sup>+</sup>	26.8±.3
89	SF <sub>2</sub> <sup>+</sup>	20.1±.3
91,8	SF <sub>3</sub> <sup>+</sup> SF <sub>4</sub> <sup>+</sup> +F	20 ±1
108	SF <sub>4</sub> <sup>+</sup>	18.9±0.2
127	SF <sub>5</sub> <sup>+</sup>	15.9±.2

An  $F^+$  ion could conceivably be found in any process in which  $SF_6$  is dissociated. However the appearance potential of  $F^+$  (35.8 volts) is higher than the appearance potential of any of the polyatomic singly charged ions. This suggests that  $F^+$  occurs from complete dissociation like the  $S^+$  ion. From the same dissociation process, the minimum energy required to produce an  $F^+$  ion and a free electron is  $22.4 + 18.6^6 = 41.0$  volts. The observed appearance potential of  $F^+$  (35.8 volts) is insufficient to produce  $F^+$  and a free electron. The minimum energy required to produce an  $F^+$  and an  $F^-$  from  $SF_6$ , however, is 37.0 volts. The observed value (35.8 volts) is close enough to leave little doubt that this is the actual process involved.

Table 3 gives the observed isotope abundance of sulfur. Also given in table 3 are the results re-

ported by Nier [10] from a study of  $SO_2$  using a specially designed mass spectrometer. The disagreement of the  $S^{36}$  abundance is greater than the estimated experimental error whether calculated from the  $SF_5^+$  ion, the  $SF_4^+$  ion or the  $SF_2^+$  ion. Other ions were not usable because of low intensity or interference by the metastable ion or doubly charged ions. From the isotopic masses listed by Pollard [11] (assuming same packing fraction for  $S^{34}$  and  $S^{36}$ ) and the conversion factor 1.000275, the authors' values give a chemical weight of 32.065. The accepted value by chemical methods is 32.066 [12].

*Carbon Tetrafluoride.*—Table 4 shows the mass spectrum of  $CF_4$  at several energy values of the ionizing electrons. The most probable dissociation process is again the loss of one fluorine atom to produce the  $CF_3^+$  ion. The abundance of the  $CF_4^+$  ion is estimated to be less than 1/1,000 relative to the  $CF_3^+$  ion. The relatively large abundance of the  $CF_2^+$  ion is unusual by analogy with other halogenated molecules (see, for example, [1] and [2], and tables 1 and 7). Doubly charged

TABLE 3. Isotope abundance of sulfur

	<i>m/e</i>			
	32	33	34	36
Mean.....	95.03	0.76	4.17	0.035
Average deviation.....	±0.02	±.01	±0.01	±.003
Nier [10].....	95.1	.74	4.2	.016

TABLE 4. Mass spectra of  $CF_4$  for 50, 70 and 100-volt electrons and  $CH_4$  for 50-volt electrons

Carbon tetrafluoride					Methane	
<i>m/e</i>	Ion	Relative intensities at—			Ion	Relative intensities at 50 volts
		50 volts	70 volts	100 volts		
12	C <sup>+</sup>	6.72	10.1	11.0	C <sup>+</sup>	2.40
13	C <sup>+</sup>	0.08	0.11	0.12		
15.5	CF <sup>++</sup>	-----	.06	.15		
19	F <sup>+</sup>	3.09	5.95	8.14	H <sup>+</sup>	3.21
25	CF <sub>2</sub> <sup>++</sup>	1.51	5.93	11.0		
25.5	CF <sub>2</sub> <sup>++</sup>	-----	0.06	0.13		
31	CF <sup>+</sup>	3.67	4.85	6.17	CH <sup>+</sup>	7.91
34.5	CF <sub>3</sub> <sup>++</sup>	-----	2.04	3.92		
50	CF <sub>2</sub> <sup>+</sup>	12.4	15.4	15.6	CH <sub>2</sub> <sup>+</sup>	15.9
51	CF <sub>2</sub> <sup>+</sup>	0.13	0.17	0.17		
69	CF <sub>3</sub> <sup>+</sup>	100	120	133	CH <sub>3</sub> <sup>+</sup>	84.6
70	CF <sub>3</sub> <sup>+</sup>	1.16	1.31	1.46	CH <sub>4</sub> <sup>+</sup>	100

ions  $\text{CF}^{++}$ ,  $\text{CF}_2^{++}$ , and  $\text{CF}_3^{++}$  were observed. No metastable ions were observed. The mass spectrum of methane is also included in table 4 for comparison. No doubly charged or metastable ions are observed in methane.

Table 5 lists the appearance potentials of various ions in the mass spectrum of  $\text{CF}_4$ . A complete analysis of the appearance potential data is impossible due to the lack of sufficient thermochemical or spectroscopic data. From Bichowsky and Rossini [8] the energy of dissociation into atoms  $\text{CF}_4 \rightarrow \text{C} + 4\text{F}$  is calculated to be 458 kcal/mole, or 19.9 electron volts. The minimum energy required to produce a  $\text{C}^+$  ion and a free electron is  $19.9 + 11.2^6 = 31.1$  volts. The minimum energy to give  $\text{F}^+$  and a free electron with complete dissociation is  $19.9 + 18.6^6 = 38.5$  volts. The observed appearance potentials of both ions are less than these values, and it must be assumed that in both cases  $\text{F}^-$  ions are formed in the ionization process and not free electrons. The process  $\text{CF}_4 \rightarrow \text{C}^+ + \text{F}^- + 3\text{F}$  requires  $31.1 - 4.0 = 27.1$  volts compared to the observed appearance potential of  $27.5 \pm 1$  volts. The process  $\text{CF}_4 \rightarrow \text{C} + \text{F}^+ + \text{F}^- + 2\text{F}$  requires  $38.5 - 4.0 = 34.5$  volts compared to the observed appearance potential of  $35.5 \pm 1$  volts.

TABLE 5. Appearance potentials of various ions in the mass spectrum of  $\text{CF}_4$

m/e	Ion	Appearance potential
		$\nu$
12	$\text{C}^+$	$27.5 \pm 1.$
19	$\text{F}^+$	$35.5 \pm 1.$
25	$\text{CF}_2^{++}$	$44.3 \pm 0.5$
31	$\text{CF}^+$	$29.8 \pm .3$
34.5	$\text{CF}_3^{++}$	$43.8 \pm .5$
50	$\text{CF}_2^+$	$21.8 \pm .3$
69	$\text{CF}_3^+$	$15.9 \pm .2$

The  $\text{C}^{12}/\text{C}^{13}$  ratio as measured from the  $\text{CF}_3^+$  and the  $\text{CF}_2^+$  ions was  $89.9 \pm 1.7$ , compared with the value of  $90 \pm 2$  reported by Nier and Gulbranson [13], using carbon dioxide from the air.

*Silicon Tetrafluoride.*—Table 6 shows the mass spectrum of  $\text{SiF}_4$  for 50, 70, and 100-volt electrons. The removal of one fluorine atom to form the  $\text{SiF}_3^+$  ion is again the most probable process. In contrast to  $\text{SF}_6$  and  $\text{CF}_4$ , however, the molecular ion has an appreciable abundance. Further dissociation to  $\text{SiF}_2^+$ ,  $\text{SiF}^+$ , and  $\text{Si}^+$  follows the general pattern of halogenated molecules, i. e., the

abundance of ions with an odd number of halogen atoms is greater than the abundance of those with an even number. The doubly charged ions  $\text{SiF}^{++}$ ,  $\text{SiF}_2^{++}$ , and  $\text{SiF}_3^{++}$  were observed. The  $\text{SiF}_2^{++}$  ion becomes more abundant than the singly charged ion above 50 volts. No metastable ions are observed.

TABLE 6. Mass spectrum of  $\text{SiF}_4$  for 50, 70 and 100-volt electrons

m/e	Ion	Relative intensities at—		
		50 volts	70 volts	100 volts
19	$\text{F}^+$	1.18	2.26	3.10
23.5	$\text{SiF}^{++}$	0.10	0.87	1.82
24	$\text{SiF}^{++}$	-----	.05	0.09
24.5	$\text{SiF}^{++}$	-----	.02	.05
28	$\text{Si}^+$	2.89	4.90	6.27
29	$\text{Si}^+$	0.18	0.28	0.38
30	$\text{Si}^+$	.11	.18	.21
33	$\text{SiF}_2^{++}$	1.35	4.56	7.48
33.5	$\text{SiF}_2^{++}$	0.08	0.23	0.38
34	$\text{SiF}_2^{++}$	.06	.16	.25
42.5	$\text{SiF}_3^{++}$	.46	1.37	2.13
43	$\text{SiF}_3^{++}$	.06	0.10	0.16
43.5	$\text{SiF}_3^{++}$	-----	.04	.05
47	$\text{SiF}^+$	3.57	4.67	4.22
48	$\text{SiF}^+$	0.20	0.24	0.23
49	$\text{SiF}^+$	.15	.17	.17
66	$\text{SiF}_2^+$	.66	.79	.66
67	$\text{SiF}_2^+$	.06	.07	.07
68	$\text{SiF}_2^+$	.03	.04	.03
85	$\text{SiF}_3^+$	100.	122.	133.
86	$\text{SiF}_3^+$	5.01	6.10	6.86
87	$\text{SiF}_3^+$	3.34	4.08	4.53
104	$\text{SiF}_4^+$	1.79	2.14	2.39
105	$\text{SiF}_4^+$	0.10	0.12	0.12
106	$\text{SiF}_4^+$	.06	.07	.08

The appearance potentials of several ions in the mass spectrum of  $\text{SiF}_4$  are given in table 7.

The relative abundance of the isotopes of silicon have recently been measured by several investigators. The results of Ney and McQueen [14], Inghram [15], and Williams and Yuster [16], together with the authors' values are given in table 8. The agreement between the present work and the previously reported values is within the experimental uncertainty. The chemical weight calculated from the isotopic masses listed by Polard [11] is 28.09 compared to the accepted chemical value of 28.06 [12].

TABLE 7. Appearance potentials of several ions in the mass spectrum of  $\text{SiF}_4$

$m/e$	Ion	Appearance potential
66	$\text{SiF}_2^+$	$v$
85	$\text{SiF}_3^+$	$27.5 \pm 0.5$
104	$\text{SiF}_4^+$	$16.1 \pm .2$

TABLE 8. Isotope abundance of silicon

	$m/e$		
	28	29	30
Mean.....	92.32	4.58	3.10
Average deviation.....	$\pm 0.03$	$\pm 0.03$	$\pm 0.02$
Ney and McQueen [14].....	92.24	4.69	3.07
Inghram [15].....	$92.28 \pm 0.08$	$4.67 \pm 0.05$	$3.05 \pm 0.03$
Williams and Yuster [16].....	92.27	4.68	3.05

#### IV. Conclusions

In a few cases in which appearance potentials could be computed from thermochemical and spectroscopic data, it was found that the observed appearance potential was considerably less than the computed potential required to give an atom ion and a free electron, but nearly equal to the calculated potential required to give a positive atom ion and a negative fluorine ion. This was observed for  $\text{F}^+$  ion from  $\text{SF}_6$  and  $\text{CF}_4$ , and for the  $\text{C}^+$  ion from  $\text{CF}_4$ . The mass spectra support the hypothesis that for these molecules, removal of a  $\text{F}^-$  ion rather than an electron is the most probable process in production of the positive ions. This would also explain the absence of the parent ions  $\text{SF}_6^+$  and  $\text{CF}_4^+$ . In the case of  $\text{SF}_6$ , the heaviest doubly charged ion is  $\text{SF}_4^{++}$ , which indicates that two  $\text{F}^-$  ions are removed to form the double positive charge. The fact that  $\text{SF}_4^{++}$  is more abundant than  $\text{SF}_4^+$  at 100 volts is not surprising if this is the mechanism of ionization. In the case of  $\text{CF}_4$ , a  $\text{CF}_3^{++}$  ion is observed although the  $\text{CF}_2^{++}$  ion is more abundant. This indicates that it is possible to ionize  $\text{CF}_4$  by removing either two  $\text{F}^+$  ions or one  $\text{F}^-$  ion and a free electron. The ap-

pearance potentials for these two processes are nearly the same.

In the case of  $\text{SiF}_4$ , the molecular ion is observed although its abundance is less than 2 percent of the  $\text{SiF}_3^+$  ion. The appearance potential of the former is actually somewhat greater than the latter, which again indicates that the  $\text{SiF}_3^+$  ion is formed by removal of an  $\text{F}^-$  ion from  $\text{SiF}_4$ . Consider the other possibility; i. e., the  $\text{SiF}_3^+$  ion arises from the removal of a free electron and a fluorine atom. This is the same as removing a fluorine atom from the  $\text{SiF}_4^+$  ion, and consequently must require work. Therefore, the appearance potential of  $\text{SiF}_3^+$  must be higher than  $\text{SiF}_4^+$  by that amount of work unless a negative ion is formed in the process.

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