

**APPEARANCE POTENTIALS OF IONS PRODUCED BY
ELECTRON-IMPACT INDUCED DISSOCIATIVE IONIZATION
OF SF₆, SF₄, SF₅Cl, S₂F₁₀, SO₂, SO₂F₂, SOF₂, AND SOF₄**

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INTRODUCTION

The identification of S₂F₁₀, a highly toxic compound,¹ in SF₆ that has been subjected to electrical discharges, including negative corona discharges,^{2,3} sparks,⁴ and arcs,⁵ has raised issues of safety and proper handling of SF₆ removed from electrical equipment, and motivates the need for trace detection of S₂F₁₀ in SF₆.⁶ A reliable measurement protocol for trace detection of S₂F₁₀ may be applied to: 1) develop safe handling procedures for SF₆ gas removed from operating machinery, 2) ensure compliance with regulatory agencies, 3) monitor the purity of SF₆ supplied both by manufacture and reprocessing, and 4) replace animal toxicity tests of commercial SF₆.

Conventional mass spectrometry is of limited value in detection of trace levels of S₂F₁₀ in SF₆ due to the similarity in their mass spectra.⁷ Two methods have shown detection sensitivity down to the peak exposure limit of 10 parts in 10⁹ by volume (ppb): a technique employing cryogenic-enrichment⁴ of S₂F₁₀ and an indirect method that relies on gas-chromatographic separation followed by chemical conversion of S₂F₁₀ to SOF₂.⁸ Both methods have their advantages and limitations. The first is time consuming and laborious, while the second has a reduced sensitivity to S₂F₁₀ when SOF₂ is present at high concentrations.⁹ Disulfur decafluoride (S₂F₁₀) normally occurs in concert with other discharge by-products, e.g., SOF₂, SOF₄, and SO₂.

The present study was undertaken to evaluate non-conventional mass spectroscopy, i.e., mass spectroscopy at electron-impact energies well below the standard of 70 eV, as a possible method to increase sensitivity of S₂F₁₀ detection. This method has been successfully used to detect SF₄ in SF₆.¹⁰ An additional purpose of this work is to obtain appearance potential data for other compounds that may be present in SF₆ that has been exposed to electrical discharge.

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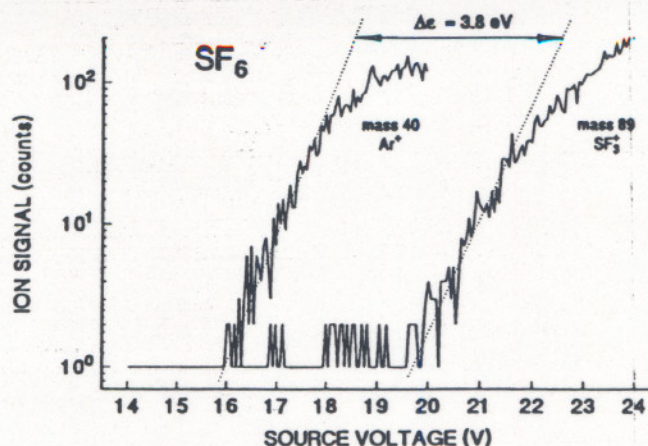


Figure 1. The observed ionization efficiency curves for Ar^+ and SF_3^+ . The semi-log plots of the curves are fit by linear functions and the difference in their x-axis intercepts, $\Delta\epsilon$. The appearance potential of SF_3^+ determined by this method is $15.76 + 3.8 \text{ eV}$ or 19.6 eV , in good agreement with earlier reported values (see Table 1 below).

EXPERIMENTAL METHOD

Near the ionization threshold, the ion signal observed using a conventional quadrupole mass spectrometer has an exponential dependence on the accelerating potential. This is due primarily to the energy distribution of the electrons emitted from the filament.¹¹ Thus a semi-log plot of the ion signal near threshold may be fit by a straight line whose intercept with the baseline noise level is, to a good approximation, the appearance potential. This technique provides a means of determining ion appearance potentials using a commercially available quadrupole mass spectrometer. The electron impact energy may be varied by changing the accelerating potential between the filament and first lens element in the quadrupole ionizer while the ion of interest is detected using single-ion monitoring.

For the results presented here, the electron energy is determined by way of reference to the spectroscopic ionization potential of argon (15.76 eV).¹² The sample gas is admixed with argon gas and the ionization efficiency curves are recorded sequentially. The results of such a measurement for SF_3^+ produced by dissociative ionization of SF_6 are presented in Figure 1.

RESULTS

Appearance potential measurements for the compounds included in this study are summarized and compared with other similar measurements in Tables 1, 2, and 3 below. Overall, agreement with earlier published results is good, i.e., in all cases, the measured appearance potential lies within the combined measurement uncertainties. The stated measurement uncertainties are influenced by the quality of the linear fit, the difference in slopes between the reference and measured ions, and the baseline noise level. For minority ions, where the ion signal is comparable to the background noise, the measurement uncertainties for this method can be large (greater than $\pm 1 \text{ eV}$). Additionally, as noted in the tables, many of the measured ionization efficiency curves

Table 1. Appearance potential measurements for SF₆, SF₄, and SF₅Cl.

Compound	Ion	Appearance Potential (eV)	
		This Work	Previous Results
SF ₆	SF ₅ ⁺	15.6±0.2	15.9±0.2 ^a , 16.2±0.2 ^b , 15.50±0.10 ^c
	SF ₄ ⁺	18.7±0.5	18.9±0.2 ^a , 19.6±1.0 ^b , 18.44±0.10 ^c
	SF ₃ ⁺	19.6±0.5	20.1±0.3 ^a , 19.6±0.5 ^b , 20.0±0.5 ^c
	SF ₂ ⁺	26±3	26.8±0.3 ^a , 27.0±0.3 ^b , 27.5±0.5 ^c
	SF ⁺	30±2	31.3±0.3 ^a , 37.6±3.0 ^b , 30.5±0.5 ^c
	S ⁺	39±5 [†]	37.3±1.0 ^a , 37.5±1.0 ^b
	F ⁺	36±5 [†]	35.8±1.0 ^a
	SF ₄ ⁺⁺	39±4	40.6±0.5 ^a
SF ₄	SF ₄ ⁺	12.2±0.5	12.08±0.10 ^c , 11.90 ^d
	SF ₃ ⁺	12±1	12.63±0.10 ^c , 12.4 ^d
	SF ₂ ⁺	18±2 [†]	17.4±0.5 ^c , 16.90 ^d
	SF ⁺	22±2 [†]	
	S ⁺	30±5 [†]	
	F ⁺	33±5 [†]	
	SF ₂ ⁺⁺	39±4 [†]	
SF ₅ Cl	SF ₅ ⁺	12.5±0.7	12.32 ^c
	SF ₄ Cl ⁺	14.5±0.5	14.76 ^c
	SF ₄ ⁺	16±1	15.87 ^c
	SF ₃ ⁺	18±4	16.2 ^c
	SF ₂ ⁺	24±3	
	SF ⁺	29±2	
	S ⁺	38±3	

[†] Observed ionization efficiency curve showed an apparent onset below the value indicated.

^a Appearance potentials determined by electron impact, Reference 14.

^b Appearance potentials determined by electron impact, Reference 15.

^c Appearance potentials determined by electron impact, Reference 16.

^d Appearance potentials from photoelectron-photoion-coincidence measurements, Reference 13.

^e Appearance potentials from photoion spectrum, Reference 17.

showed an apparent onset for ion production at low energies, which tended to obscure the threshold. Two possible explanations are offered for this behavior. First, the hot filament in the ionizer may introduce unwanted thermochemical reactions that produce species with ionization potentials lower than that of the sample gas. The mass spectra of SOF₂ shown in Figure 2, for example, show mass peaks corresponding to the presence of SO₂ and provide clear evidence of chemical conversion in the ionizer. Second, polar dissociation may produce positive ions at impact energies below dissociative ionization. This process is known to produce SF₃⁺ from SF₄ at an excitation energy of 9.00 eV,¹³ approximately 3.4 eV below the corresponding ionization appearance potential.

The potential for improved sensitivity to S₂F₁₀ is demonstrated by data presented in Figure 3. With even modest electron energy resolution (the energy resolution for these measurements was approximately 1 eV), SF₃⁺ from SF₆ and S₂F₁₀ may be resolved.

Table 2. Appearance potential measurements for SOF_2 , SO_2F_2 , SOF_4 , and SO_2 .

Compound	Ion	Appearance Potential (eV)	
		This Work	Previous Results
SO_2	SO_2^+	12.0 ± 0.5	12.4 ± 0.1^a , 12.3^b , 12.50^c
	SO^+	$15.0 \pm 0.5^\dagger$	16.2 ± 0.2^a , 15.930 ± 0.005^d
	S^+	$17 \pm 2^\dagger$	17.5 ± 0.2^a , 16.334^d
	O^+	$21 \pm 2^\dagger$	20.6^a
SO_2F_2	SO_2F_2^+	13.3 ± 0.5	13.3 ± 0.1^a , 13.0^c , 13.04 ± 0.01^e
	SO_2F^+	14.9 ± 0.5	15.1 ± 0.2^a
	SOF^+	17.9 ± 1.0	18.6 ± 0.1^a
	SO_2^+	$21 \pm 2^\dagger$	19.9 ± 0.3^a
	SO^+	$25 \pm 3^\dagger$	24.3 ± 0.3^a
	S^+	$33 \pm 3^\dagger$	
SOF_2	SOF_2^+	12.5 ± 0.5	12.25^c , 12.19^f
	SOF^+	13.8 ± 1.0	
	SO^+	$16.0 \pm 1.0^\dagger$	
	S^+	$25 \pm 4^\dagger$	
SOF_4	SOF_4^+	12.7 ± 0.5	
	SOF_3^+	13.0 ± 0.2	
	SF_3^+	17.4 ± 0.5	
	SOF_2^+	$18 \pm 1^\dagger$	
	SF_2^+	$24 \pm 2^\dagger$	
	SOF^+	$20 \pm 2^\dagger$	
	SF^+	$29 \pm 2^\dagger$	
	SO^+	$28 \pm 3^\dagger$	
	S^+	$36 \pm 3^\dagger$	

[†] Observed ionization efficiency curve showed an apparent onset below the value indicated.

^a Electron impact, Reference 18.

^b Vertical ionization potential from photoelectron spectrum, Reference 19.

^c Adiabatic ionization potential from photoelectron spectrum, Reference 20.

^d Appearance potentials from photoelectron-photoion-coincidence measurements, Reference 21.

^e Adiabatic ionization potential from photoelectron spectrum, Reference 22.

^f Adiabatic ionization potential from photoelectron spectrum, Reference 23

These data indicate that use of an electron energy of about 16 eV in the ion source will completely suppress SF_3^+ production from SF_6 .

DISCUSSION AND CONCLUSIONS

The principle ions produced by electron-impact ionization of S_2F_{10} are clearly distinguished from those produced in SF_6 by their appearance potentials. The lower appearance potentials of the larger fragment ions such as SF_5^+ and SF_4^+ from S_2F_{10} is expected from the relatively weak S-S bond strength compared to the S-F bond strength

Table 3. Appearance potential measurements for S_2F_{10} .

Compound	Ion	Appearance Potential (eV)	
		This Work	Previous Results
S_2F_{10}	SF_5^+	13.0 ± 0.2	13.2 ± 0.3^a
	SF_4^+	$12.8 \pm 0.7, 18 \pm 1^\dagger$	
	SF_3^+	12.9 ± 0.2	13.3 ± 0.3^a
	SF_2^+	$20 \pm 2^\dagger$	
	SF^+	$33 \pm 3^\dagger$	

[†] Observed ionization efficiency curve showed an apparent onset below the value indicated.

^a Electron impact Reference 7.

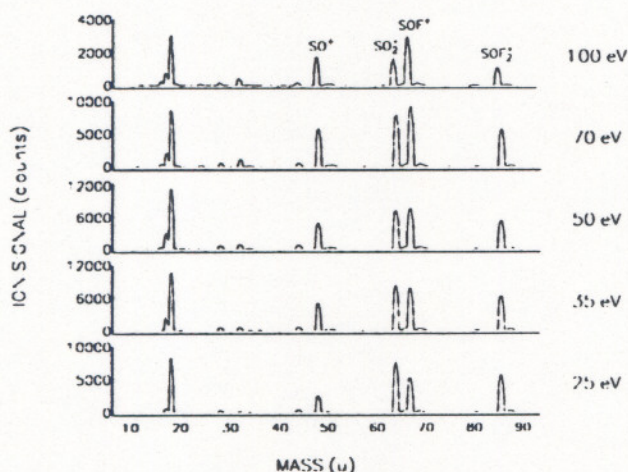


Figure 2. Mass spectra for SOF_2 . The electron impact energy for each spectrum is indicated on the right. Note the presence of a mass peak corresponding to SO_2^+ , a clear indication of the presence of SO_2 . The presence of SO_2 is an artifact that is most likely due to the exposure of SOF_2 to the hot filament in the quadrupole ionizer.

in SF_6 .^{24,25} At the present time there is no explanation for why the appearance potentials of the fragments SF_5^+ , SF_4^+ , and SF_3^+ from S_2F_{10} all have nearly the same values. Although this could be due to contributions from polar dissociation near threshold, there is no evidence from other measurements²⁶ of significant negative-ion formation from S_2F_{10} at electron energies above 13 eV. The results presented here suggest that a judicious choice of electron-impact energy holds promise for improved sensitivity to S_2F_{10} in SF_6 when using a conventional quadrupole mass spectrometer and ionizer with or without a gas chromatograph.

The presence of SO_2 in the mass spectrum for SOF_2 shown above in Figure 2 suggests that thermochemical reactions may be catalyzed on the hot filament in the ionizer. Such reactions may also occur for many of the compounds examined here and may contribute to the low-energy onset for production of positive ions noted above. Polar-dissociation, i.e., electron impact followed by unimolecular dissociation to form

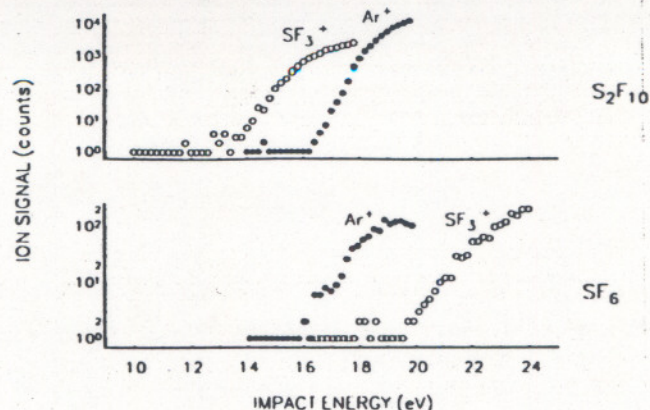


Figure 3. Comparison of the observed ionization efficiency curves for SF_3^+ from S_2F_{10} and SF_6 .

stable positive and negative ions, may also contribute to low-energy production of positive ions.

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DISCUSSION

S. R. HUNTER: Why are there such large uncertainties stated for the appearance potentials of some ion fragments?

J. K. OLTHOFF: As can be seen in Fig. 2, there is evidence that the hot filament in the electron impact source affects the gas in the source region. For the ion fragments for which we have quoted large uncertainties, structure is observed in the ionization efficiency curves, which we attribute to excitation or dissociation occurring on the filament. This structure makes it impossible to get a unique linear fit to the efficiency curve (see Fig. 1) and therefore increases the uncertainties.

J. CASTONGUAY: (1) What detector absolute sensitivity reduction did you observe by lowering the electron energy from 70 to 16 eV? (2) How has lowering the electron energy affected the intensities of the SOF_2 ion fragments present in the mass spectrum of S_2F_{10} ?

J. K. OLTHOFF: Lowering of the electron energy from 70 eV to 16 eV reduces the ion signal by nearly 2 orders of magnitude for S_2F_{10} . We have not yet attempted to adjust the electron impact energies for improved detection of S_2F_{10} by GC/MS. Obviously we must investigate the trade-off between the increased selectivity and the reduced sensitivity inherent in reducing the electron energy.