Mass Spectrum of Sulfur Vapor

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The mass spectrum of sulfur vapor has been measured by evaporating sulfur from a heated tube directly into the ionization chamber of a mass spectrometer. Ions S_x^+ with x ranging from 1 to 8 are observed with S_2^+ most abundant. Isotope abundances were computed from the S_x^+ ions. The appearance potentials of S_2^+ and S_4^+ are respectively 8.9 ± 0.2 and 8.3 ± 0.2 electron volts. This suggests that the vapor in the ionization chamber is a mixture of molecules containing S_2 and S_8 and possibly other molecules.

1. Introduction

The mass spectrum of sulfur vapor has been studied in connection with a program to establish reference samples of natural isotopic abundance [1].[1] While one objective of this study was to check the isotope ratios and the chemical purity of the reference sample, the mass spectrum and the appearance potentials are of research interest. The molecular weight of sulfur vapor indicates that the vapor in equilibrium with sulfur at 175° C is predominantly S_8 [2]. This is a relatively unstable configuration, and in the presence of an electric discharge an S_2 band spectrum is observed [3]. The vibration series and predissociation spectra give with some uncertainty a value of 4.4 ev for the S_2 bond energy, indicating that S_2 is quite stable.

2. Experimental Procedure

The sulfur from the reference-sample stock is virgin sulfur from a dome in Wharton County, Tex. The sulfur-vapor pressure is too small to measure the mass spectrum at room temperature, and the measurements were made by evaporating the sulfur from a heated tube into the ionization chamber of a 60° mass spectrometer. A few milligrams of coarse powder were held in a capillary tube with a thermocouple in contact with the tube. This in turn was in a 6-mm tube, which extended about 2 cm to the entrance port of the ionization chamber. The ionization chamber reached a temperature of 186° C during operation, and the sample attained a steady temperature of 94° C by heat conduction and radiation. This proved to be a convenient temperature for recording the spectrum.

Sulfur dioxide was made by burning the sulfur in air, and the mass spectrum of SO_2 and the air oxygen was measured with a 180° gas-analysis mass spectrometer. This is the conventional method of measuring sulfur-isotope abundances.

3. Results

3.1. Mass Spectrum

Table 1 gives the principal ions observed in the mass spectrum of sulfur vapor. Column 3 gives the relative abundance of the ions S_x^{32}, whereas column 4 gives the monoisotopic spectrum. It is the sum of the isotope peaks in each S_x group relative to the S_8 ions taken as 100. The rather complicated isotope structure identifies all these ions as predominantly singly charged ions, except for the following: Mass 16 from S^{++} was 0.05 percent of the 64 peak in a spectrum where O^+ from O_2 and CO_2 was negligible. Mass $32\frac{1}{2}$ from $S^{32}S^{33++}$ was 0.06 percent of the 64 peak, and is about 4 percent of the 65 peak. Hence, doubly charged ions of mass 64 contribute 4 percent to the 32 peak. A peak at mass 80 from S_5^{++} is 0.06 percent of the 64 peak.

Impurities that can be ascribed to the sulfur rather than the mass-spectrometer background are volatile gases, which decrease with time. H_2S^+ ranged from 1.2 to 0.15 percent of the 64 peak, and CS_2^+ was 0.13 to 0.07 percent. A 48 peak ranging from 0.17 to 0.02 percent may be SO^+ from SO_2. The molecule ion masked by S_2^+ would be about twice the SO^+ peak.

TABLE 1. *Mass spectrum of sulfur vapor*

m/e	Ion	Relative intensity	Monoisotopic spectrum
32	S^{32}	13. 5	12. 8
64	S_2^{32}	100. 0	100. 0
96	S_3^{32}	4. 7	5. 0
128	S_4^{32}	8. 1	9. 0
160	S_5^{32}	5. 2	6. 1
192	S_6^{32}	3. 2	3. 9
224	S_7^{32}	0. 33	0. 43
256	S_8^{32}	6. 4	7. 3

3.2. Isotope Ratios

Sulfur has four isotopes of abundance S^{32}, 95.0; S^{33}, 0.76; S^{34}, 4.2; S^{36}, 0.014 (see table 2). The relative intensity of the isotope peaks in a molecule containing x atoms can be expressed formally by means of the x power of the expression,

$$S^{32} + a_1 S^{33} + a_2 S^{34} + a_3 S^{36},$$

where the a's are abundances relative to that of S^{32} as unity, but the S terms are chemical symbols, not algebraic terms. Thus the isotopes of S_2 give the terms:

$$S^{32}S^{32} + 2a_1 S^{32}S^{33} + 2a_2 S^{32}S^{34} + a_1^2 S^{33}S^{33} + 2 a_1 a_2 S^{33}S^{34} +$$

$$2a_2 S^{32}S^{36} + a_2^2 S^{34}S^{34} + 2a_1 a_3 S^{33}S^{36} + 2a_2 a_3 S^{34}S^{36} + a_3^2 S^{36}S^{36}.$$

Collecting terms of equal-mass numbers gives the relative intensities of the S_2 ions as listed in column 2 of table 2. Because of intensity and resolution, the S_2 ions are best adapted to deriving isotope ratios, and mass peaks 64, 65, 66, and 68 were used to determine a_1, a_2, and a_3. Five successive slow scans of the S_2 peaks under steady conditions gave the relative intensities listed in column 3, where uncertainties listed are the maximum spread of the data. In these measurements the 64 peak was about 5,600 scale divisions on the most sensitive scale, and a small drift in the 64-peak height was corrected by a linear interpolation to the positions of the measured peaks on the record. The fourth column gives the derived relative abundances.

TABLE 2. *Isotope abundances and relative intensities of S_2 ions*

m/e	Relative intensities	Observed intensities	Derived relative abundances
64	1	1	----------
65	$2a_1$	0.01596 ± 7	$a_1 = 0.00798 \pm 4$
66	$2a_2 + a_1^2$	$.08897 \pm 20$	$a_2 = 0.04445 \pm 20$
67	$2a_1 a_2$	----------	----------
68	$2a_3 + a_2^2$	$.00228 \pm 2$	$a_3 = 0.00015$
69	$2a_1 a_3$	----------	----------
70	$2a_2 a_3$	----------	----------
72	a_3^2	----------	----------

Table 3 gives percentage abundances from data of table 2 and values derived from the mass spectrum of SO_2 made from this sulfur. The correction for O_2 isotopes was based on measurements of the air oxygen used in making SO_2. The table also includes published values from SO_2 spectra.

The S_2 ions are not favorable for the computation of a_3, for the contribution of $2a_3$ to the 68 peak is only 15 percent of the a_2^2 term. A source of uncertainty in evaluating a_1 from the 65 peak arises from the possibility that a trace of $S_2^{32}S^{34++}$ may be present. The comparative values of table 2 give no evidence of this.

TABLE 3. *Sulfur-isotope abundances*

	Mass number			
	32	33	34	36
S_2^+ (sulfur vapor)	95.0	0.76 ± 0.004	4.22 ± 0.01	0.014
SO_2 (same sulfur)	95.0	$.77_2 \pm .01$	$4.23 \pm .07$	....
Nier [5]	95.1	$.74 \pm .02$	$4.20 \pm .1$	$.016 \pm .0016$
Thode [6] sulfur from same region	....	....	4.259	....

3.3. Appearance Potentials

Some measurements of appearance potentials were made to see whether or not S_2^+ was a fragment ion from S_8 ionization. The experimental conditions were not well adapted to accurate measurements. The ion-repeller voltage was kept rather high to maintain sensitivity, and there were irregularities in the current-voltage curves that may come from surface charges on adsorbed sulfur. Mercury vapor was introduced with the sulfur vapor, and the appearance potentials of sulfur ions were measured relative to that of Hg^+ (spectroscopic value 10.34 ev) [4]. Measurements are based on semilog plots, with current plotted on a scale to make the ion current at 50 v unity. Values of the appearance potentials at an ordinate of 0.003 of the current at 50 v are: S_8^+ 8.9 ± 0.2 ev and S_2^+ 8.3 ± 0.2 ev. Variations in the slopes of the current-voltage curves give some added uncertainty. Some measurements on S^+ indicate an appearance potential roughly 2 v higher than S_2^+ and S_8^+. A search for negative ions gave negative results, but there was no basis to appraise the sensitivity for negative-ion detection.

4. Discussion

The fact that the appearance potential of S_2^+ is somewhat less than that of S_8^+ suggests that S_2 molecules are present and 8.3 ev is the ionization potential of S_2. Ionization resulting in a pair of positive and negative ions could give fragment ions at an appearance potential less than the ionization potential of the S_8 molecule, but there is no evidence that this occurs. As vapor in the ionization chamber is at a pressure less than 10^{-4} mm and at a temperature of 186° C, dissociation of S_8 into the relatively stable S_2 molecule is not unexpected. The mass spectrum of sulfur vapor given in table 1 is probably to be interpreted as the spectrum of a mixture of molecules.

The appearance potentials are unexpectedly low. Smyth and Blewett [7] reported an appearance potential of 10.7 ± 0.3 ev for S_2^+ from thermally dissociated CS_2, as compared with 8.3 ev found in this work. An ionization potential of S_2 lower than that observed by Smyth and Blewett is suggested by analogy with O_2. The ionization potential of O is 13.61 ev [4] and that of O_2 is 12.2 ev [8]. As the ionization potential of S is 10.36 ev [4], the ionization potential of S_2 is expected to be considerably lower than this, not slightly higher as reported by Smyth and Blewett.

The isotope ratios of sulfur are fairly consistent with published values, as is evident in table 2, but there is considerable variation in isotope abundances of sulfur. Thode and his colleagues [6] have made an intensive survey of relative abundances of S^{34} in sulfur from various sources and find values ranging from 4.39 to 4.19 percent, with a value of about 4.29 percent reported for native sulfur from the same region as the reference sample.

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5. References

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