

LETTER TO THE EDITOR

Electron-energy dependence of the S_2F_{10} mass spectrum

J K Olthoff†, R J Van Brunt† and I Sauers‡

† National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

‡ Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

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Abstract. The positive-ion mass spectrum of S_2F_{10} has been measured as a function of electron-impact energy in the range 20–70 eV using a quadrupole mass spectrometer. Contrary to recent results reported by Farber and co-workers from mass spectrometric analysis of arc-decomposed SF_6 there was no evidence of $S_2F_9^+$ or $S_2F_{10}^+$ ion formation from S_2F_{10} at any energy. The largest ion observed at all electron energies is SF_5^+ . It was found, however, that the appearance potentials for SF_5^+ and SF_3^+ , the two most prominent ions from S_2F_{10} , are significantly lower than the appearance potentials of these same ions from SF_6 . The differences between the mass spectra of S_2F_{10} and SF_6 are delineated and the implications for detection of S_2F_{10} in the presence of SF_6 are discussed.

Evidence was presented in a recent Letter by Farber and co-workers [1] for formation of the ions $S_2F_{10}^+$ and $S_2F_9^+$ from direct electron-impact ionisation of S_2F_{10} at an electron energy of 20 eV in a mass spectrometer. The gas samples used by these authors were prepared by subjecting SF_6 to an electrical discharge in which the S_2F_{10} was presumed to be formed. Other than the appearance of ions at mass-to-charge ratios (m/e) of 254 and 235, which were surmised to be formed from S_2F_{10} , there was no other evidence presented for the presence of S_2F_{10} . No corresponding tests were reported using reference gas samples known to contain S_2F_{10} .

In the present work, mass spectrometric measurements were performed using gas samples known to contain 1500 PPM_v of S_2F_{10} in either Ar or N_2 buffer gas. The gas mixtures were prepared using pure S_2F_{10} as discussed previously [2]. The mass spectra were measured using a differentially pumped RF-quadrupole mass spectrometer with a mass range from $m/e = 2$ to $m/e = 2000$. The instrument was equipped with an electron-impact ioniser which allowed electron energies from 11 to 70 eV to be selected with an estimated energy spread between 1 and 2 eV. The electron energy scale was calibrated by the method established previously [3] using the ionisation potential for Ar of 15.76 eV.

§ Pure S_2F_{10} was synthesised in a high-temperature reactor containing sulphur and fluorine by Dr Darryl DesMarteau, Clemson University, Clemson, SC, USA. The identity of the sample was determined by IR absorption spectroscopy.

Table 1. Percentage relative abundances of ions from SF_6 and S_2F_{10} at 70 eV for $m/e \geq 51$.

Ion	m/e	Relative abundances (%)			
		SF_6		S_2F_{10}	
		a	b	a	c
SF_5^+	127	100	100	100	100
SF_4^+	108	12.4	8.9	3.3	<3.1
SF_3^+	89	30.7	26.3	33.0	36.0
SF_2^+	70	5.2	5.3	10.3	14.0
SF_4^{2+}	54	6.7	7.4	0.4	<3.1
SF^+	51	5.2	7.6	2.6	5.9

^a Present work.

^b Cornu and Massot.

^c Cohen and MacDiarmid.

Examples of mass spectra obtained from SF_6 and S_2F_{10} at 70 eV are shown in figure 1 for $m/e \geq 50$. The corresponding relative abundances of the different ions from these molecules at 70 eV are given in table 1 in comparison with the 'standard' SF_6 mass spectrum [4] and with results published previously by Cohen and MacDiarmid [5] for S_2F_{10} . These abundances are expressed in per cent as obtained by computing areas under the peaks shown in figure 1 and normalising to the peak area for the most abundant ion, namely SF_5^+ at $m/e = 127$. The relative abundances obtained from the present measurements are seen to be in acceptable agreement with those published previously. The differences are undoubtedly due in part to differences in relative-mass discrimination associated with the dif-

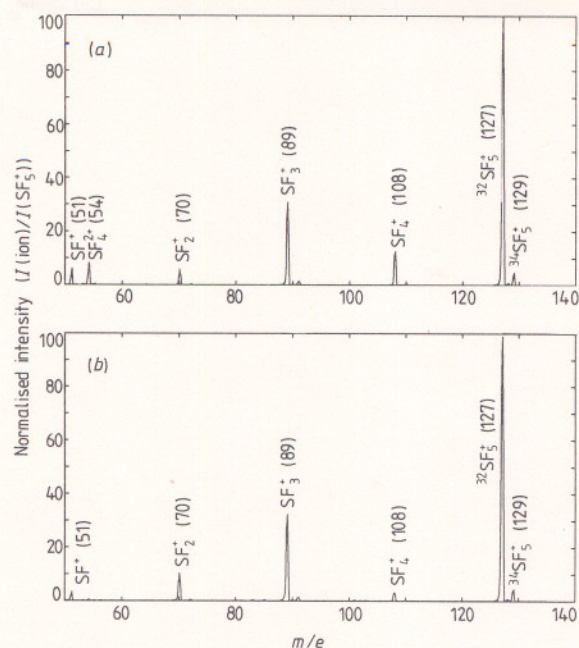


Figure 1. Observed mass spectra of (a) SF_6 and (b) S_2F_{10} at an electron-impact energy of 70 eV.

ferent instruments used. For the quadrupole mass spectrometer used in this work, the relative-mass discrimination depended significantly on the operating conditions which were not always adjusted to minimise discrimination over the mass range of interest. Consistent with previous work [4, 5], no ions from either SF_6 or S_2F_{10} were observed above $m/e = 129$ corresponding to $^{34}\text{SF}_5^+$.

Table 2 shows ratios of relative S_2F_{10} ion fragment intensities to corresponding SF_6 ion fragment intensities, e.g. $I(\text{SF}_3^+, \text{S}_2\text{F}_{10})/I(\text{SF}_3^+, \text{SF}_6)$, where the numerator and denominator are respectively the normalised SF_3^+ peak areas from the S_2F_{10} and SF_6 spectra at the same electron energy. The ratio $I(\text{SF}_5^+, \text{S}_2\text{F}_{10})/I(\text{SF}_5^+, \text{SF}_6)$ is always equal to 1.0 because the SF_5^+ peak is always the largest in both spectra. These ratios were found to be insensitive to relative-mass discrimination associated with different operating conditions for the instrument, and give a quantitative indication of the extent to which the mass spectra for these two molecules differ.

The data shown in figure 1 and tables 1 and 2 indicate that at 70 eV the mass spectra of SF_6 and S_2F_{10}

Table 2. Ratios of relative S_2F_{10} peak intensities to corresponding relative SF_6 peak intensities at different electron-impact energies (20–70 eV).

Ion	m/e	$I(\text{ion}, \text{S}_2\text{F}_{10})/I(\text{ion}, \text{SF}_6)$			
		70 eV	50 eV	35 eV	20 eV
SF_5^+	127	1.0	1.0	1.0	1.0
SF_4^+	108	0.27	0.29	0.28	0.70
SF_3^+	89	1.09	1.12	1.09	57.0
SF_2^+	70	1.99	1.75	2.34	26.0
SF^+	54	0.05	0.05	†	†
SF^+	51	0.50	0.45	1.92	†

† Ion not present for one or both species.

are quite similar. With the possible exception of SF_4^{2+} at $m/e = 54$, all of the significant ion peaks that appear in the SF_6 spectrum also appear in the S_2F_{10} spectrum. However, at lower electron energies, particularly at 20 eV, the mass spectra of these two species exhibit considerable differences. In particular, the relative intensities of the SF_3^+ and SF_2^+ ions in the S_2F_{10} spectrum are seen to be much higher than the corresponding relative intensities of these ions in the SF_6 spectrum at 20 eV. This is due in part to the fact that the appearance potentials of these ions are significantly lower for S_2F_{10} than for SF_6 .

The appearance potentials for the ions SF_5^+ and SF_3^+ from S_2F_{10} were measured by the usual method [3, 6] and found to be 13.2 and 13.3 eV, respectively. The corresponding appearance potential values for these ions from SF_6 were found to be 15.7 and 19.7, respectively, in favourable agreement with values reported previously [7].

There was no evidence for formation of either $\text{S}_2\text{F}_{10}^+$ or S_2F_9^+ at electron energies in the range 11–70 eV and for ion source pressures from 1×10^{-6} Torr to 8×10^{-5} Torr. From a consideration of the measured detection sensitivity, we estimate that the maximum allowable relative abundance, $I(\text{ion})/I(\text{SF}_5^+)$, for the ions at masses 254 and 235 to be about 0.07%. To ensure that ions at these masses could have been observed, the instrument response was checked up to $m/e = 502$ using perfluorotributylamine [8]. The present observations, therefore, do not lend support to the assignment of S_2F_{10} to the observed peaks at $m/e = 254$ and $m/e = 235$ made by Farber and co-workers [1] from their analysis of SF_6 decomposed in an arc discharge. It should be noted that the arc-discharge cell which they used was made of a polymeric material (Teflon). There is evidence from the measurements of Gilbert and co-workers [9] that polymers can significantly degrade when exposed to electrical discharges in SF_6 giving rise to volatile compounds of relatively large mass such as $\text{CF}_3\text{--S}_x\text{--CF}_3$, $x \geq 2$. It is conceivable that the high-mass ions reported by Farber and co-workers are associated with molecular species resulting from polymer degradation. Certainly the ion intensity ratio of $m/e = 254$ to $m/e = 256$, apparent from the data of Farber and co-workers (their figure 1), is not in agreement with the known ^{34}S to ^{32}S isotope abundance ratio of 0.0443. The failure to obtain the correct isotope ratio suggests that the observed ions were not derived from the same sulphur-containing compound.

The present results demonstrate that $\text{S}_2\text{F}_{10}^+$ and S_2F_9^+ ions are not likely to be formed from S_2F_{10} and therefore cannot be used as indicators for the presence of this species in SF_6 using electron-impact mass spectrometry. It is clear from the similarity of the SF_6 and S_2F_{10} mass spectra at 70 eV that it would be very difficult to unambiguously detect the presence of small quantities of S_2F_{10} in SF_6 using a mass spectrometer operated at this energy. Because of the rather large differences in appearance potentials for the ions

SF_5^+ , SF_3^+ and SF_2^+ observed from SF_6 and S_2F_{10} , it may be possible to use a lower electron-impact energy (20 eV or lower) to detect S_2F_{10} in SF_6 . However, the level of detection sensitivity by this method is yet to be determined.

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