SPECTRA AND REACTIONS OF ELEMENTAL SULFUR

by

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A thesis submitted in partial fulfillment

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We have carefully read the dissertation entitled Spectra and Reactions of Elemental Sulfur

submitted by Thottathil V. Oommen in partial fulfillment of the requirements of the degree of Doctor of Philosophy and recommend its acceptance. In support of this recommendation we present the following joint statement of evaluation to be filed with the dissertation.

The first section of this thesis presents a well-documented investigation of the electronic spectrum of elemental sulfur in solution, in a single crystal, in the vapor phase, and in liquid form at various temperatures. The study focuses on the temperature dependent shift of the absorption edge of pure sulfur. It proposes, for the first time, an explanation for the change of the color of liquid sulfur in the temperature range above 160°C. The color change is explained as a combination of the shift of the absorption edge of S_8, and the absorption due to high temperature species, probably S_4 or S_3.

In the second section, a short exploratory study on fluorosulfanes is reported. This work confirms that fluorosulfanes can be prepared from silver fluoride and elemental sulfur, and indicates that species containing four and more atoms in a chain can be prepared.

The third part constitutes a summary of an introductory study on diatomic sulfides.

This thesis contributes to the knowledge of elemental sulfur. It is a very worthy one.

DISSERTATION READING COMMITTEE: Basil Meyer.

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Many providential circumstances have contributed to the progress and completion of this work. My concluding words are therefore, "SOLI DEO GLORIA".

INTRODUCTION

Elemental sulfur has been known and used since antiquity. Its physical and chemical properties have been extensively studied by numerous workers. In recent years excellent reviews (1,2,3) have appeared which enable one to reach out for detailed information.

Even a cursory inspection of the literature reveals many interesting features of this element. Sulfur has the largest number of allotropes among all the elements. These vary from well-defined, ordered species such as the cyclo-S_8 or orthorhombic variety to macromolecules consisting of a few hundred thousand atoms. Several of these forms can co-exist in solid, liquid, vapor and solution phases. Thus elemental sulfur can exhibit a vast range of physical and mechanical properties. The behavior of the element is therefore complex.

Part I of the present work is devoted to the study of the several allotropic forms of sulfur, including the common, orthorhombic form. Our knowledge of these allotropic species is still very inadequate. One often finds in the literature many ambiguous and contradictory statements about the behavior and characterization of sulfur species. This study is an attempt to clarify some of the puzzling features of the element

and to obtain a better understanding of the allotropic forms.

The chief tool in this investigation is absorption spectroscopy in the visible and UV ranges. The reasons for selecting this tool are:

1. Compared with other methods of investigation, this type of spectroscopy has not been applied extensively to the problems of elemental sulfur chemistry. Only the solution and vapor phases have received some degree of attention from spectroscopists. The solid and liquid phases have been only poorly studied. As a result, many common observations such as color change on heating have not been well understood.

2. Spectroscopy is a valuable tool in identifying new species. Although a complete characterization is possible only with supplementary methods of investigation, the existence of well-defined species can at least be recognized by spectroscopic studies.

3. Even the widely investigated solution and vapor phases were in need of re-investigation on account of the incomplete and sometimes conflicting nature of the data available.

In obtaining the spectra the main interest in this work was centered around identification of the species present in terms of their characteristic absorption peaks. Since the allotropic composition of sulfur is strongly temperature dependent, this study had to be carried out in the large temperature range from 77°K to 1000°K. The wavelength range was usually 2000 $\mathring{A}$ - 7000 $\mathring{A}$.

Of all the phases in which elemental sulfur can exist, liquid sulfur is the most complex. Its composition undergoes

drastic changes on heating. The color changes from a translucent yellow to opaque red. Viscosity increases and decreases; many physical properties show discontinuity at certain temperatures. The study of liquid sulfur is described in Chapter I. The subsequent chapters deal with the solid, vapor and solution phases. A broad study of the various phases was found very useful in understanding the nature of elemental sulfur, especially the liquid state. The last chapter of Part I is an investigation of sulfur-iodine system in solution. This is essentially a re-investigation of earlier work because there is considerable ambiguity about the existence of sulfur-iodine compounds and charge-transfer complexes.

In addition to the visible and UV spectra, infrared, nmr and mass spectra have been studied. Infrared spectra were studied for their own interest and for supplementary evidence to support conclusions from visible and UV spectra. NMR and mass spectra were used as confirmatory tools in characterization of species.

Part II describes some work on fluorosulfanes. The existence of these compounds has been indicated by nmr studies (Chapter VIII). The present work is an attempt to prepare fluorosulfanes from elemental sulfur and a suitable

fluorinating agent, and to characterize them by nmr. The work described is mainly exploratory in nature. Further work in this field is being planned.

Part III is a literature study of diatomic species containing sulfur. Since no review on this subject has appeared, part of this study is a review of the preparative methods and important properties of these compounds. The remaining part of this section is an attempt to correlate spectroscopic and thermodynamic properties in terms of group trends. A comparison of sulfides with the corresponding oxides is also attempted. This study has enabled prediction of some spectroscopic and thermodynamic parameters of the less studied diatomic species. Part III was undertaken as an introduction to the experimental study of sulfur.

PART I

SPECTRA OF ELEMENTAL SULFUR

CHAPTER I

A STUDY OF LIQUID SULFUR

Introduction

Sulfur has been studied extensively in the liquid state by a variety of physical methods. The latest survey summarizes the work done up to 1965 (4).

The tremendous interest shown in liquid sulfur is justified by its complexity. The liquid state extends from about 114°C to 444°C under normal pressure. Almost all the physical properties show abnormal changes at certain temperatures in this range. The most remarkable transition point is at about 160°C. Figure 1 illustrates several physical properties studied as a function of temperature.

A search of the literature revealed that comparatively little work had been done on the spectra of liquid sulfur. For the purpose of this study, optical and infrared spectra are considered. More detailed investigations of these spectra are described in this chapter.

The study of UV-VIS spectra and infrared spectra will be discussed in sections A and B respectively.

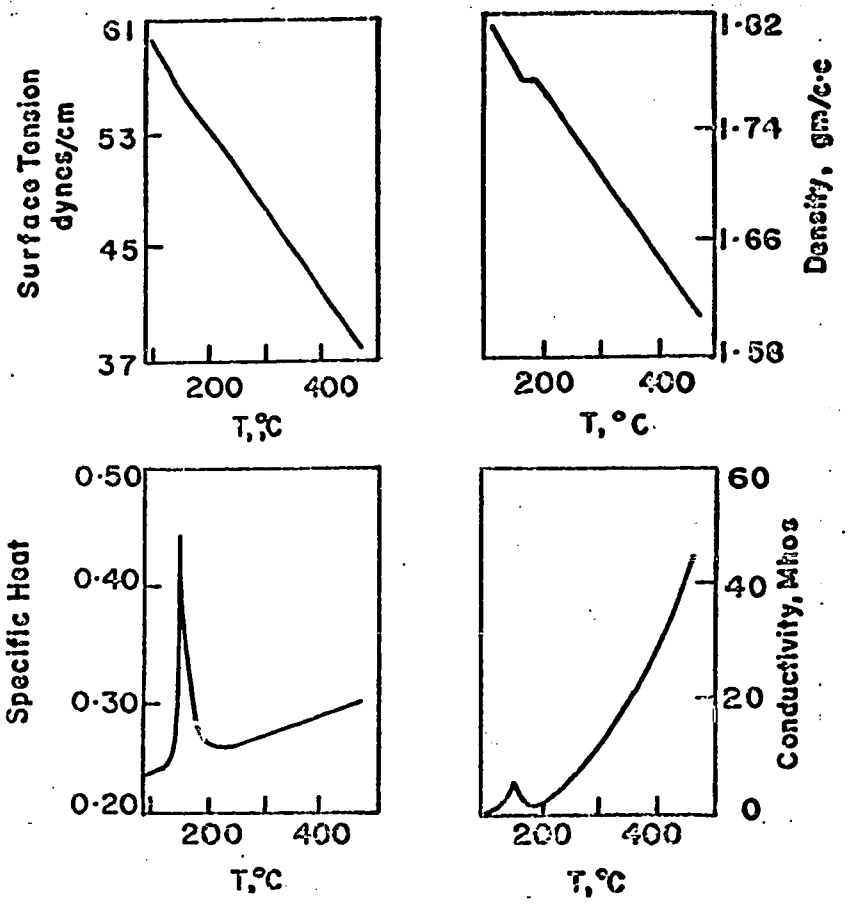


Figure 1. Liquid Sulfur: Physical Properties as a Function of Temperature. Reference (5)

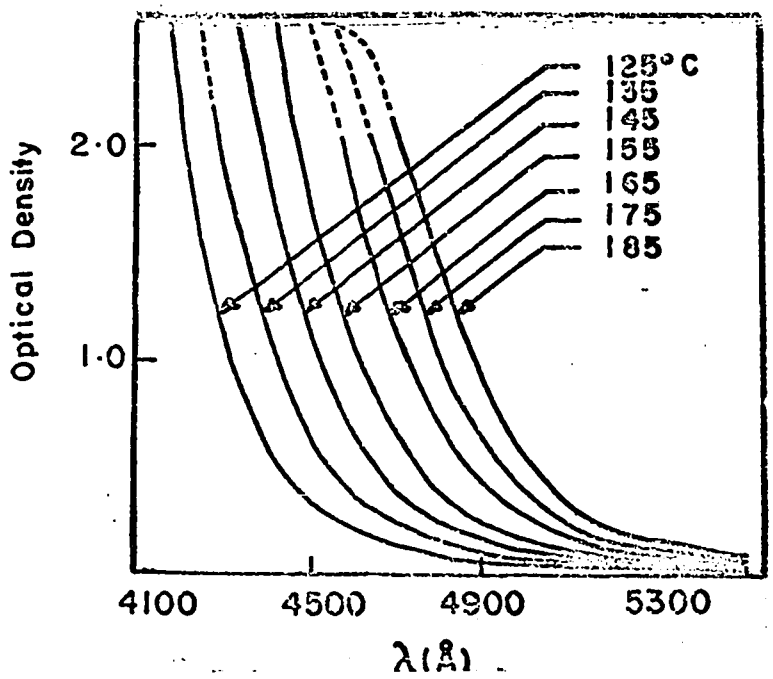


Figure 2. Liquid Sulfur: Absorption Edges, 125-185°C. Sample Thickness: 123μ . Reference (8)

A. UV-VIS Spectrum of Liquid Sulfur (2000-7000 Å range)

1. Previous work

The earliest reported work on the optical spectrum is by M. Fukuda, 1921 (6). The spectrum was re-examined by Mondain-Monval, 1930 (7) and A.M. Bass, 1953 (8). These authors have reported that liquid sulfur has an exceedingly high absorption in the UV region and therefore only the absorption edge extending to the visible could be studied.

One of the most remarkable observations made by all investigators is the appreciable shift in the absorption edge towards the red when liquid sulfur is heated. The specimen becomes deeper red as a result of this shift. The spectrum shown in Figure 2, obtained by Bass, is the only illustration of the shift found in the literature. Fukuda reported a uniform shift of 2Å/°C; Mondain-Monval observed two shift rates: below 160°C, 2.94 Å/°C and above 160°C, 7.4 Å/°C. Bass found a discontinuity at about 160°C but no details were given. The average shift reported by him was 6.2 Å/°C. The thickness of the sulfur film varied from 123 μ to 317 μ.

2. Purpose of the present work

The main objective of this work was to record the spectrum of liquid sulfur in the UV-VIS region as a function of temperature. It was hoped that the results obtained would

lead to an increased understanding of the nature of the spectral shift, especially in the temperature range 160° - 200°C where abnormalities have been found. It was also necessary to test the results obtained by earlier workers because of the discrepancies with respect to shift rate.

3. A discussion of the experimental problems in studying optical absorption of liquid sulfur

Two major experimental difficulties experienced by previous workers are discussed in this section. Possible solutions are suggested.

(i) High absorption of liquid sulfur:

To appreciate this problem, a comparison with the solution spectrum is useful. Figure 25 shows that for S_8 species the highest absorption peak in the 2400 - 4000 Å region is the 2640 Å peak, having a molar extinction coefficient of about 6.5×10^3.

Liquid sulfur, with a density ca. 2.0 g/cc. has a molar concentration of about 8 since a liter of it would contain about eight S_8 units. As a very rough approximation, liquid sulfur at the melting point is assumed to be composed of S_8 molecules and to obey the Beer-Lambert Law: Optical density (O.D.) = εcl where ε is the molar extinction coefficient, c, the molar concentration and l, the path length. For a one cm.

path, the optical density for the 2640 Å wavelength would be

$$(O.D.) = 6500 \times 8 = 52,000.$$

If the path length had been reduced to 100μ , O. D. would be 520. Since it is very difficult to construct cells of lower than 100 μ thickness, the problem seems formidable. Usual spectrophotometers cannot record optical densities higher than 2.4, under normal conditions.

If, however, absorption intensity increases at a much slower rate for condensed phases (since Beer's law is not applicable to these systems), there is some possibility that the absorption is considerably lower than the calculated value and is measurable with the aid of neutral density filters. The use of these filters will be referred to in several studies and hence a brief description is given below.

In a double beam spectrophotometer such as a Cary 14, absorption recorded is the difference between the absorption of the sample and reference beams. Since the reference beam has practically no absorption, the absorption of the sample beam determines the net absorption. If, on the other hand, a filter is placed in the reference beam and if its absorption is less than that of the sample, the difference will be the net absorption. Using strong filters, this resultant absorption can be brought within the range of the spectrophotometer.

Such filters can be solutions or metal-coated surfaces, whose absorption curves are known.

Recently, neutral density filters with flat absorption curves in the UV-VIS region have been prepared by applying a metallic coating between two layers of ground and polished, low fluorescence UV grade fused silica. Filters with transmission from 50 per cent (O.D. 0.3) to 0.01% (O.D. 4) are available (e.g. from Oriel Optics Corporation, Conn.,).

The use of these filters at high absorptions is limited by the intensity of the light source used. It was found that with the usual hydrogen arc-lamp (UV) and the high intensity quartz-iodine lamp (VIS), optical densities up to 6 (transmission, 0.0001%) could be measured. This was sufficient for the present purpose.

Instead of the very expensive commercial filters, a rather inexpensive type of filter was used. This was made from optically pure quartz plates by grinding either or both of the polished surfaces. The ground surface scatters light and serves the same purpose as the absorption filter. The transmission curve of this type of filter was found to be smooth and nearly flat. One precaution in using these filters is that they should be standardized each time and their relative distances (if more than one is used) should be unaltered.

(ii) Instability of the film at higher temperatures.

A thin film of liquid sulfur shows great tendency to break on heating. This is partly due to the rapid decrease in surface tension with increase in temperature (Figure 1). Another reason is the formation of gaseous products such as CS_2 (Chapter IV). It was felt by this author that the rupture of the film was aided by the cavity type of cell used by earlier workers (8). A partly sealed cell would perhaps keep the film intact.

Details of the procedure used to solve these experimental problems are given in the next section.

4. Experimental

For practical reasons, described later in this section, the study was carried out separately for two ranges (120 - 300°C) and (300 - 700°C)

a. Temperature range 120 - 300°C.

Optical cell. Cells with optical paths in the region of 100 μ were constructed by sealing together two flat quartz plates (1" X 1" X 1/16", optosil grade, manufactured by Amersil quartz division, New Jersey) at the edges, providing a uniform gap (about 100 μ wide) in between, and a narrow neck joined to a quartz tubing. The optical path was measured accurately from the volume of water required to fill the cell.

The uniformity of the spacing between the plates was tested by a micrometer screw.

Heating Block (Figure 3)

This served as cell holder and heating block. Brass was used in the construction. The heating block is illustrated in Figure 3 along with the optical cell. Heating was done with a firerod heater (115 V, 300 W). The temperature was controlled by a variac and was measured by a Chrome-Alumel thermocouple and potentiometer arrangement.

Preparation of the sample

Spectroscopically pure sulfur (99.999%) was used. A few milligrams of it were placed at the neck of the cell. The cell was placed in the block and was gently heated to about 120°C. The sulfur melted down and filled the cell. Gentle shaking of the cell ensured complete filling.

UV-Visible Spectrum

The heating block, holding the cell, was transferred to the sample compartment of a Cary 14 H spectrophotometer. When a steady temperature was attained, the spectrum was scanned from 7000 Å to lower wave lengths. At about 4300 Å, the absorption increased rapidly and exceeded the limits of the instrument (2 O.D.). At this point neutral density filters

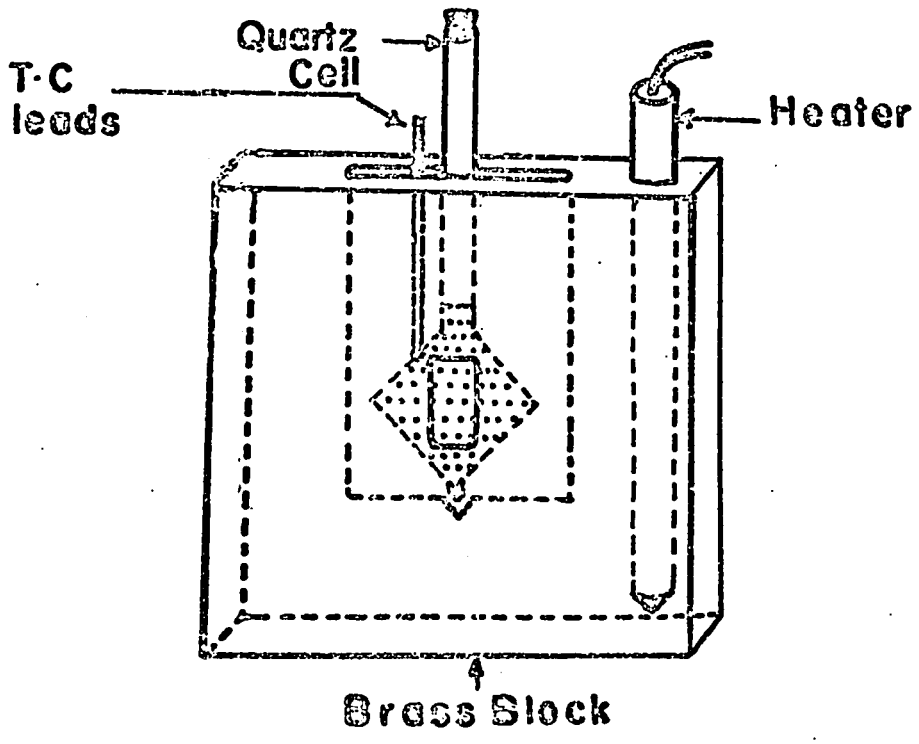


Figure 3. Cell and Heating Block

were introduced into the reference beam. Fortunately, the maximum absorption was less than 5 O.D. and could be measured with the filters. The spectrum was not scanned below 2400 Å because the absorption was too high and the hydrogen lamp was not powerful enough when filters were introduced. In the visible range, a high intensity quartz-iodine lamp was used.

Spectrum was scanned for every ten degrees from 120 to 300°C. Scanning time was about 10 minutes in each case. Temperature was kept constant within 1°C during the experiment.

Above 300°C the film started breaking, and hole-transmission decreased the absorption considerably, hence higher temperatures were not used in the study.

A second technique, involving no use of filters was also adopted to scan the spectrum. The optical cell was partly raised in the sample beam till the absorption was lowered to within 2 O.D. This technique was not good for quantitative results but gave absorption curves similar to those obtained with filters. The use of this technique is justified by the following example: if we have a 200 μ cell raised 50 per cent in the optical path, the absorption should be lowered by 50 per cent which is equivalent to using a 100 μ cell in the full beam. In practice, however the absorption of a 100 μ sample was found to be different from the absorption of a 200 μ

sample raised halfway. The reason is Beer-Lambert Law is not obeyed by concentrated solutions or pure liquids. Absorption of a 100 μ specimen was found to be between 50 and 90 per cent of the absorption of a 200 μ specimen, in different parts of the spectrum. The advantage of this technique is that qualitative spectra can be obtained even though the absorption intensity is very high.

Since it was thought that the composition of the liquid and the vapor was roughly the same, a spectrum of the liquid film with a vapor bubble was taken at 270°C. The second technique was used because the absorption was beyond the limit of the filters.

b. Temperature range 300 - 700°C

Cell and heating equipment

A thicker cell (ca. 300 μ) was used in this range because the film could be kept intact only by increasing the thickness. This however, limited the usefulness of the spectrum because only part of the absorption edge could be recorded.

It was necessary to seal the cell under vacuum because the sample had to be studied up to 700°C, far above the normal boiling point (444°C).

Since heat loss was considerable at high temperatures, effective insulation had to be provided. The heating block

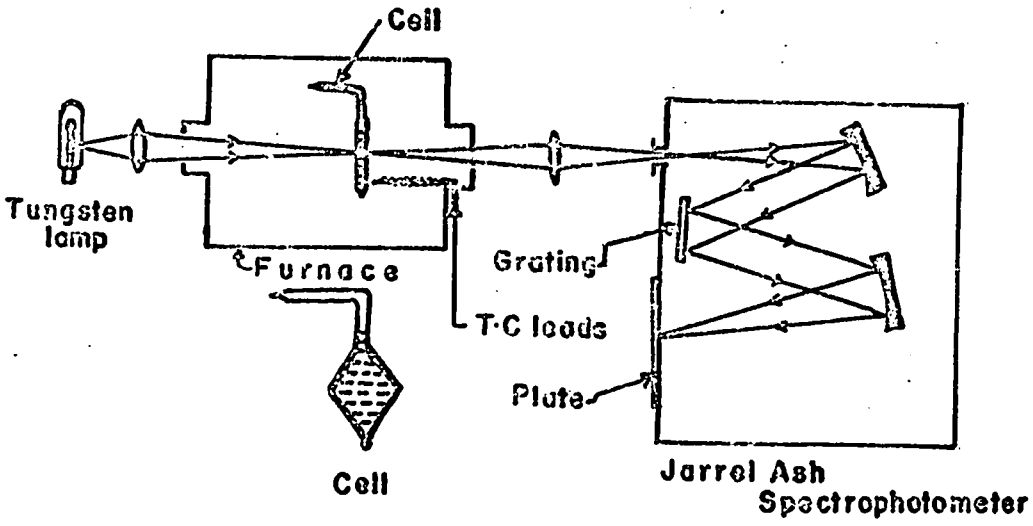


Figure 4. Optical Arrangement for the Study of Liquid Sulfur (300-700°C)

previously used was not efficient for high temperatures. Hence an electric furnace was chosen for the purpose. The furnace had an interior space 12" X 5" X 4" and could be heated to 1000°C.

The cell, containing the sulfur, was placed at about the center of the furnace. Temperature was measured with thermocouple and potentiometer. The furnace had open windows (1" dia.) at each end so that an optical beam could pass through it.

Spectrophotometer

Ir was found very convenient to use a Jarrel-Ash (Model 75 - 000) type spectrophotometer with photographic recording. The optical arrangement is shown in Figure 4.

To decide the right exposure times and to get an approximate idea of the absorption, polaroid films (Black and white, type 57, speed 3000) were used at first. Polaroid films are sensitive from visible to about 2600 Å.

KODAK photographic plates and films were used to record the spectra accurately. The exposure times for these were about three times that for polaroid films. In the visible and UV region, KODAK TRI-X PAN films were used. Since the spectrum shifted to the near infrared region at higher temperatures, infrared sensitive plates had to be used after a while. KODAK

Type 1 - N spectroscopic plates, specially made for this purpose were used. A mercury arc was used as reference.

To obtain correlation with spectra obtained using a Cary Model (section A), one of the spectra was taken at a temperature common to both ranges (here, 300°C). This spectrum agreed with the spectrum at 300° obtained with the Cary 14. Density tracings were obtained from the processed photographic plates and films with a McPherson microphotometer.

Precautions

A precaution is to keep the sealed end of the cell tubing near the furnace walls where the temperature is higher. It was found that this had the effect of keeping the film unbroken.

Since the cell is sealed, vapor pressure reaches a few atmospheres at 700°C, and under high pressure the cell may burst. This did happen in the present experiment at about 725°C.

5. Results and Discussion

5.1. Spectral displays

The spectra of liquid sulfur under the following situations are shown in Figure 5:

(a) complete range (UV-VIS): specimen spectra at 120°C and 185°C

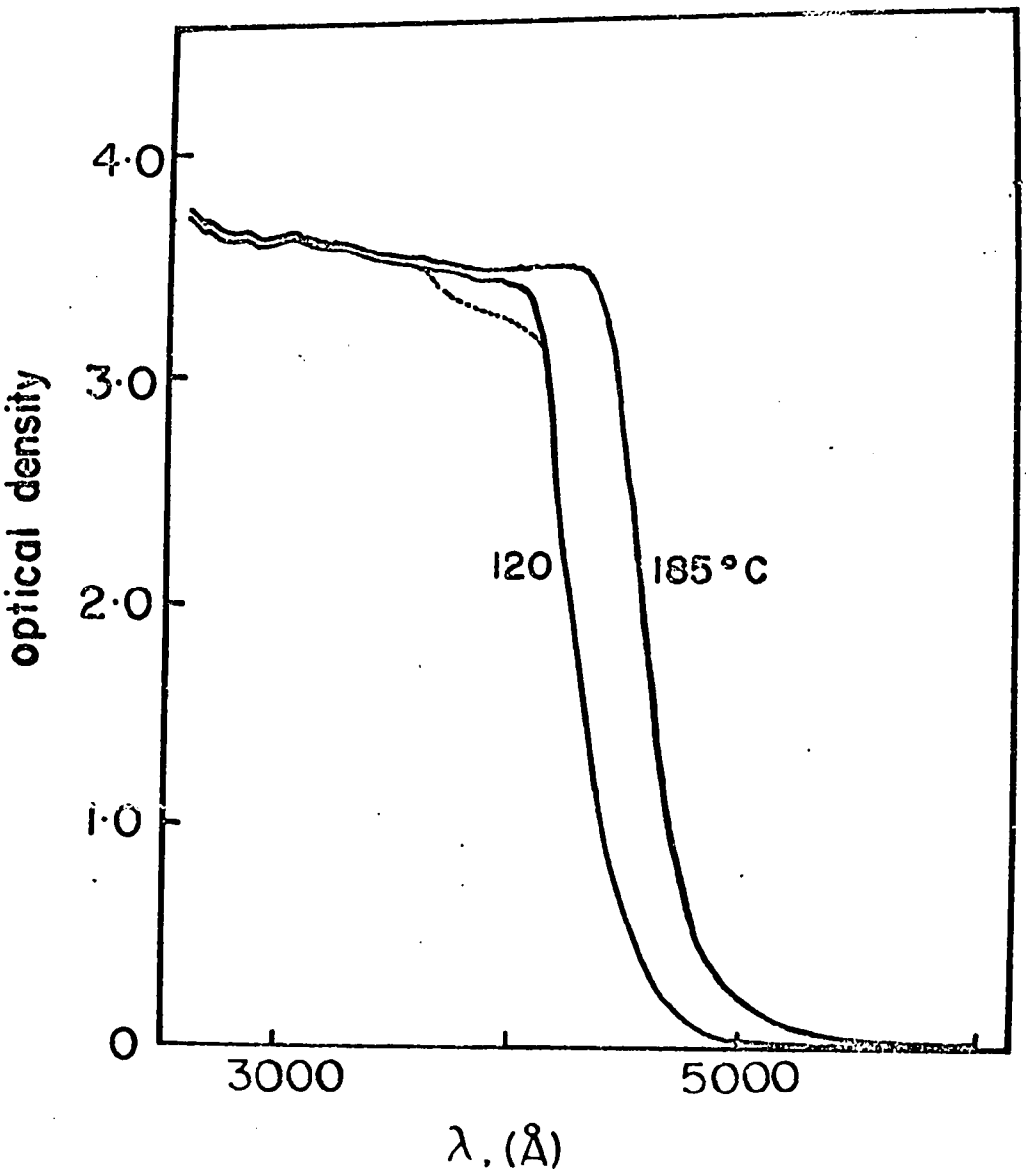


Figure 5a. Spectrum of Liquid Sulfur at 120° and 185°C. Sample Thickness: 105μ

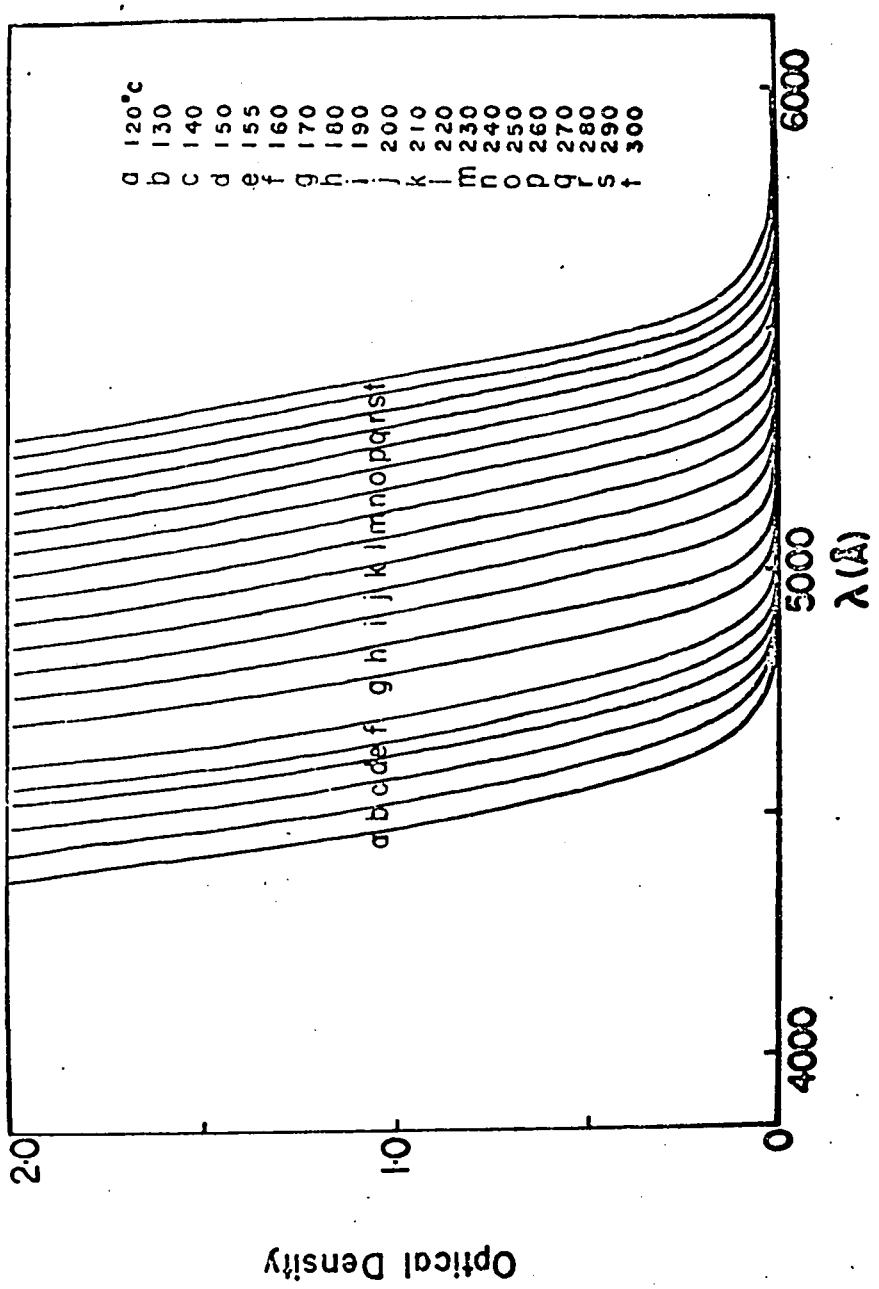


Figure 5b. Liquid Sulfur: Absorption Edges, 120-300°C.
Sample Thickness: 160 μ

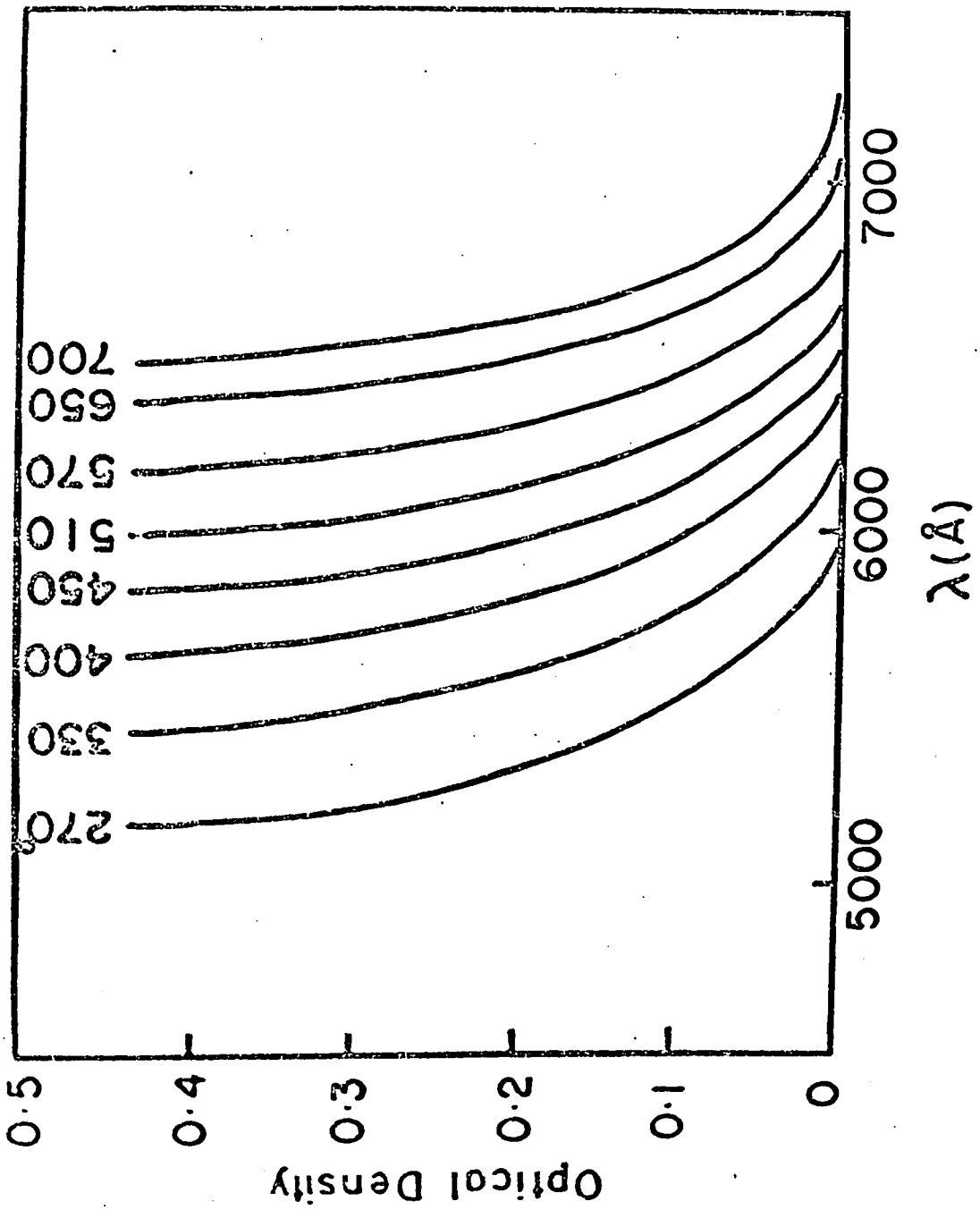


Figure 5c. Liquid Sulfur: Absorption Edges, 270-700°C.
Sample Thickness: 300 μ

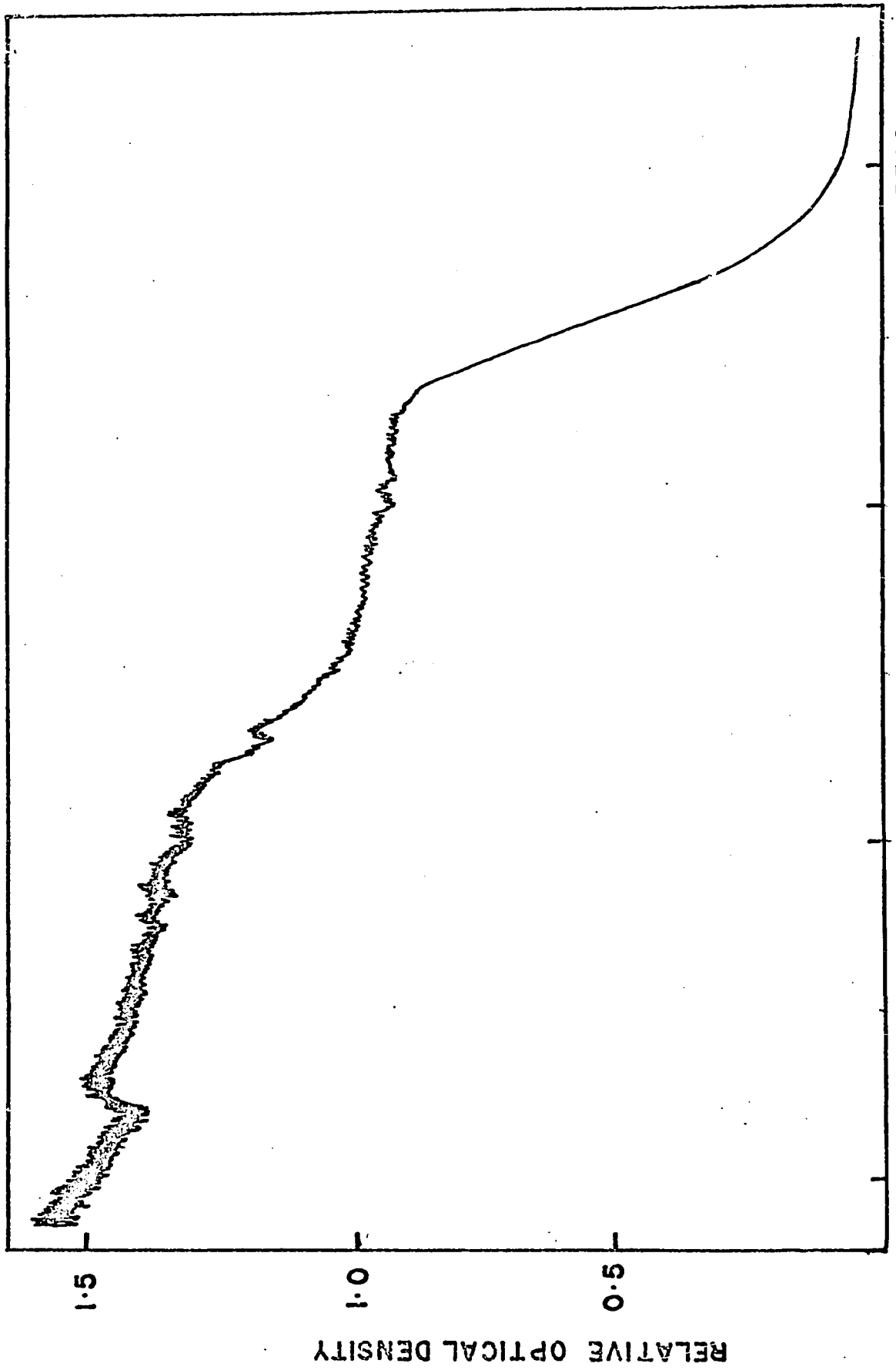


Figure 5d. Spectrum of Liquid Sulfur Containing Vapor Bubble at 270°C. Sample in 100μ thick cell, partly raised.

(b) absorption edges: 120 - 300°C

(c) absorption edges: 300 - 700°C

(d) partly raised cell: spectrum for vapor bubble and liquid at 270°C (region below 2200 Å omitted).

5.2. General observations

Examination of the spectra revealed the following:

(i) agreement with spectrum of crystal:

The general nature of the absorption curves resembled the spectrum of sulfur crystal (Figure 16). Absorption was very high in the UV region and the spectrum was broad. Characteristic peak positions for S_8 species were faintly visible in the 2600 - 2800 Å region. The absorption edge was almost straight and steep.

(ii) Shift in absorption curve with temperature:

With increase in temperature, the absorption edge shifted to the red, i.e., to longer wavelengths, and absorption intensities increased. The increase in absorption for a given wave length was considerably less in the broad absorption region than in the region of the absorption edge. The lower parts of the curves merged together to zero absorption.

This observation explains qualitatively the change in color, viz., from yellow to red, when liquid sulfur is heated. With a 100 μ sample, the color became distinctly red at about

300°C. A thicker sample darkened at lower temperatures. This is merely a result of increased absorption with increased thickness.

(iii) Shift rate:

The average shift rate was 5.76 Å/°C or 23.6 cm^{-1}/°C for the temperature range studied. This was slightly lower than the latest reported value of 6.2 Å/°C (8) but higher than earlier values (6). Shifts were measured at a constant O.D. of 0.6.

The shift rate decreased gradually with increase in temperature from 5 Å/°C at 120° to 3.5 Å/°C at 300° and 2.5 Å/°C at 700°C, except for an abnormal rise at 160°. From an almost steady shift rate of 5 Å/°C it rose up to 14 Å/°C at 160° and then decreased rapidly to about 4.5 Å/°C at 200°C. (Figure 6)

(iv) For a preheated sample of sulfur (heated above 160°) the absorption curves showed a distinct shoulder at about 3600 Å (Figure 5a).

(v) The spectrum of the liquid with a vapor bubble at 270° showed broad peaks in the high absorption region. Peaks at 2800 Å, 3590 Å, 3750 Å, 4300 Å, 4550 Å and 4700 Å were indicated.

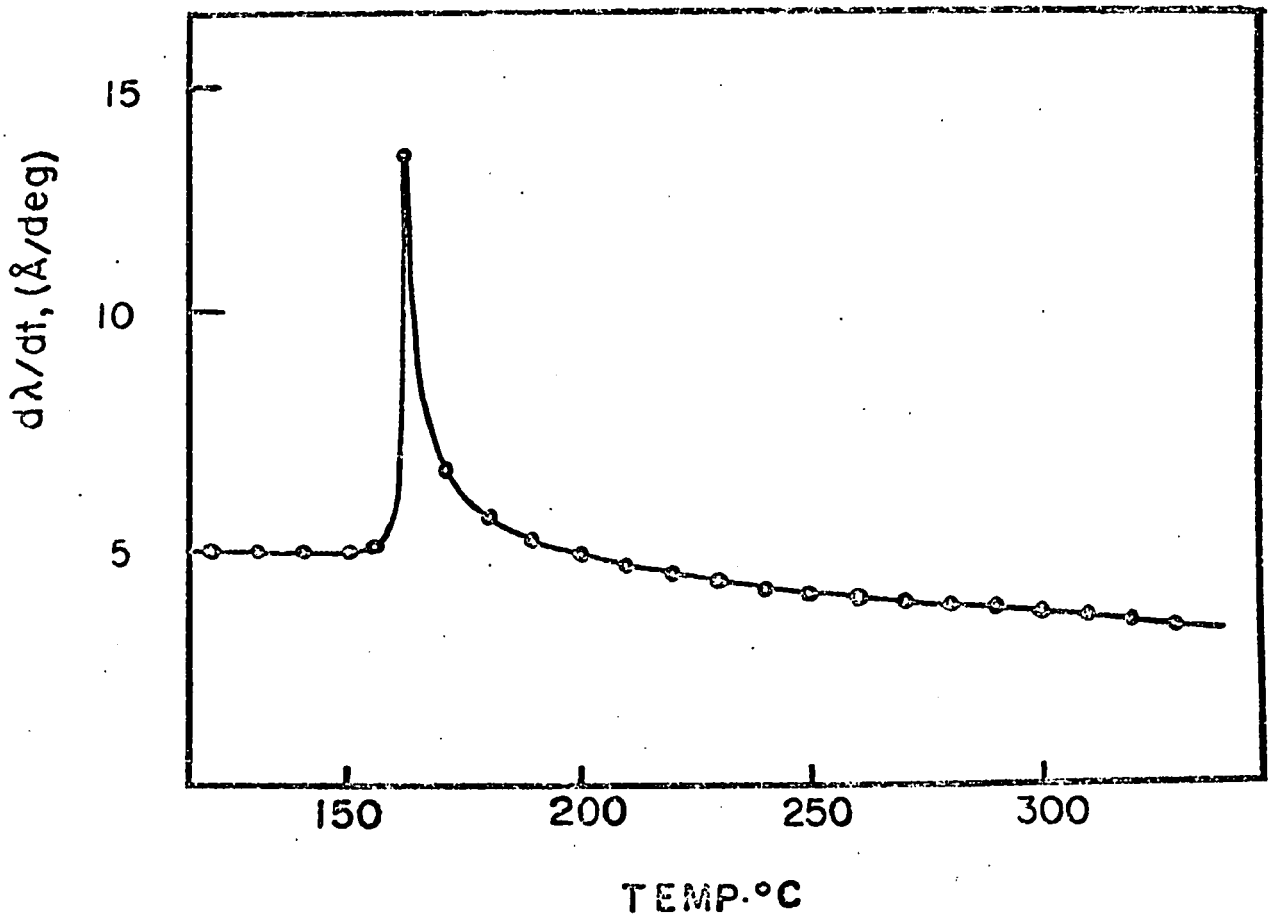


Figure 6. Liquid Sulfur: Shift rate in absorption edge

5.3. Examination of the cause of spectral shift

Two explanations are offered for the observed shifts:

(a) Effect of temperature on vibrational level populations.

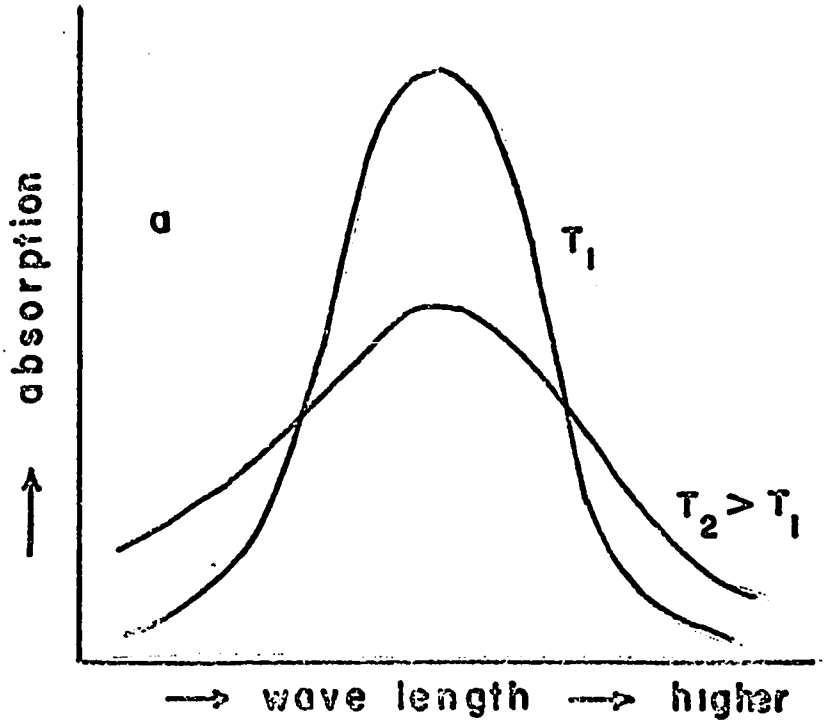
(b) Change in molecular composition on heating.

A discussion of each is given below:

(a) Effect of temperature on vibrational levels

It is generally observed that absorption bands intensify with decrease in temperature and broaden with rise in temperature. Figure 7a shows this behavior qualitatively. At very low temperatures almost all molecules are in the lowest vibrational level, hence transition to upper state is sharp; at elevated temperatures higher vibrational levels are populated and transitions from these levels also are possible. Since these transitions are of lower energy a shift of the absorption curve towards longer wavelengths is expected. At the same time, the intensity maximum decreases because transitions from the lowest level are reduced. The total number of absorbers must remain the same, which means that the integrated absorption under the absorption band is unchanged.

To understand this phenomenon more clearly, we consider the vibrational energy level population in a molecule at a given temperature T (°K), governed by the Boltzmann factor



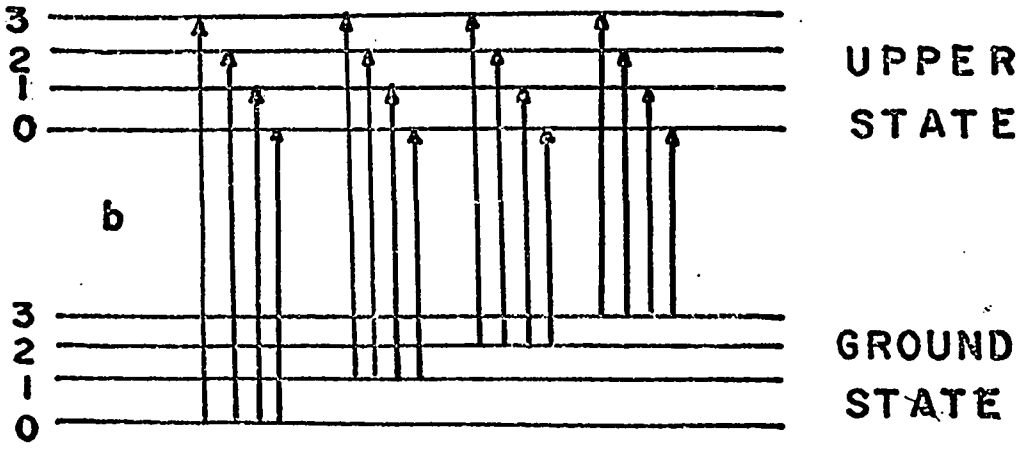


Fig. 7a. Schematic representation of temperature dependence of absorption

$\exp(nh\nu/kT)$ where n is the vibrational quantum number for the frequency ν. Since absorption is proportional to the number of absorbing molecules, the Boltzmann factor governs the transition probabilities from the various vibrational levels in the ground state to levels in the upper electronic state. This means that absorption is a function of frequency and temperature. The temperature dependence could be expressed in a simple way as

$$\log (O.D.) = a - \frac{b}{T}$$ where O.D. = optical density; a & b are constants.

The plot of log (O.D.) vs. $\frac{1}{T}$ should therefore be a straight line with a negative slope.

Figure 7b shows typical plots. The curves were approximately linear for optical densities below 1.0. The slopes were negative. Similar observation has been made on the spectrum of selenium (9).

The following observations revealed that factors other than a mere temperature dependence were present.

1. The log (O.D.) vs. $\frac{1}{T}$ curves were not straight at high optical densities.

2. In the temperature range 160 - 200°, the above plot was not linear even at low optical densities. The shift rate is 23.6 $cm^{-1}/°C$ in the liquid as compared to 2.3 $cm^{-1}/°C$ in frozen solution at 196°, and showed a maximum at 160°.

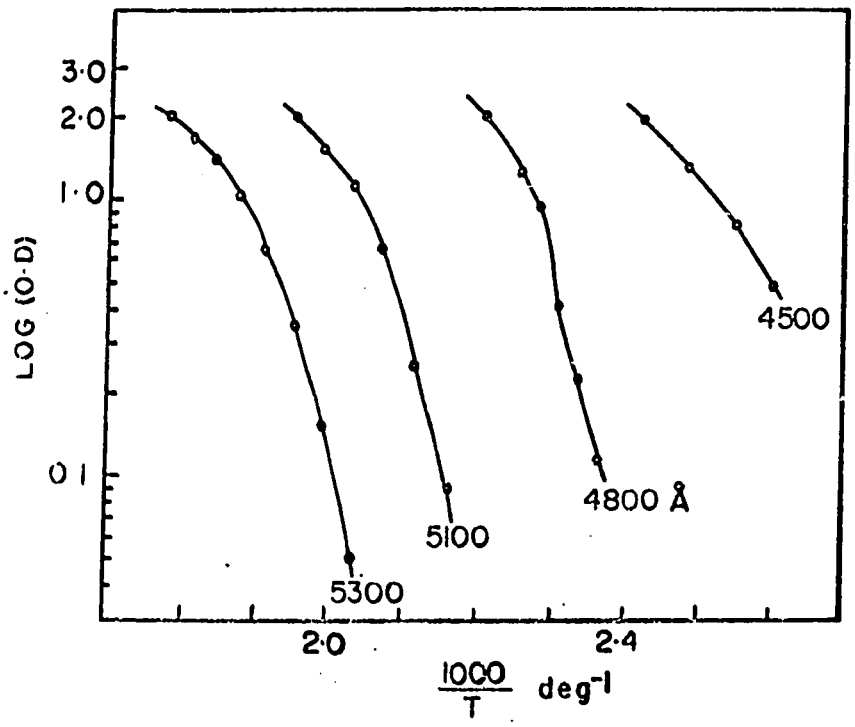


Figure 7.b Plot of log (O.D.) vs. Reciprocal Temperature

3. The vapor spectrum showed a few absorption peaks at higher temperatures. This was indicative of new molecular species. The color of the vapor and the liquid were almost the same. Hence these species could also be present in the liquid and contribute to the color.

These considerations lead to a discussion of a possible structural change in liquid sulfur, given below.

(b) Change in molecular composition on heating

An attempt is made to explain the spectrum and spectral shifts in terms of structural changes.

It was mentioned in the introduction that several physical properties show a sudden discontinuity at 160°. Extensive study of other physical properties, especially viscosity, has led to the theory of equilibrium polymerization. This was introduced by Powell and Eyring, 1943 (10) and developed by Gee, 1952 (11), Tobolsky and Eisenberg, 1959 (12). According to them, the existence of at least two equilibria must be assumed to explain the observed facts:

(i) $\text{cyclo} - S_8 \overset{K_1}{\rightleftharpoons} \text{catena} - S_8$; $\Delta H_1 = 32.8$ kcal/mole

(ii) $(\text{catena} - S_8)_n + \text{cyclo} - S_8 \overset{K_2}{\rightleftharpoons} (\text{catena} - S_8)_{n+1}$

$\Delta H_2 = 3.17$ kcal/mole

This would imply that on heating liquid sulfur, S_8 rings are opened up to form S_8 catena (open chains) which

attack other S_8 rings to form larger polymer chains. The presence of free radicals in polymer sulfur has been demonstrated using esr techniques by Fairbrother, Gee and Marrall (13). The transition point at 160° is considered to be the starting point in the formation of polymers in appreciable quantities by the rupture of S_8 rings (Figure 8).

It is necessary to examine whether this theory is capable of explaining the spectrum. If S_8 rings are converted to open chains, the absorption spectrum in the longer wavelength region must be due to the catena species. The abnormal shift at 160° could then be correlated to catena species appearing suddenly in the liquid in appreciable quantities. One should expect a characteristic absorption peak for the new species. At least one new peak has been observed in the present study which could be associated with the new species. This was at about 3600 Å. Although a fresh sample of liquid sulfur did not show this peak (perhaps due to the broad nature of the spectrum) at 160°, a preheated (above 160°) specimen showed a shoulder at 3600 Å. The vapor spectrum (Figure 5d) showed a peak at 3590 Å. In Chapter V the same observation will be made in connection with solution spectrum at 160°.

Several difficulties arise when we attempt to identify the new species. According to polymerization theory there can be numerous catena species in liquid sulfur above 160°.

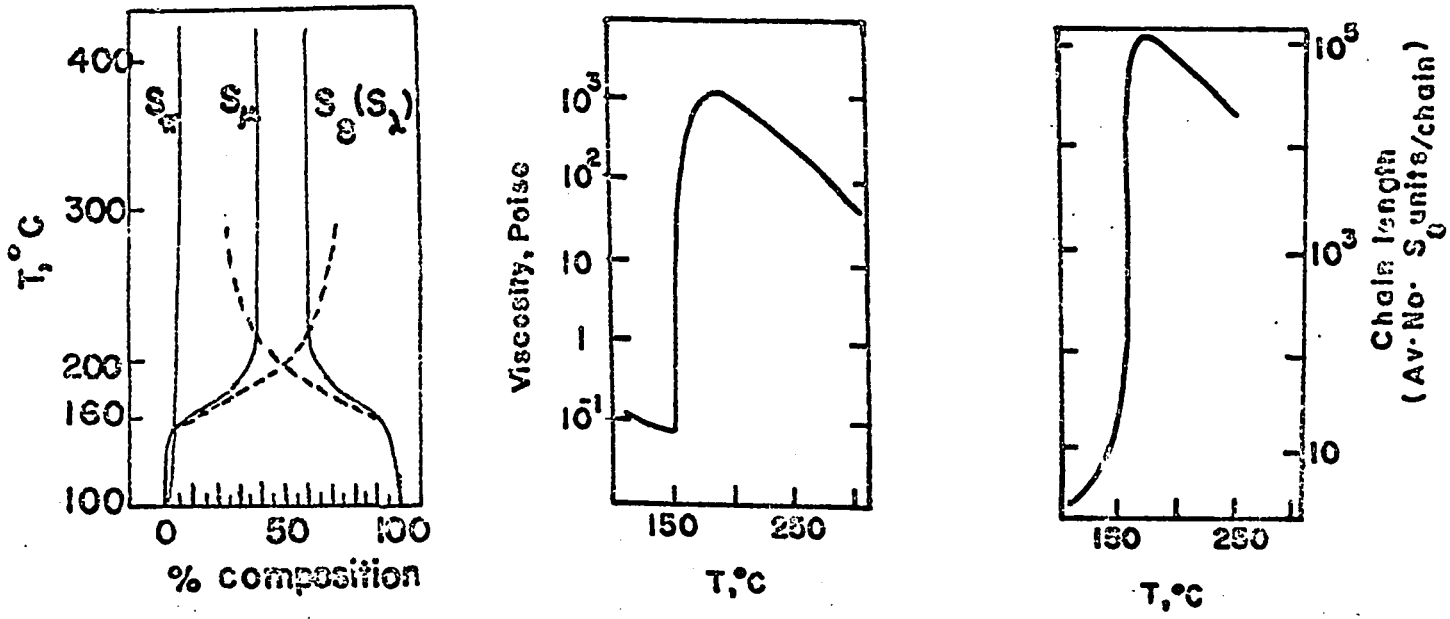


Figure 3. Liquid sulfur: composition and properties

a. composition: —— Data from Aten, Z.Physik Chem., 86,(1914)
- - -Data from Ward & Myers, J.Phy.Chem., 73, 1374 (1969)
S_π, S_μ and S_λ probably correspond to small molecules, long polymers and cyclo-S_8 respectively.

b. viscosity as a function of temperature, reference (14)

c. chainlength at different temperatures, reference (15)

The chain length increases to a maximum of 10^5 S_8 units at about 190°, and then decreases (Figure 8). The relation between chain length and UV absorption has not been studied for sulfur. However, Raymonda and Simpson, 1967 (16) studied the vacuum UV absorption spectra of a homologous series of aliphatic hydrocarbons (carbon atoms 2 to 9) and found the absorption to increase with increase in chain length (Figure 9a). At the same time the absorption edge shifts towards longer wavelengths, the shift decreasing with chain length assymptotically. These observations were explained by the interaction between adjacent atoms in the chain. Polysulfide chains in organic polysulfides show a linear increase in absorption with increase in chain length. (Figure 9b) (17). In liquid sulfur, since the chain length very suddenly becomes high after 160°, absorption should change rapidly and reach a limit at about 190° when chain length reaches a maximum. Above 190°, the shift should be reversed. This was not the case; absorption continued to increase with increase in temperature, even after 200° when chain length starts decreasing.

The comparison with carbon chains or even with polysulfide chains is not however, very meaningful in the present case because liquid sulfur contains open diradical chains in contrast with the bound chains of hydrocarbons and organic polysulfides.

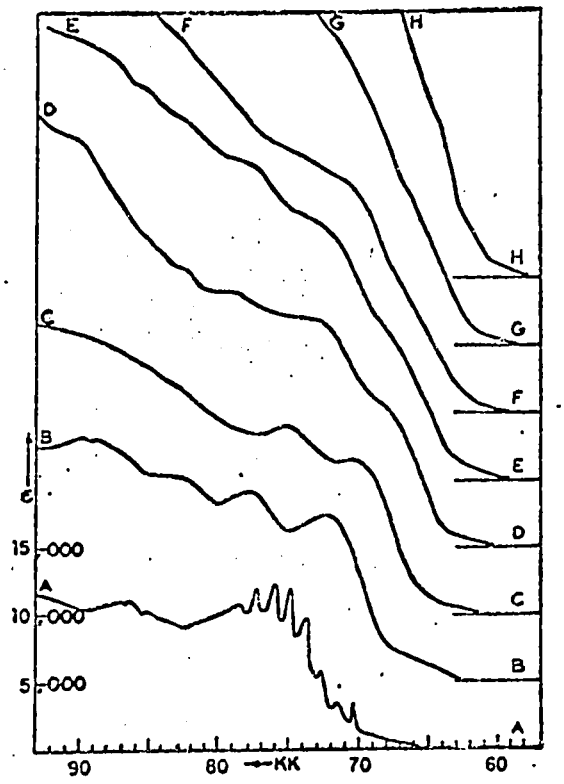


Figure 9a Spectra of Some Linear Alkanes: (A) Ethane, (B) Propane, (C) Butane, (D) Pentane, (E) Hexane, (F) Heptane, (G) Octane, (H) Nonane. Reference (16)

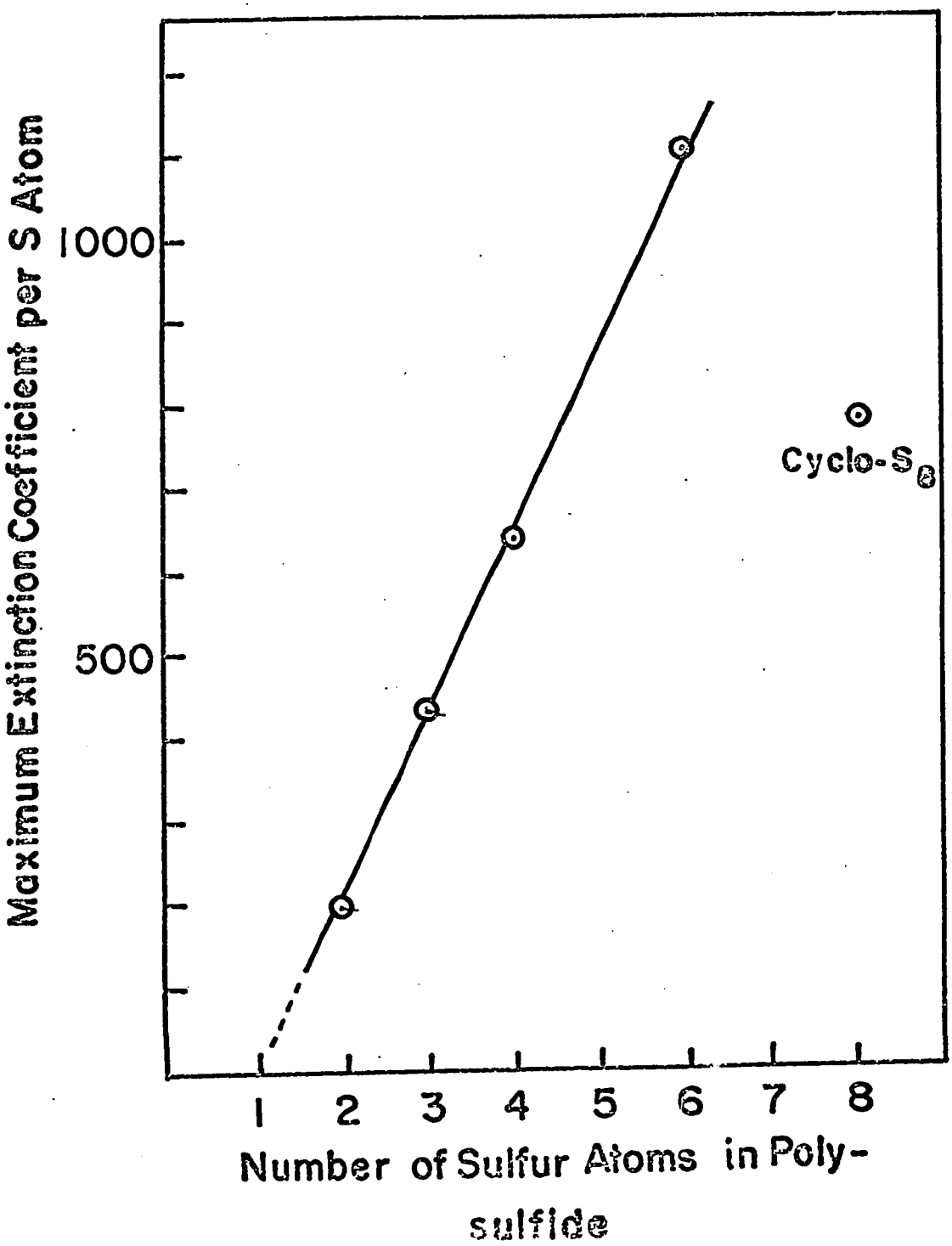


Figure 9b. Intensity correlation of the first band of the polysulfides. Ref (17).

Another approach to explaining the color change of liquid sulfur is provided by a comparison with the color of the vapor. The vapor and the liquid always have a similar color, and both become dark at high temperatures. Long-chain polymers are not expected in the vapor on account of their high molecular weight and low volatility. Hence the absorbing molecule must be small. The color of liquid sulfur should then be attributed to small molecules rather than to long polymers. Berkowitz and Marquart, 1962 (18) have proven by mass spectrometric studies that sulfur vapor contains molecules with two to at least ten atoms. Bond energy relations showed that these species (except S_2) are perhaps cyclic. Of these, cyclo-S_8 has the maximum stability. The proportion of these species in saturated sulfur vapor is shown in Figure 10a. Data independently obtained by Detry et al. (19) are shown in Table I, which lists vapor compositions at various temperatures, and in Table II which summarizes thermodynamic data. Only the spectra of cyclo-S_8, cyclo-S_6 and S_2 are presently known. From their absorption curves (Figures 25,29,22) one would not expect them to account for the red color. Braune and Steinbacher, 1952 (20) observed from spectroscopic studies of sulfur vapor (288 to 990°C temp. range), a peak at 5100 Å (Fig. 10b) which they attributed to S_4. The postulation of this species was necessary to obtain a closer fit with the observed molecular

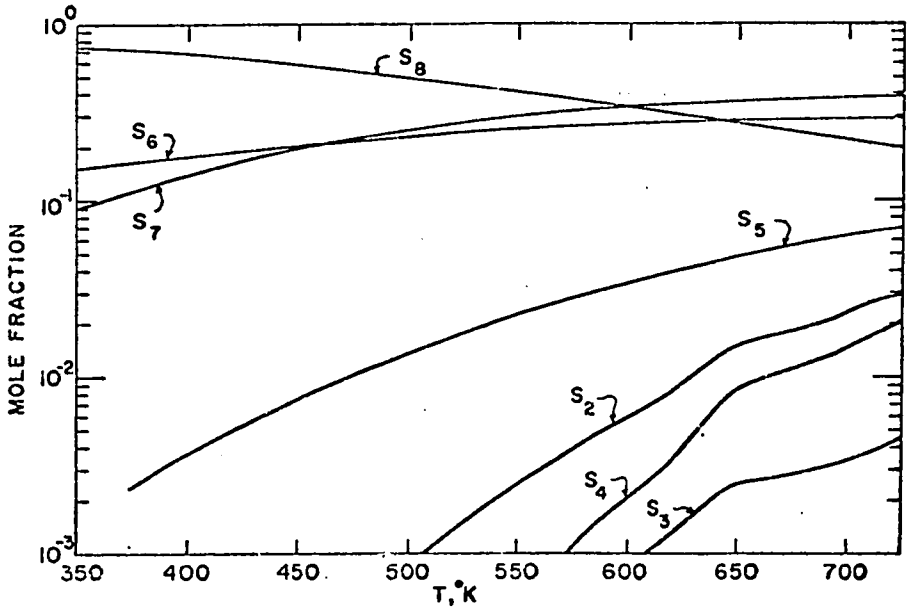


Figure 10a. Mole Fraction of the Sulfur Species S_n (n-2,3, . . .8) in the Saturated Vapor from Room Temperature to the Boiling Point of Sulfur. Reference (18)

TABLE I

TOTAL PRESSURE, p_T ACCORDING TO WEST AND MENZIES AND PARTIAL PRESSURE p_{S_x} OF SATURATED SULFUR VAPOR IN THE TEMPERATURE RANGE OF 200 - 400°C REFERENCE (19)

Pressure (atm)	Temperature (°C)				
	200	250	300	350	400
p_{S_2}	$1.40.10^{-6}$	$2.60.10^{-5}$	$2.68.10^{-4}$	$1.90.10^{-3}$	$9.40.10^{-3}$
p_{S_3}	$1.70.10^{-7}$	$3.38.10^{-6}$	$3.66.10^{-5}$	$2.68.10^{-4}$	$1.34.10^{-3}$
p_{S_4}	$1.65.10^{-7}$	$3.04.10^{-6}$	$3.25.10^{-5}$	$2.15.10^{-4}$	$1.04.10^{-3}$
p_{S_5}	$1.56.10^{-5}$	$1.72.10^{-4}$	$9.64.10^{-4}$	$4.20.10^{-3}$	$1.43.10^{-2}$
p_{S_6}	$5.50.10^{-4}$	$3.60.10^{-3}$	$1.60.10^{-2}$	$5.25.10^{-2}$	$1.37.10^{-1}$
p_{S_7}	$3.28.10^{-4}$	$2.63.10^{-3}$	$1.27.10^{-2}$	$4.55.10^{-2}$	$1.26.10^{-1}$
p_{S_8}	$1.89.10^{-3}$	$1.02.10^{-2}$	$3.64.10^{-2}$	$9.70.10^{-2}$	$2.14.10^{-1}$
p_T	$2.79.10^{-3}$	$1.66.10^{-2}$	$6.62.10^{-2}$	$2.00.10^{-1}$	$4.98.10^{-1}$

TABLE II

THERMODYNAMIC DATA OF SULFUR MOLECULES. REFERENCE (19)

ΔH_T^o enthalpy of reaction; ΔS_T^o entropy of reaction; S_T^o entropy of S_x molecule; $\Delta H_v H_o^o$ entholpy of vaporization of S_x molecule.

Molecule	Equilibrium Reaction	Temperature °K	ΔH_T^o kcal mol^{-1}	ΔS_T^o cl mol^{-1}	$S_T^o(S_x)^a$ cl.mol^{-1}	$\Delta_v H_o^o$ keal mol^{-1}
S_2	$2S(s) \rightleftharpoons S_2(g)$	460 to 670	28.08±0.35	32.6	59.6 (565°K)	30.86±0.35[b]
S_3	$2S_3(g) \rightleftharpoons 3S_2(g)$	566 to 669	26.6±2.0	(37.6±3.0)	(71.8±1.5)(618°K)	33.3±1.3
S_4	$S_4(g) \rightleftharpoons 2S_2(g)$	615	28.2±2.0	(36.7±2.5)	(83.9±2.5)(615°K)	33.5±2.2
S_5	$2S_5(g) \rightleftharpoons 5S_2(g)$	565 to 620	95.5±4.0	(111.4±8.0)	(94.3±4.0)(592°K)	29.1±2.5
S_6	$3/4S_8(g) \rightleftharpoons S_6(g)$	435 to 625	6.26±0.33	7.6±0.8	(101.6±3.3)(512°K)	24.8±2.7
S_7	$7/8S_8(g) \rightleftharpoons 4S_2(g)$	435 to 625	5.77±0.31	7.2±1.0	116.9±3.8 (512°K)	28.1±2.7
S_8	$S_8(g) \rightleftharpoons 4S_2(g)$	460 to 625	96.8±2.2	110.2±4.2	126.8±4.2 (530°K)	26.0±2.7

a. The value for S_6, S_7 and S_8 were calculated from experimental data and the literature value for the entropy of S_2. For S_2, S_3, S_4, S_5 statistically calculated entropy values were used.

b. Literature value: H_o^o = 30.81 kcal mol^{-1}.

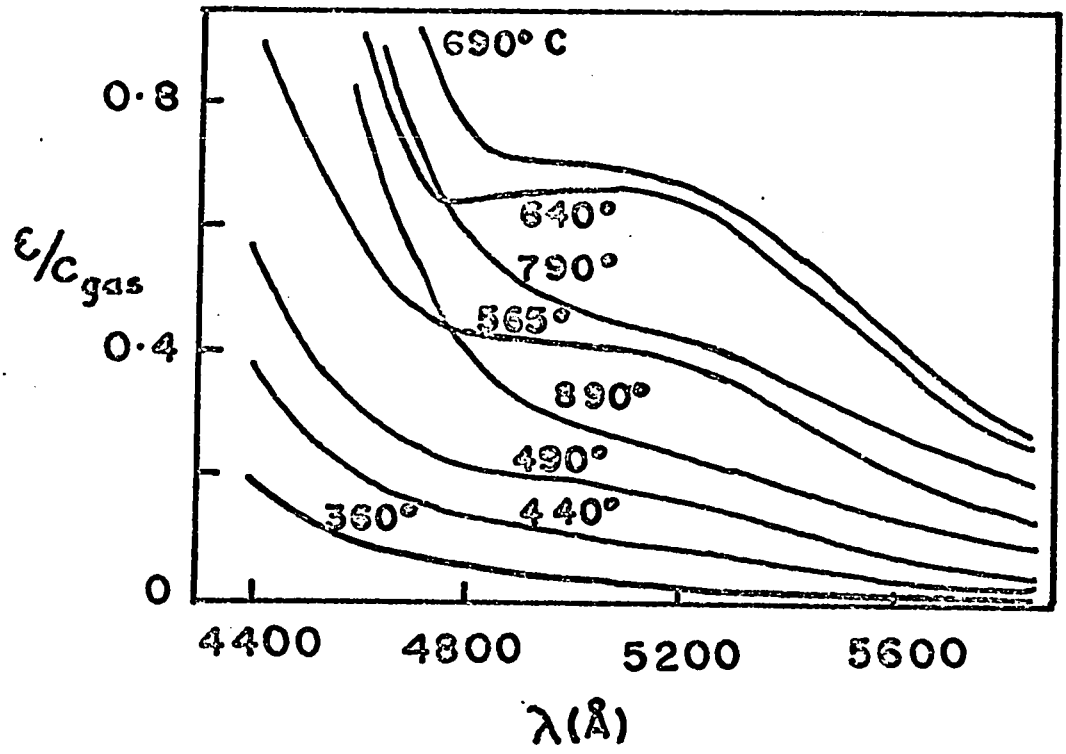


Fig. 10b. Spectrum of sulfur vapor, ref.(20)
(concentration: 1060 mg/l)

weight of the vapor. This species and its spectrum are not yet well known and it is not clear whether it is a chain or a ring. However, it could explain at least part of the absorption spectrum. Erdmann, 1908 (21) suggested that at 160°, thiozone is formed. Kellas, 1918 (22) deduced the existence of S_{18} from surface energy measurements.

Molecules with odd number of sulfur atoms are yet less known. If these consist of open chains they are expected to be deeply colored because they contain two only partly bound electrons. It should be pointed out that the concentration of free radical chains in liquid sulfur is much less than expected. This has so far been taken as an indication that open sulfur chains are not present in significant quantities. However, recent theoretical calculations (23) indicate that chains may very well be present, because in chain the free electron can stabilize by resonance or by charge-transfer complex formation with S_8 rings. At higher temperatures the chains are destabilized and a more mobile electron system results. This might account for the increase in absorption with rise in temperature. A complete identification of the species will not be possible until each species is isolated. At present, attempts are being made (24) to synthesize unusual sulfur rings, and S_7, S_{10}, S_{12} and S_{24} have been prepared. However, the species of prime interest to us are not stable

enough to prepare under normal conditions. They will have to be made in low temperature matrices.

6. Conclusion

Although polymerization influences most physical properties of liquid sulfur, it does not account for color. Polymeric sulfur separated from liquid sulfur by quenching shows yellow color whereas liquid sulfur at high temperatures is dark red. Moreover, the color of the vapor which is similar to that of the liquid cannot be explained as due to long chain species. The color may be attributed to small molecules S_x, $2 < x < 10$, whose concentration is a function of temperature. These cannot be cyclo S_8, cyclo S_6 or S_2 because the absorption spectra of these molecules do not agree with the spectrum of liquid sulfur. It could be one or several other species such as S_3, S_4, S_5, etc.

However, new species alone are not sufficient to explain the spectrum. The overall absorption is a function of both temperature and molecular composition. Only the temperature aspect had been considered by former workers. This study places emphasis upon the molecular composition of the liquid in explaining the spectrum.

Further Remarks

A few explanations for discrepancies in previous results may be given. Different shift rates could result from measuring shifts from different parts of the absorption edge. For example, the lower parts of the edges tend to merge together and hence the shift in this region would be less. Reliable results could be obtained only if the middle parts of the edges, where they are straight and parallel, are considered. In a thick specimen, this part is far above the limits of the instrument. The anomalous shift rate is not conspicuous in the lower parts of the absorption edges. Rupture of the film is another cause of incorrect results. Many earlier workers were mistaken about the color change thinking it had resulted from impurities. This was partly justifiable because high purity sulfur was not available until 1943 (14). The purity grade used here was quite satisfactory for the study of liquid sulfur. This was verified by a study of infrared spectrum, described in the next section.

B. Infrared Spectrum of Liquid Sulfur

1. Introduction: Previous work

The first IR spectrum of liquid sulfur was obtained by Taylor and Rideal, 1927 (25). These authors measured the spectrum of the liquid at 25°C in a wavelength range from 2

to 15 μ . They found that the spectrum was similar to that of the solid but the absorption bands were extended and slightly shifted towards shorter wave lengths. Srb and Vasko, 1963 (26) studied the spectrum up to 25 μ (400 cm^{-1}) using KBr windows, at temperatures 153, 252, 313 and 396°C. Greenhouse and Strauss, 1964 (27) re-examined the same region at temperatures 95 - 130°C and 187 - 192°C.

2. Purpose of the present work

The main purpose of this study was to extend the spectral investigation to 200 cm^{-1}. In the previously studied range (4000 - 400 cm^{-1}) band positions showed agreement for the solid and the liquid spectra (27). Similar confirmation was expected from this study for the 400 - 200 cm^{-1} range. Band positions for solid orthorhombic and solution phases in this range are known (44).

A re-investigation of the higher frequency range was considered necessary for the following reason: Srb and Vasko (13) reported a parasite absorption band at about 1100 cm^{-1} in the spectrum of the surface layer of the cell window (KBr) used for the study of liquid sulfur above 300°C. This band has not been reported by other workers. It was therefore decided to investigate whether this band was due to any reaction product.

3. Experimental

Infrared cell

The cell designed for the purpose was essentially a modification of the infrared cell described by Wiewiorowski et al. (28). The essential improvement was in the spacer which held the liquid specimen. Figure 11 illustrates the cell assembly. It consisted of two cesium iodide windows (2" dia. X $\frac{1}{4}$" thick), a spacer (an open Teflon O-ring, 1/16" thick, 1" i.d.) and two heating blocks. The O-ring spacer was found to be superior to a flat metallic plate to hold liquids. Aluminum rings cut from tubing (not shown in Figure 11) served to separate the supporting plate from the heating block near it. Fire-rod heaters (115V, 300 W) were used in a heating block. Temperature was controlled by a variac and measured by chrome-alumel thermocouple and potentiometer.

I.R. Spectra

The cell was filled with sulfur (spectroscopic grade) and placed in the sample beam of a Perkin-Elmer Model 225 Infrared Grating spectrophotometer. The specimen was heated slowly to melting. More sulfur had to be added to make up for incomplete filling and for loss from any leakage. Temperature was kept steady at about 135°C for about 30 mins. and the spectrum was scanned in 4000 - 400 cm^{-1} and 400 - 200

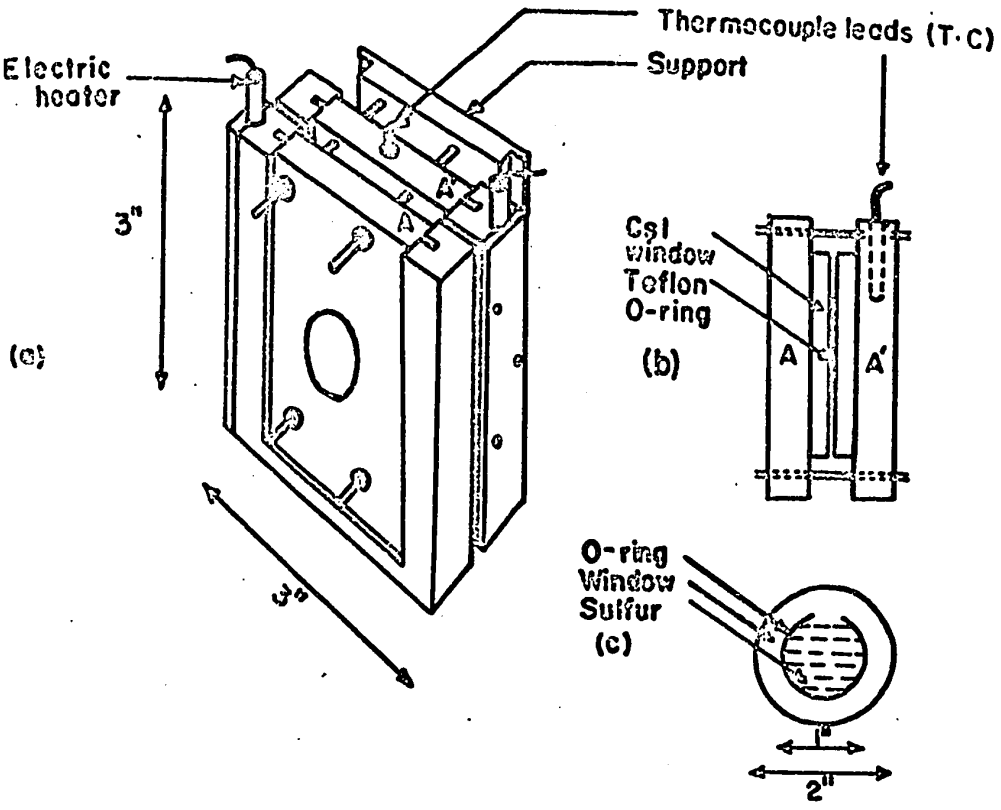


Figure 11. Infrared Cell for the Study of Liquid Sulfur

cm^{-1} ranges. Another spectrum was scanned at 190°C.

The cell windows remained clear at 135°C but when heated to 190°C, they became yellow on the surface in contact with liquid sulfur. When the cell was cooled down to room temperature, a slight yellow color still persisted. The spectrum of the window was recorded. In another experiment, a CsI crystal was heated with sulfur above 200°C for 15 minutes . This crystal became permanently colored deep yellowish-brown. Some parts of the crystal were colored light pink. The spectrum of this crystal also was recorded.

4. Results and conclusion

1. 1600 - 400 cm^{-1} region

(a) Absorption bands due to sulfur

Figure 12 is a typical spectrum of liquid sulfur at 130°C. All the peaks could be identified as due to sulfur by comparison with previous data (27). Hence, this aspect need not be discussed further. The 4000 - 1600 cm^{-1} region is omitted in the display. Only a small peak due to sulfur could be identified in this region (at 2919 cm^{-1}). The peaks were broader for the liquid than for the solid. Further broadening was observed in the spectrum at 190°. This is assumed to be a thermal effect, discussed elsewhere. Peak positions became less definite due to the broadening effect but

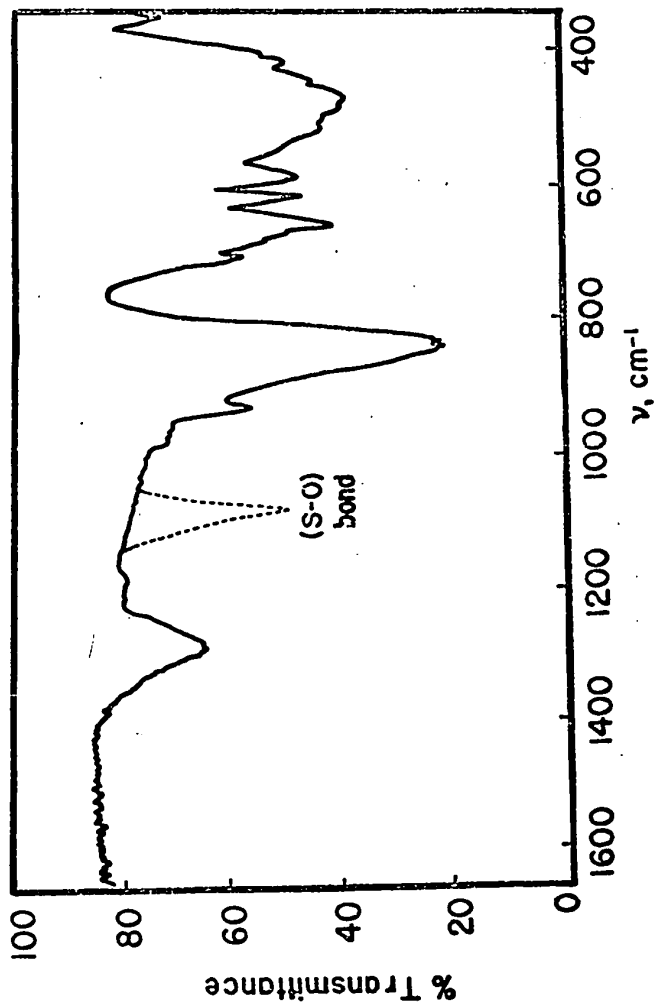


Figure 12. Infrared Spectrum of Liquid Sulfur at 130°C. Sample Thickness: 1.6 mm. Dotted lines Represent S-O Band Appearing at 190°.

there was no appreciable shift.

(b) Other absorption bands (Figure 12)

A strong band at 1088 cm^{-1} appeared in the spectrum when the specimen was heated to 190°C. This band persisted on cooling the specimen, but was less intense. The same band appeared as a highly intense and broad peak for the CsI crystal treated with sulfur above 200°C. In this case, a peak of low intensity could be found at 1600 cm^{-1} in addition to the strong peak. An attempt is made below to identify these bands.

(c) Identification of the parasite bands

It was mentioned in the introduction that a previous worker (13) had observed a parasite absorption band at 1100 cm^{-1} when liquid sulfur was studied above 300°C using KBr windows. The presently observed band (at 1088 cm^{-1}) confirms the possibility of such a band.

Among the various possible causes for a peak at this position, the most logical one was to associate it with a reaction product between sulfur and oxygen. This was justified for the following reasons:

(i) Sulfur reacts with air to for SO_2 in the temperature range studied.

(ii) SO_2, SO_3, SO_4 -- and SO_3 -- have absorption bands in the range 1000 - 1200 cm^{-1}. SO_2 and SO_3 bands are at 1151 cm^{-1} and 1069 cm^{-1} respectively (29). These bands do not agree with the observed band; other bands due to SO_2 and SO_3 could not be identified. Moreover, these compounds are gases at the temperature studied.

SO_3^{--} and SO_4^{--} have absorption bands in 1070 - 1100 cm^{-1} region. Miller and Wilkins (30) studied the infrared spectra of several sulfites and sulfates, including those of alkali metals Li, Na and K. Among the alkali metal sulfites, potassium sulfite has a band at 1100 cm^{-1}. Calcium sulfite and zinc sulfite also have this band. For Barium sulfite the band is at 1070 cm^{-1}. A few other bands are also present for SO_3^{--} of which a band in 1625 - 1645 cm^{-1} region is worth mentioning because in the present spectrum a weak band at 1600 cm^{-1} was observed. However, the presence of SO_3^{--} was not established because the characteristic band of SO_3^{--} is in the 900 - 950 cm^{-1} region. This band was not observed in the spectrum of the cell window.

Another possibility is SO_4^{--}. A strong absorption band at 1110 cm^{-1} has been observed for Li, Na and K sulfates. (17). These sulfates do not show a band in 900 - 950 cm^{-1} region. For heavier metals, the 1100 cm^{-1} band is shifted to 1080 - 1090 cm^{-1}. A weak band in 1600 - 1630 cm^{-1} is present

for sulfates.

These considerations lead us to the conclusion that the 1088 cm^{-1} and the 1600 cm^{-1} bands are probably due to sulfate ion. Since Cesium is a heavy alkali metal, the band position for cesium sulfate should be in the region 1080 - 1090 cm^{-1}. This was found to be the case. A possible reaction to form the sulfate is discussed in the next section.

(d) Further investigations on the reaction products

The CsI crystal treated with sulfur above 200°C was dissolved in water. The solution acquired a pale yellow color. Test with starch solution showed the presence of iodine (as I_3^-). A UV spectrum of this solution agreed with that of KI_3 solution (Chapter VIII). A test with barium chloride solution showed the presence of a trace amount of SO_4^{--}. Free iodine was observed visually in the crystal of CsI. Traces of sulfur particles settled down from the aqueous solution when the window was dissolved.

To account for these observations, the following reactions are suggested:

(i) $S + O_2 = SO_2$ (liquid phase)

(ii) $2\ SO_2 + 2\ I^- = S + SO_4^{--} + I_2$ (on surface layer of crystal)

It can be seen that part of the sulfur is regenerated. An alternate course for (ii) can be:

$$3\ SO_2 + 2\ I^- = S + 2\ SO_3^{--} + I_2$$ (reversible at lower temperature)

$$2\ SO_3^{--} + O_2 = 2\ SO_4^{--}$$

The possibility of reaction between SO_2 and CsI was tested by heating a small piece of CsI crystal in a flask containing pure SO_2. Above 140°, violet vapors of iodine filled the flask, and the crystal was slowly colored pale yellow. Further analysis was not carried out. It is easy to understand why a band at 1100 cm^{-1} was observed when KBr window was used. A similar reaction could be visualized in this case, with the liberation of bromine. K_2SO_4 would also be formed. This reaction takes place at a higher temperature because Br^- is less easily oxidized than I^-. The position of K_2SO_4 band is at 1110 cm^{-1} and agrees with the observed location. Formation of SO_4^{--} peak is unlikely if a NaCl window is used because SO_2 cannot oxidize Cl^-. No such peak has been observed.

5. 400 - 200 cm^{-1}

About eleven absorption bands were observed in this region. All these bands were also identified in the spectrum of sulfur crystal (Chapter II).

Figure 13 is a typical spectrum of liquid sulfur at 130°C. Shoulder peaks due to water vapor are not shown. The

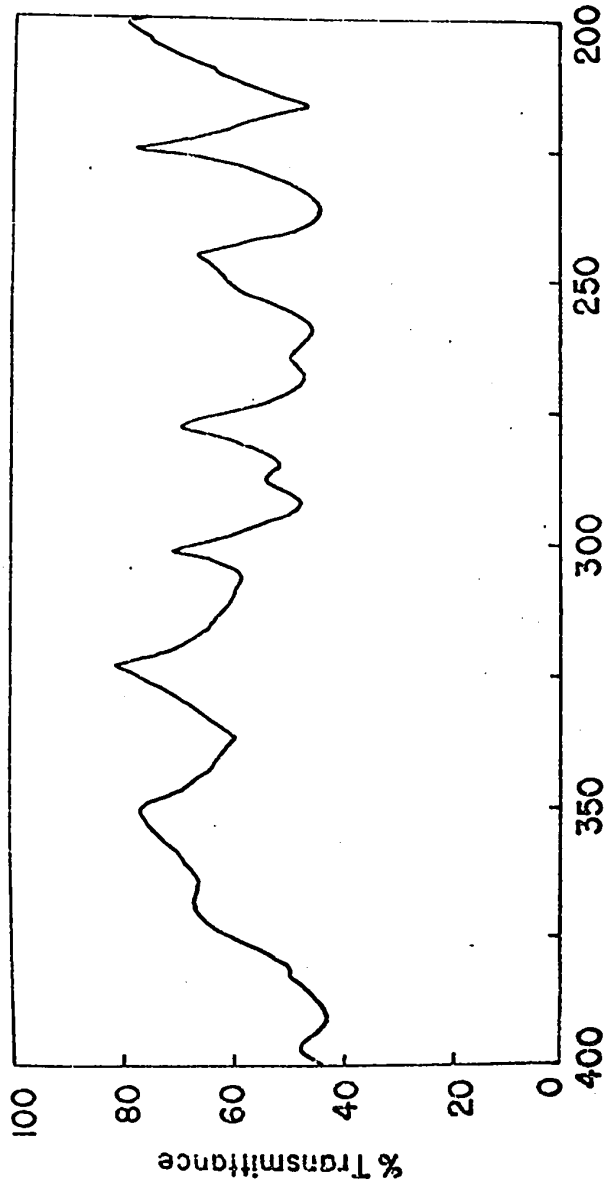


Figure 13. Far Infrared Spectrum of Liquid Sulfur, 130°C. Sample Thickness: 1.6 mm.

spectrum at 190°C was similar but the peaks were broader. No shift could be noticed for the peak positions.

The positions of peaks in this region for the temperature rang 130 - 190°C were (cm^{-1}):

216, 238, 260, 270, 285, 293, 306, 331, 343, 379 and 389

An assignment of these peaks will be given in the next chapter.

Comparison with previous data is not possible because this region has not been studied before for liquid sulfur. The results obtained, however, are in agreement with those obtained for other phases, such as the crystal and the solution.

The study of the infrared spectrum of liquid sulfur confirms that the predominant molecular species in the liquid below 200° is cyclo-S_8 molecules, as in the solid. The broadening of the peaks can be attributed to interaction with neighboring molecules, in addition to thermal effects.

Summary

A spectroscopic study of liquid sulfur was described in this chapter. Absorption in UV, Visible and infrared regions were studied.

The UV-VIS spectra were recorded as a function of temperature from the melting point of sulfur to 300°C. An incomplete spectral study was conducted from 300 - 700 °C. The extremely high absorption in the UV region could be recorded

by using a thin cell (ca. 160 μ) and neutral density filters. Absorption was found to be broad in the UV region. The absorption edge was found to shift towards longer wavelengths at an average rate of 5.76 A/°C. The shift was abnormal in the 160 - 200°C temperature range (Figure 6). The abnormal rise in absorption at 160° is possibly related to the appearance of a small molecular species, formed in the liquid. The color of liquid sulfur at high temperature may be due to small molecules rather than to long polymers in the liquid because of at least three reasons: (1) the vapor has the same color as the liquid (2) polymeric sulfur is not red and (3) the chain length decreases after 190° but absorption continues to increase.

Infrared spectra were studied at 135° and 190°C. The low frequency region (400 - 200 cm^{-1}) was studied for the first time. A parasite absorption band at 1088 cm^{-1} was observed at 190°C which persisted on cooling. This could be attributed to SO_4^{--} ion, formed possibly from SO_2 reacting with CsI window.

Suggestions for Further Work

A very useful project is the study of reactions in or with liquid sulfur. Infrared spectroscopy is more suitable for this purpose because absorption bands are better

identified. Wiewiorowski (31) has studied a few systems such as H_2S - S, SO_2 - S, CS_2 - S and H_2S-SO_2 in molten sulfur. Reactions of carbon, oxygen and halogens with sulfur could be attempted. The best region of the spectrum for such studies would be 4000 - 1400 cm^{-1} because sulfur is almost free of absorption in this frequency range.

A second suggestion is the investigation of the transition point (160°) when impurities are added to sulfur. Recent work by Ward and Myers (32) has shown that addition of 2 per cent (by weight) of arsenic lowers the transition point to about 122°C. The effect on the spectral shifts could be investigated by studying the absorption edge of the optical spectrum when such impurities are added. For a preliminary study, arsenic, selenium and carbon could be used as impurities.

CHAPTER II

SPECTRA OF SULFUR CRYSTAL

Introduction

The present chapter describes a spectroscopic study of sulfur in the solid state. On account of the more ordered state of the solid, the spectrum is expected to be simpler than that of the liquid. In the liquid drastic structural changes take place at different temperatures whereas in the solid, under the conditions used very little structural change is observed. However, certain common features in the spectra are expected because both are condensed phases and contain cyclo S_8 species.

Previous Work on Spectra of Single Crystal of Sulfur and Scope of the Present Work

Spectroscopic work on sulfur crystal has been confined to infrared and Raman spectra. The first infrared spectrum of orthorhombic sulfur was taken by Coblentz in 1905 (33) and the first Raman spectrum by Krishnamurti, in 1930 (34). The latest available data indicate that the spectrum has been studied down to 100 cm^{-1} (35).

The UV-VIS absorption spectrum of sulfur crystal has not been reported. Possible reasons are:

1. Highly intense absorption in the UV-VIS region.
2. Difficulty in preparing thin crystals of high purity.

The present work was intended mainly to record the spectrum in the UV-VIS region. A low temperature study was also planned, since preliminary investigation revealed that the color of sulfur crystal is lost upon immersion in liquid nitrogen. Infrared study was conducted for two reasons:

1. To examine the presence of solvent (CS_2) in a freshly prepared crystal and to observe the effect of degassing the crystal.
2. To observe the spectrum in the low frequency region (400-200 cm^{-1}) for a crystal exposed to atmosphere and to note the changes when air and water vapor are removed from the environment of the crystal. It was suspected that the published data (35,36) did not take into account the effect of atmospheric contamination.

A. UV-VIS Spectrum of a Single Crystal of Sulfur At Room Temperature

Preparation of the crystal from CS_2 solution

Two methods were used to obtain a thin, pure crystal. First, a tiny seed crystal was grown in a nearly saturated solution of sulfur in CS_2 (Baker Analytical grade). The crystal was allowed to grow with one face (111) resting on the bottom surface of the container. A 2 cm. long, 2.5 mm. thick crystal thus obtained was polished on smooth carborundum papers to a thickness of ca. 1 mm., and finally washed with CS_2

liquid. Secondly, a shallow pool of nearly saturated CS_2 solution was slowly evaporated. The crystals obtained were thin (ca. 0.2 mm.) and clear but too small for the present purpose.

The crystal prepared by the first method was used for this study. Further polishing was not attempted since the crystal showed tendency to break. A second reason will be given at the end of the next section.

UV-VIS Spectrum

The crystal was supported on a holder in the sample beam of a Cary 14 Model Spectrophotometer and the spectrum was scanned from 2400 Å to 6500 Å. The absorption was found to be too high (above 2 O.D.); only the absorption edge could be recorded. Neutral density filters were used at this stage to record the absorption. The use of these filters was preferable to the use of a thinner specimen because on reduction of crystal thickness the absorption was not decreased correspondingly. Moreover, preparation of a very thin crystal involved the risk of fracture of the crystal.

Results and conclusion

Figure 14 shows the spectrum of a fresh crystal of sulfur from CS_2 solution. The lower portion of the absorption edge is not shown for convenience. The absorption edge

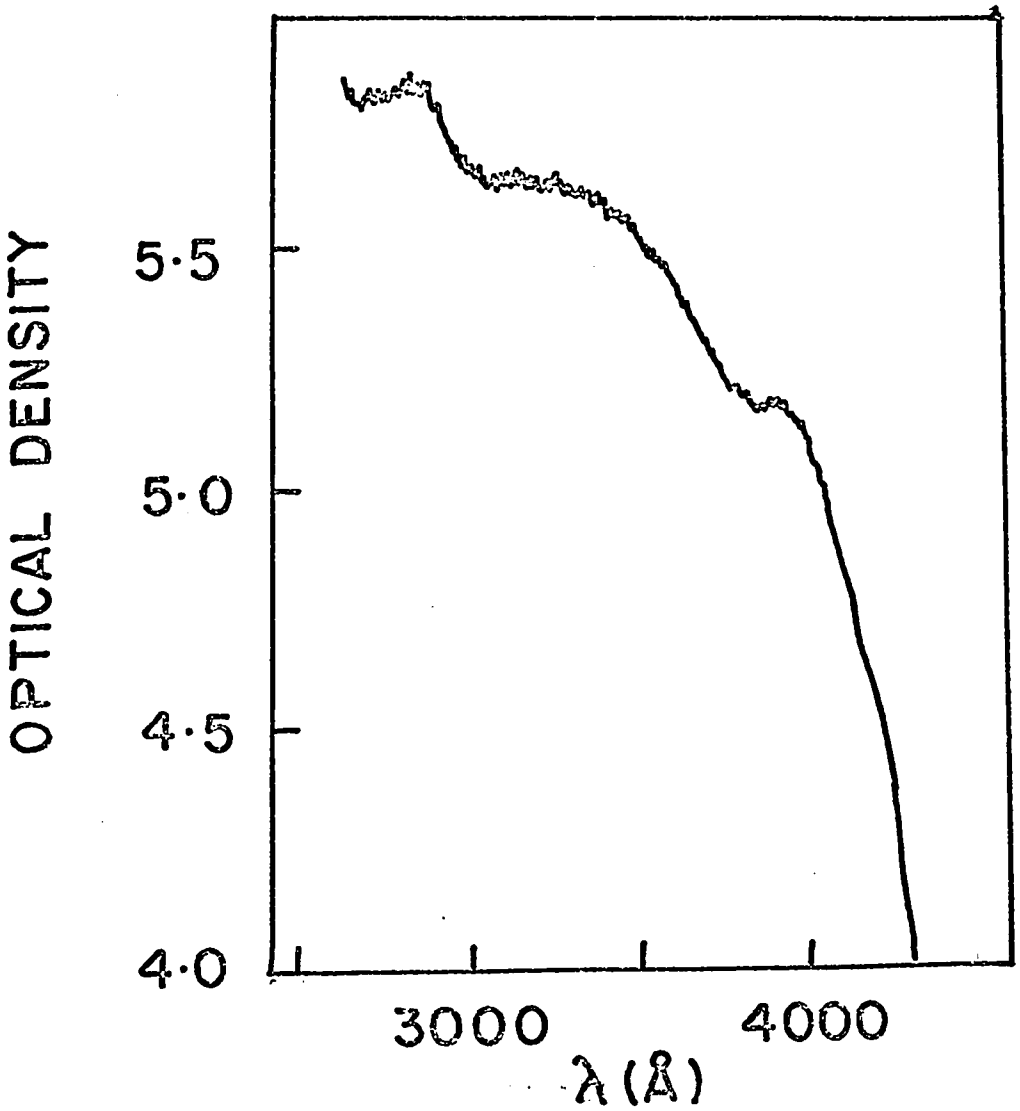


Figure 14. Spectrum of a fresh sulfur crystal, 1.4 mm thick.

Was straight and steep, rising almost abruptly from zero absorption at about 4400 Å. Absorption in the region 2600 - 4000 Å is broad, but shows faint maximum around 2800 Å, as expected for S_8 species. The broad nature of the absorption is perhaps due to interaction of S_8 molecules with neighboring S_8 molecules in the condensed state. It was suspected that the crystal contained some trapped CS_2. Characteristic absorption bands of CS_2 in the 3000 Å - 3400 Å region are known from a study of the vapor (Figure 24). The shoulder in the absorption between 3000 Å and 4000 Å is supposed to be the result of superposition of CS_2 and sulfur spectra. When the crystal was degassed, this shoulder disappeared and a smooth, broad absorption resulted (Figure 16). The infrared spectrum of the crystal (section D) confirmed the presence of CS_2.

B. UV-VIS Spectrum, 76°K.

The loss of color when a sulfur crystal was cooled to liquid nitrogen temperature was already mentioned. This phenomenon was more carefully studied spectroscopically.

Experimental

Sulfur crystal. Preparation has been described in Section A.

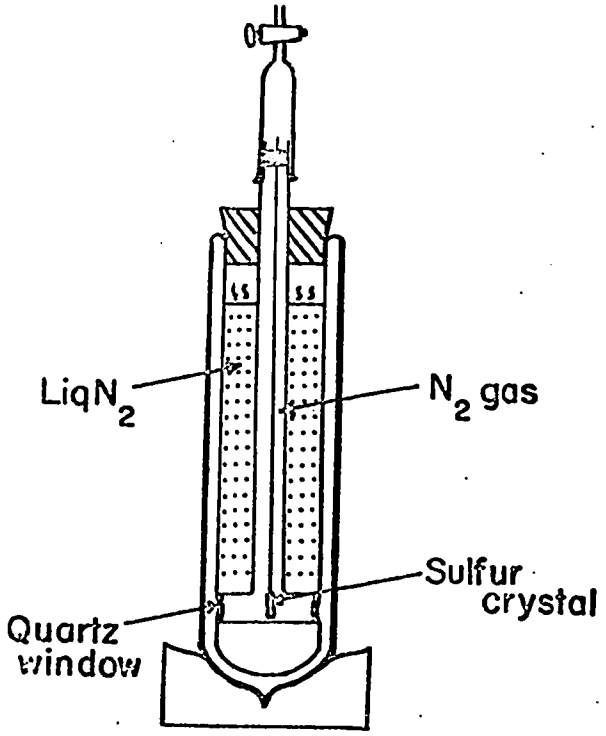


Figure 15. Low Temperature Cell Equipment for the Study of Sulfur Crystal.

Low temperature cell. The cell (Figure 15) is essentially a specially adapted Dewar flask. The sulfur crystal was supported in the optical path as shown. The inner tube incorporating the cell was evacuated and closed. This ensured the removal of oxygen in the space above, and CS_2 in the crystal (to the extent that it was not detected in the spectrum). The tube was filled with nitrogen gas at ordinary pressure. The crystal was cooled slowly to 76°K. Spectra were scanned at room temperature and at liquid nitrogen temperature (ca. 76°K), using a Cary 14 H Model spectrophotometer. Neutral density filters (Chapter I) were used to scan the high absorption region.

Results and conclusion

Spectrum at room temperature and 76°K are shown in Figure 16 for a crystal of 1.4 mm thickness. The absorption edge was at about 4500 Å at room temperature and accounts for the familiar yellow color of sulfur. At 76°K, the edge was shifted to about 3950 Å, in the UV region. This shift explains the loss of color on cooling (the color reappears on warning to room temperature). Tiny fractures appeared on cooling. This explains the slight opaqueness in the previously transparent regions of the spectrum. Absorption in the 2800 - 4000 Å region was still broad. The 2600 - 2800 Å

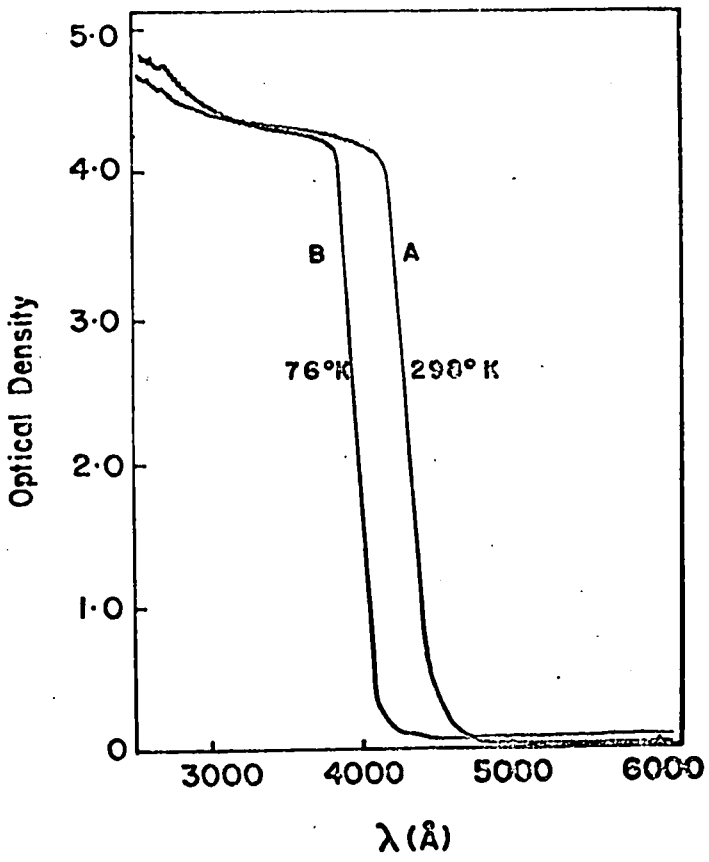


Figure 16. Spectrum of sulfur crystal at 76°K

region showed increased absorption at low temperature.

These results are anticipated from the general observation about temperature dependence on absorption discussed elsewhere (Chapter I). The reappearance of the color on warming confirmed that the change was reversible and temperature-dependent.

C. Spectrum of Sulfur Film

This experiment was conducted to verify the results obtained when a crystal was used. Elaborate pieces of equipment were not necessary. A small quantity of sulfur was placed in between two flat quartz plates and melted by slow heating. The plates were pressed together and then allowed to cool to room temperature. Tiny crystals of sulfur appeared as a translucent coating on the plates. The spectrum of the film is shown in Figure 17.

This spectrum resembles that of the crystal and confirms the broad nature of absorption in the UV region in contrast with the absorption of S_8 monomers in solution.

D. Infrared spectrum of Sulfur Crystal from CS_2 Solution

The purpose of studying the IR spectrum was stated earlier. Details of the experimental procedure and a discussion of the results will be presented in subsequent sections.

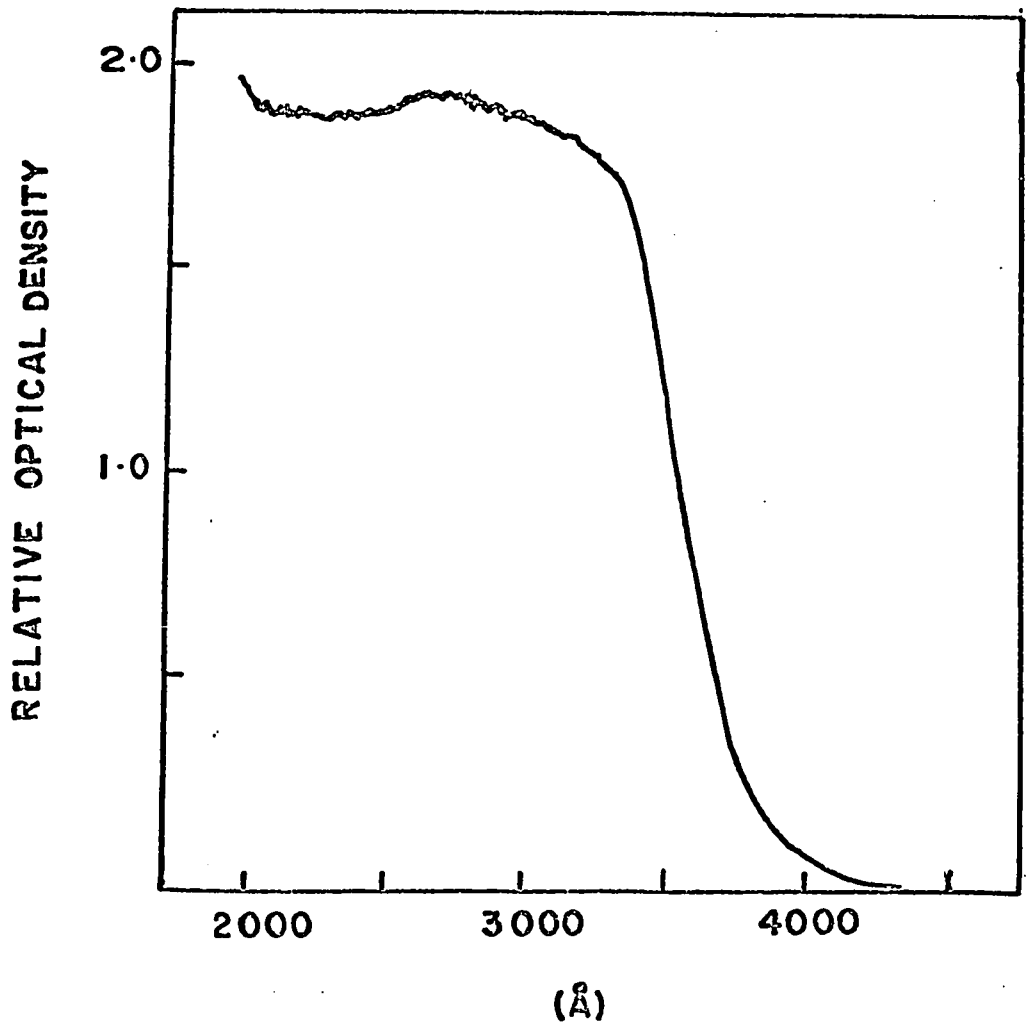


Figure 17. UV-VIS Spectrum of a Thin Film of Sulfur at 25°C.

Experimental

Sulfur crystal. Preparation has already been described (Section A). A crystal of 1.4 mm. thickness was used. The same crystal was degassed for 24 hours in vacuum to observe the effect of removal of solvent.

IR spectrum

Recording was made on a Perkin-Elmer 225 Grating Infrared Spectrophotometer. The crystal was mounted on a holder provided with a slot and was placed in the sample beam. An identical slot was cut in another holder placed in the reference beam. Spectrum was scanned from 4000 - 400 cm^{-1}. The low frequency region, 400 - 200 cm^{-1} was scanned separately for higher resolution. Other experimental conditions were different for each spectrum and are given below:

1. Sulfur crystal, freshly prepared, from CS_2 solution.
2. Sulfur crystal, degassed for 24 hours in vacuum.

Results and conclusion

Figure 18 shows the spectrum of sulfur crystal. The region 4000 - 1600 cm^{-1} is omitted because this region was free of absorption except for a small peak at 2919 cm^{-1}, attributed to sulfur (37). The remaining part is divided into three sub-regions:

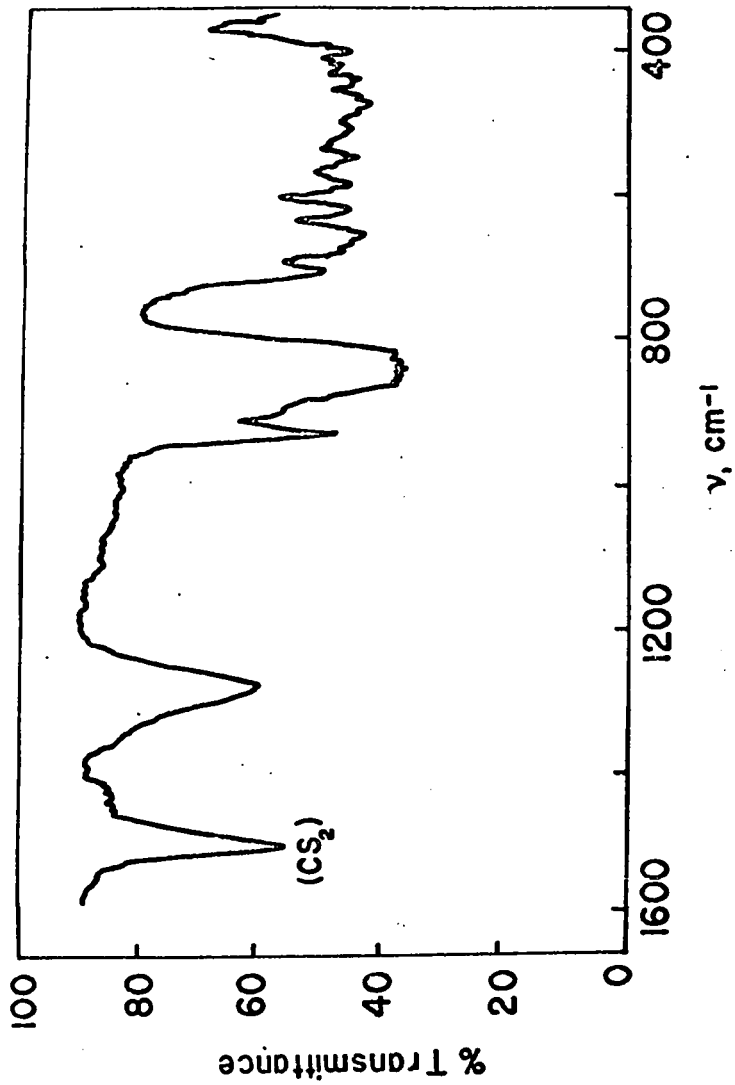


Figure 18a. Infrared Spectrum of a Fresh Sulfur Crystal from CS_2 Solution. Thickness: 1.4 mm.

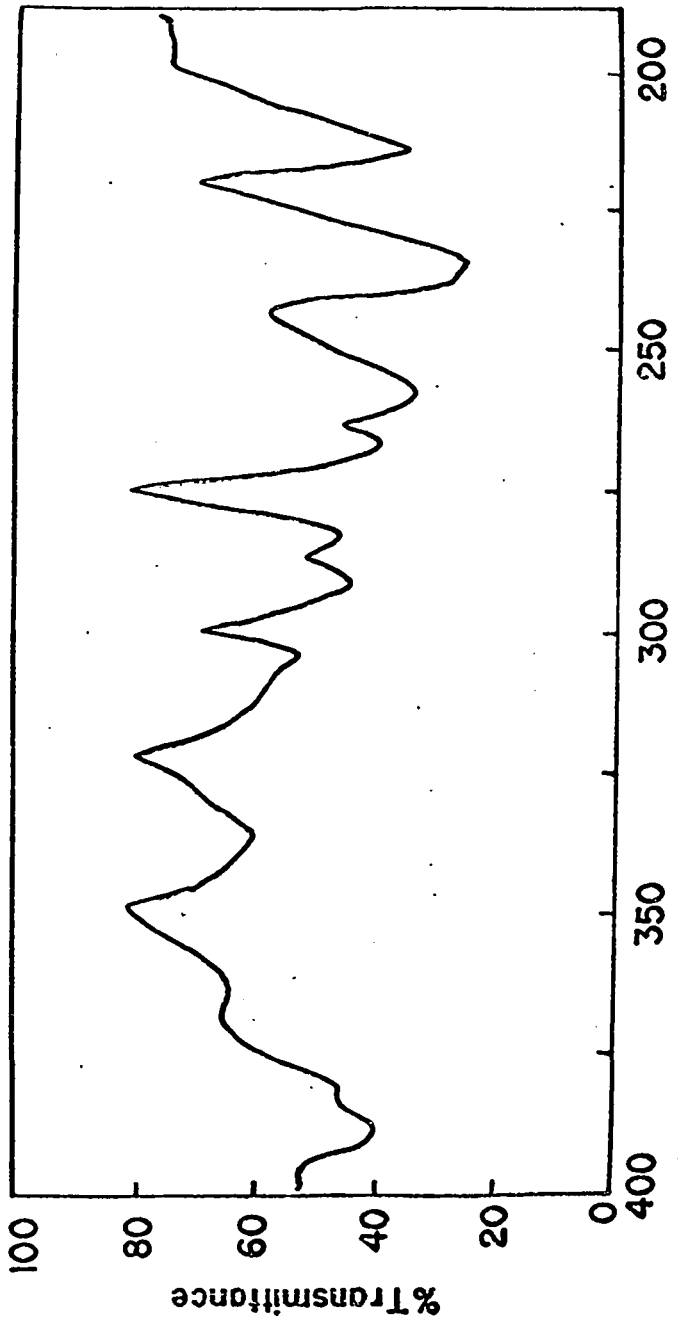


Figure 18b. Far Infrared Spectrum of Sulfur Crystal Thickness: 1.4 mm.

(i) 1600 - 1400 cm^{-1}.

An intense peak was observed at 1510 cm^{-1} for the fresh crystal and a faint one at the same position for the degassed crystal. A natural orthorhombic crystal does not show this peak (38). Hence this peak was suspected to be due to CS_2. Earlier investigators have reached the same conclusion. The spectrum of pure CS_2 consists of a few peaks of which the most intense is found at 1523 cm^{-1} (39,40). This is identified with the presently observed peak.

The effect of degassing was seen in the considerable weakening of the solvent peak (by about 95 per cent). Complete removal of the solvent could not be achieved. Hence crystallization from CS_2 is not a good method to obtain very pure sulfur.

(ii) 1400 - 400 cm^{-1}.

The various peaks in this region (about 15) were all found at positions confirmed by previous investigations (37). This region did not show clearly one of the peaks due to CS_2 (at 656 cm^{-1}). A spectrum of pure CS_2 (40) shows that this peak is much less intense than the 1523 cm^{-1} peak. A second reason could be that the strong 659 cm^{-1} peak due to S_8 masked the 656 cm^{-1} peak of CS_2. It is also possible that the peak was shifted from its expected location. In any

case, CS_2 in the crystal could not be identified with the help of this peak.

(iii) 400 - 200 cm^{-1}.

This region of the spectrum contained about 12 peaks (Figure 18b). The observed peak positions were: (cm^{-1})

215, 237, 258, 270, 284, 292, 305, 330, 343, 360, 378 and 388.

When the instrument was not dry the spectrum contained many shoulder peaks. These were recognized as due to water vapor because they disappeared when the instrument was dried (41).

The only other contaminant that could give absorption peaks was CS_2. A vibrational peak at 396.7 cm^{-1} has been reported for this molecule. (42) The intensity of this peak is low and therefore an exact location was not possible. Rotational peaks are not expected for CS_2 because it is a symmetrical linear molecule (42).

It is interesting to compare the present spectrum with those obtained by previous workers. Barnes, 1932 (43), reported bands at 400 cm^{-1}, 267 cm^{-1} and in 250 - 200 cm^{-1} region for a natural crystal of sulfur. The band positions were not clear or definite. Catherine MacNeill studied the spectrum of sulfur crystal from CS_2 solution and reported the results for the 400 - 350 cm^{-1} region in 1963 (36) and for the 350 - 100 cm^{-1} region in 1969 (35). Band positions

estimated from the spectrum are: 380, 340, 294, 272, 248, 244, 227 and 208 c,$^{-1}$. These peaks resembled peaks in the present spectrum but the positions were 8 to 12 cm^{-1} lower. This could be an experimental error. Another observation is that the intensity of these peaks are appreciable. Hence sulfur is unsuitable as a window material for infrared studies. A peak at 388 cm^{-1} has been reported by Strauss and Greenhouse (37) in the infrared spectrum of orthorhombic crystal.

Spectra of sulfur in other phases are also known. The solution phase was studied by Scott et al. (44) in 1964. Only one peak could be observed in the 400 - 200 cm^{-1} region, at 243 cm^{-1}. Comparison with peaks in the higher frequency region shows that in the crystal, peaks are shifted to lower frequencies by about 6 cm^{-1} (reference (44) for comparative table). Assuming a similar shift in the low frequency region, the position of the peak would be at 237 cm^{-1}. In fact a strong peak at this frequency was observed in the sulfur spectrum. Absence of other peaks suggests that higher concentration is required for the appearance of the weaker peaks.

Evidence obtained from a study of liquid sulfur was presented in Chapter I.

A tentative assignment of the various peaks in the low frequency region for sulfur crystal and liquid sulfur is given in Table I. This is based on the fundamental vibrational modes

TABLE III

ASSIGNMENT OF PEAKS IN SULFUR SPECTRUM
($400 - 200^{-1}$)

Band Positions Cm^{-1}	Assignment*
215	215
237	243
258	86x3
270	216+152
284	191+86
292	?
305	152x2, 216+86
330	86+243
343	152+191
360 ?	?
378	191x2
388	152+243

*based on Cyclo-S_8 Fundamentals, Reference (45)

a_1	475,218 cm^{-1}
b_1	411
b_2	243
e_1	471,191
e_1	475,152,86
e_3	437,248

of S_8 molecule, worked out by Scott et al. from a study of the infrared and Raman spectra (45). The fundamental modes selected for the assignment are: (cm^{-1})

86, 152, 191, 216 and 243.

Strict selection rules forbid the appearance of some of the peaks in the infrared region. In practice, however, Raman active fundamentals appear in infrared spectrum and vice versa. Explanations have been given for the breaking down of the selection rules (42). Observed Raman frequencies in the region are 216 cm, 248 cm^{-1} (46).

Summary

The UV-VIS and infrared spectra of sulfur crystal prepared from CS_2 solution were studied. The results obtained from the former indicated that UV-VIS absorption of a crystal is broader than the absorption of a dilute solution. This was attributed to the condensed environment in the crystal where absorption may be influenced by neighboring molecules.

Low temperature study of the optical spectrum confirmed the general assumptions about the temperature dependence of absorption.

Infrared studies proved a useful method of testing the presence of CS_2 in sulfur crystal. The spectrum of low frequency region (400 - 200 cm^{-1}) was re-examined. A number of

well defined peaks observed were assigned on the basis of the fundamental vibrational modes of S_8 molecule.

Suggestions for Further Work

Sulfur crystals grown from other solvents can be studied for solvent inclusion effects. A temperature dependence study can be carried out in the region of the absorption edge. Any unusual shift of the edge would be interesting. The only known, definite change in the solid phase between room temperature and melting point is the phase transition, rhombic $\overset{95.5°C}{\rightleftharpoons}$ monoclinic (47). Whether this can give rise to an abnormal shift might be examined.

CHAPTER III

COLORED ALLOTROPES OF SULFUR

Introduction

Sulfur is known to exist in several molecular states and allotropic forms (48). At least five well defined molecular species can be prepared. These are: the atom, disulfur, cyclohexasulfur, cyclooctasulfur and cyclododeca sulfur. (48) In a previous chapter reference was made to the existence of several other molecular species (Chapter I). In the vapor, for example, molecules S_2 through S_{11} have been observed. Liquid sulfur at high temperature contains an appreciable amount of many catena forms. In solid state, the same molecular species may exist in different crystalline forms as in the case of S_8 (orthorhombic and monoclinic).

In this chapter, species formed at high temperatures alone are considered. These are generally obtained from liquid sulfur or sulfur vapor. The change in color of liquid sulfur from yellow to red was attributed partly to the formation of new species, especially the catena forms (Chapter I). Two unusually colored species, known as purple sulfur and green sulfur have been obtained by condensing sulfur vapor on a cold target (49,50). These two forms are considered in

greater detail below.

The purple variety was first observed by Rice and Sparrow in 1953 (50) when they condensed sulfur vapor at 0.1 - 1.0 torr from a temperature above 450°C to liquid nitrogen temperature (77°K). A green variety was reported by Rice in 1953 (49). This resulted when sulfur vapor from a solid sample at 80 - 110°C was heated to 200 - 400°C and condensed on a cold finger at 77°K. Species of intermediate colors have also been observed. Table IV, due to Meyer (51), summarizes the correlation of color with temperature of vapor (v_f) and rate of deposition.

These colored species should be of great interest to spectroscopists. A search of the literature revealed that very little work has been done on the optical spectra. Meyer, 1960 (52) investigated the 4000 - 5500 Å region for green sulfur and observed a continuous absorption with a maximum at ca. 5070 Å. The UV spectrum of purple sulfur in inert gas matrices at 20°K was examined by Brewer, Brabson, and Meyer, 1965 (53). They observed the characteristic bands of S_2 in the 2600 - 3200 Å region and concluded that S_2 was present in trapped species at 20°K.

The purpose of this study was to record the optical spectra of purple and green sulfur formed at liquid nitrogen temperature, in the absence of matrices, and to interpret the

TABLE IV

COLORED SULFUR ALLOTROPES
REFERENCE (51)

V_s °C	V_f°C	V_t°C	mgms/cm^3/min	Color of deposit, approx. 10μthick	
				Reflected Light	Transmitted Light
160	200	-188	0.3	Yellowish-green	Yellowish-green
160	275	-188	0.3	Dark green	Red-brown
160	300	-188	0.3	Blue-green	Red
160	380	-188	0.3	Violet	Yellow-red
105	600	-188	0.01	Green	Reddish
145	600	-188	0.2	Dark green	Red
200	600	-188	1.6	Violet	Yellow-red

V_s = temperature of sulfur reservoir

V_f = temperature of front oven

V_t = temperature of target

results as far as possible.

Experimental

Two experimental systems were combined for the study of the spectra: a molecular beam furnace, and a cryostat with windows for optical studies. The former produced high temperature species in the vapor and the latter enabled deposition at liquid nitrogen temperature.

A. Molecular beam furnace.

This was a quartz double furnace (Figure 19) of the same type used for matrix studies of S_2 (53). Pure sulfur (99.999 per cent) was placed in the lower part of the sample tube. The bent, horizontal part of the tube narrowed down to a small orifice (about 0.5 mm). This part of the tube was provided with an electric heating coil. The sulfur reservoir was immersed in an oil bath. A water cooler separated the orifice from the window flange of the cryostat and was shaped so that only a few square millimeters of hot surface were visible to the target (inside the cryostat). The furnace was connected with a window flange to the metal cryostat.

B. Cryostat

It consisted of a diffusion pump and a cylinder containing the target. A sapphire window, 1" diameter, 1/16"

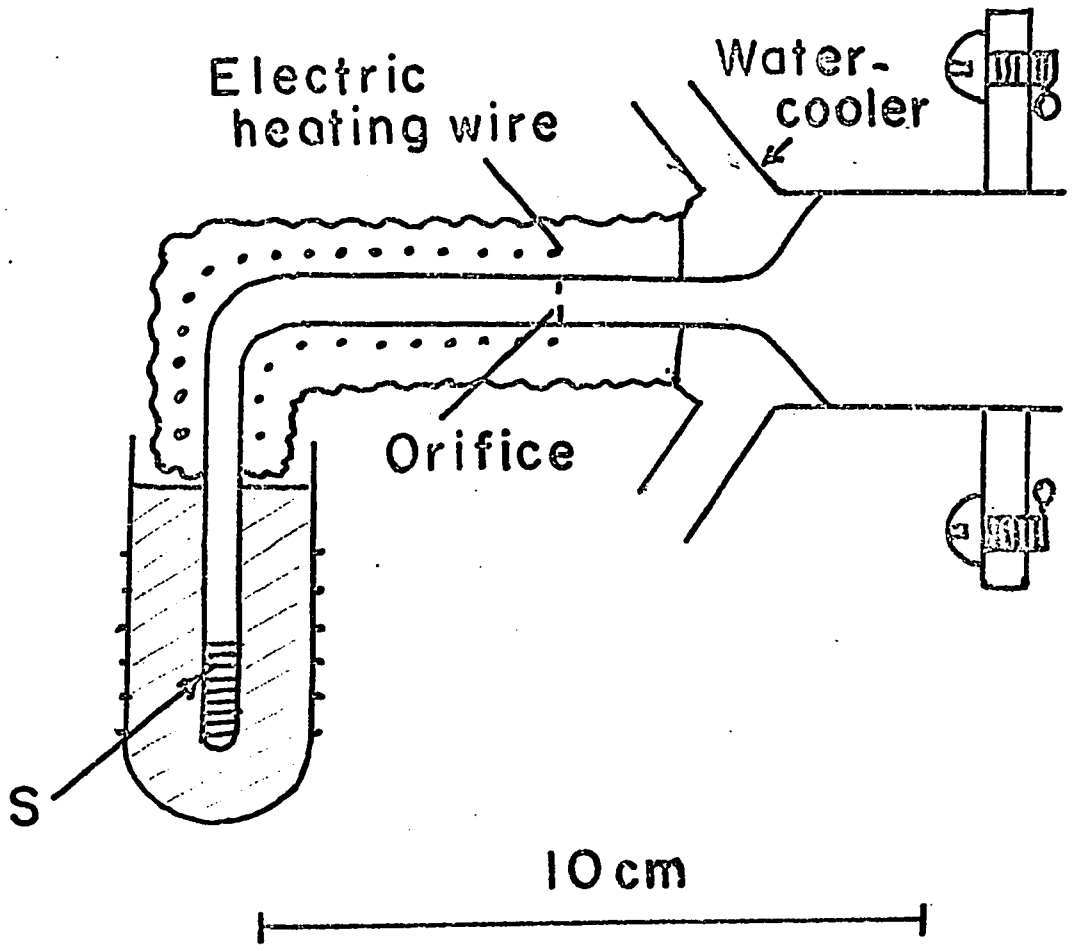


Figure 19. Molecular beam furnace

thick, served as target. It was mounted on a stainless steel frame with indium metal gaskets (for better thermal contact). An O-ring seal made it possible for the target to be turned 90° during the course of an experiment in such a way that it either faced the molecular beam or that it was lined up in the optical path of a spectrometer. Liquid nitrogen was poured into a metallic tube the lower end of which carried the metallic frame and target. The interior of the cylinder was evacuated to a pressure of a few microns with the help of the diffusion pump.

The assembly of the cryostat is shown in PLATE I.

C. Formation of colored deposit

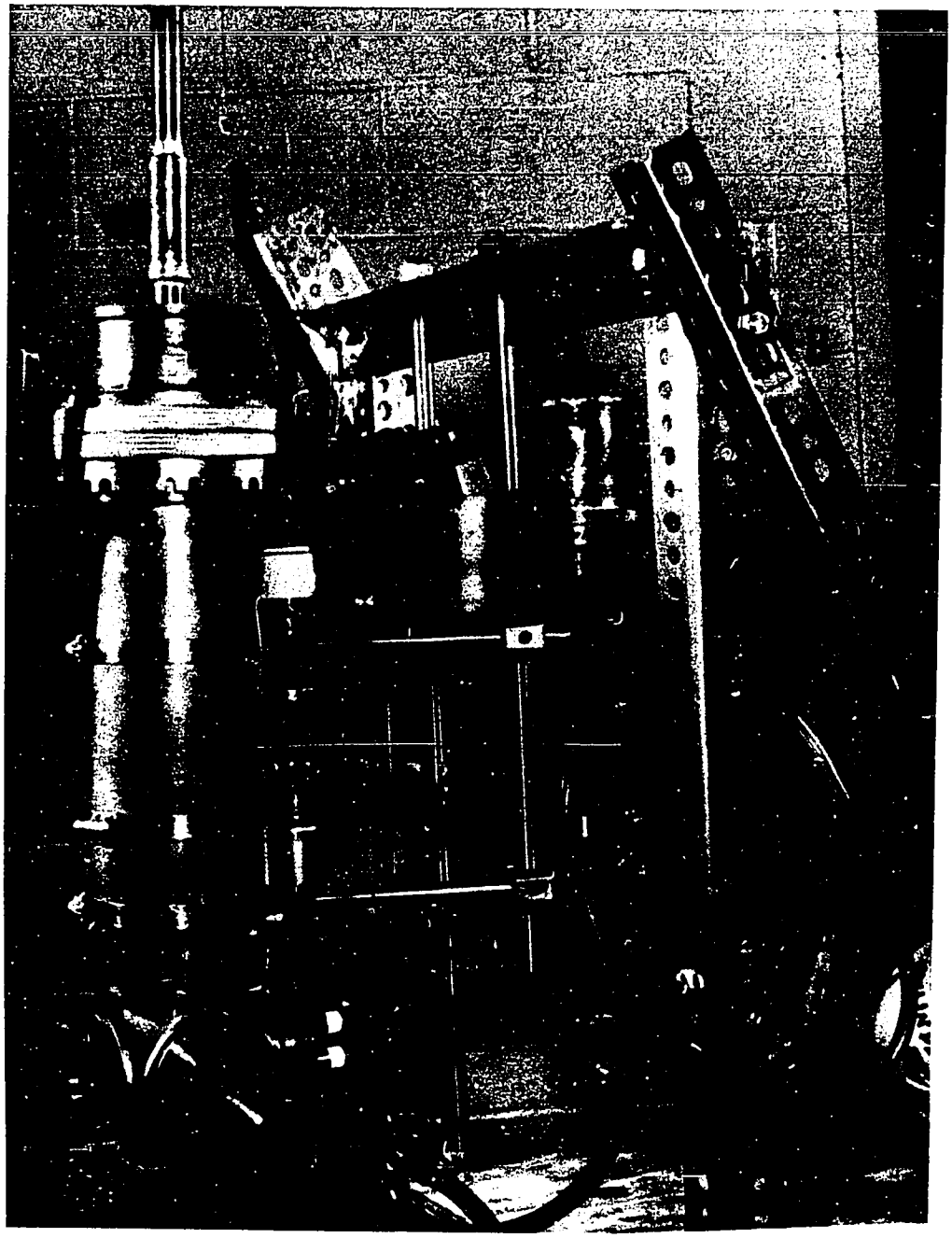
The front oven (horizontal part of the tube) was turned on first. In a few minutes the heating wire became red-hot (about 800°C). Water cooling was started simultaneously with the heating. The sulfur reservoir was slowly heated to about 125°C. At this temperature the vapor pressure of sulfur is about 0.05 torr. The target was turned to face the beam and deposition was made for a few minutes. Absorption of the deposit depended on the thickness of the deposit and hence on the time of deposition. About 3 minutes of deposition gave a thin film suitable for study of UV region and a 7 minute deposition gave a thicker film suitable for the study of

PLATE I

CRYOSTAT ASSEMBLY

Used for the Preparation

of Colored Sulfur Allotropes



visible region.

D. Recording the spectra

The cryostat was placed in the optical path of a Cary 14 H Model spectrophotometer and the target was turned so that it was lined up with the sample beam. Spectra were scanned in the visible and UV regions. For a thin film, the visible region was almost transparent but the UV region showed considerable absorption. A thicker film was used to record the spectra in the visible region. In this case, neutral density filters had to be used to record UV absorption. Absorption in the UV region was examined also by Jarrel-Ash spectrophotometer (Figure 4, Chapter I) using polaroid films.

Spectra were recorded for the following situations in the order given:

1. Deposit at 77°K, thin and thick deposits.
2. Warm up to room temperature.
3. Room temperature (25°C).
4. Back to 77°K.
5. Back to room temperature.

Results and Conclusion

1. General observations

In these experiments, the deposit was colored purple at 77°K. Warming-up changed it to yellow with slight greenish

hue. At room temperature the color was pale yellow and back at 77°K, almost white. This showed that the colored species were destroyed irreversibly by warming up. Fluorescence was not observed for the purple deposit. The film had a plastic texture but at room temperature it crumbled into yellow powder resembling orthorhombic sulfur.

2. Spectral displays with brief explanation

Figure 20 shows typical results obtained from the study. Figure 20a: a thin deposit at 77°K. The visible region was almost transparent. Absorption in UV region was high and broad. The absorption edge was not as steep as for crystal and liquid. This showed that the film was very thin. A broad shoulder with a maximum in 3500 - 3600 Å was observed. This is remininscent of similar maximum observed for solution (Figure 29, Chapter V) and the liquid (Figure 5a, Chapter I) at higher temperatures. The deposit therefore appeared to consist of catena species. Peaks were not observed in 2600 - 2800 Å region, hence the presence of S_8 or S_2 species was not established.

Figure 20b: A thicker deposit at 77°K. The deposit was purple. Absorption in the visible region was appreciable but still low. Peaks could be located at about 4700 Å, 5550 Å and 6800 Å. Absorption in the UV region was very high, and

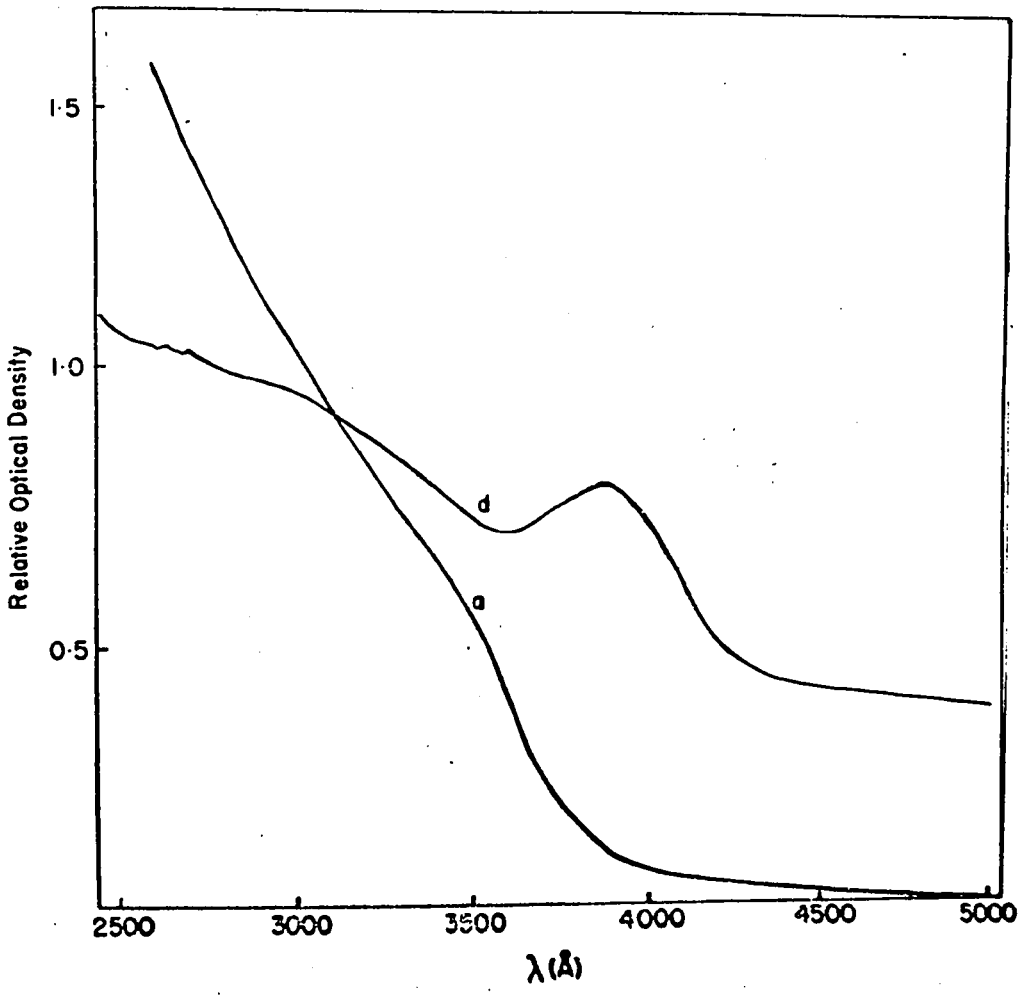


Figure 20. Optical Spectra of Colored Sulfur Allotropes
a. Thin Film at 76°K. d. Room Temperature, Thicker Film

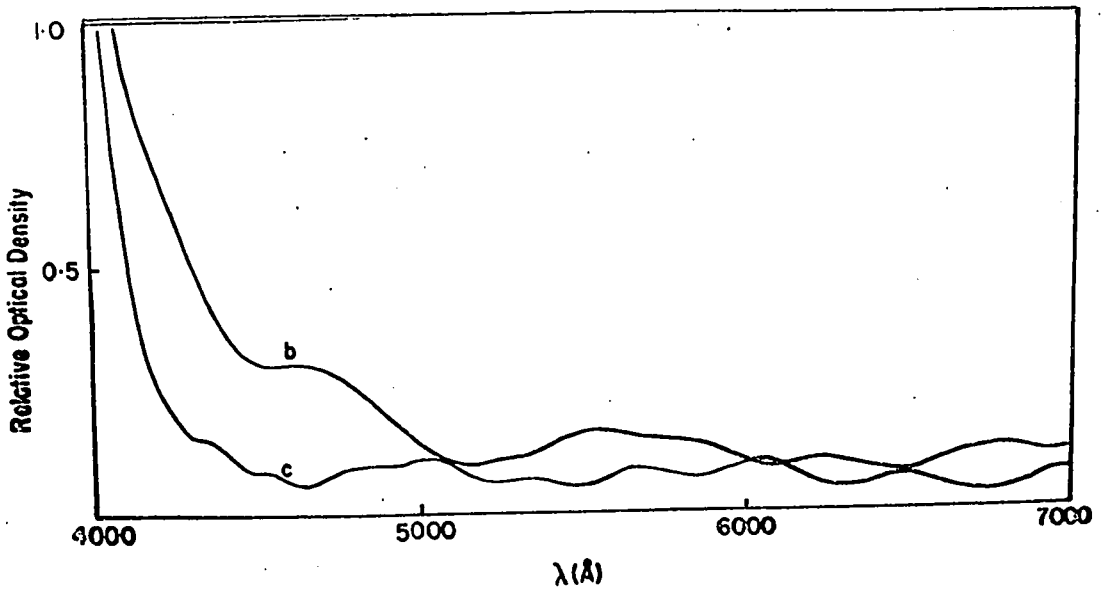


Figure 20. Optical Spectra of Colored Sulfur Allotropes b. Thicker Film at 76°K. c. Warm up Stage

the absorption edge was steeper than for the very thin deposit. Two faint peaks appeared in 2600 - 2800 Å region. This could be attributed to S_8 or S_2. The resolution and intensity of the peaks were so poor that no definite conclusions could be reached.

Figure 20c shows spectrum of the deposit on warm-up. There was a general decrease in the absorption; the edge shifted to slightly lower wavelengths. It appeared that the concentration of the species absorbing in the visible was decreasing. Peaks were observed at 4350 Å, 4550 Å, 4775 Å, 5050 Å, 5330 Å, 5650 Å, 5050 Å, 6460 Å, and 6950 Å. The 5050 Å maximum agrees fairly well with a previous result reported for green sulfur (51). The conclusion is that green sulfur may be an intermediate in the warming up process.

Figure 20d shows spectrum at room temperature. All absorption bands in the visible nearly disappeared. The deposit was pale yellow and the absorption edge shifted further toward lower wavelengths. The specimen became rather opaque as seen from the absorption curve in the visible. The most remarkable feature of this spectrum was a single absorption peak at 3900 Å. Two faint peaks in the 2600 - 2800 Å region

When the specimen was cooled down to 77°K again, the only change from Figure 20dwas the shift in the absorption edge and the peak to lower wavelengths. This could be the

purely temperature-dependent change described earlier (Chapter I)

3. Further discussion

It is evident from the foregoing explanations that the deposit resulted from high temperature species. The plastic texture of the film would indicate that polymer chains could be present in the deposit.

The appearance of several peaks suggests that the deposit may not be just a single molecular species. Some investigators had thought that purple sulfur was pure S_2 condensate. But later studies showed that S_2 was only one of the species in the purple variety (54,55).

The various peaks found in the visible region may be correlated with the results obtained in the last chapter. The spectrum of a liquid-vapor system at 270° (Figure 5d) showed peaks at about 2800 Å, 3590 Å, 3840 Å, 4350 Å, 4450 Å, 4650 Å and 4750 Å. All these peaks, and a few more, were observed in the present study. From the general shift of the absorption edge (Chapter I), one would expect peaks at higher wavelengths at still higher temperatures. Hence the peaks beyond 4750 Å must be due to high temperature species. It is reasonable to expect a lower fraction of the low temperature species at high temperatures. This is offered as an

explanation for the absence of a few peaks in the blue part of the spectrum of purple sulfur. If one peak is assigned to each species, at least eleven species have been encountered in the present study. It is not possible to identify the molecular species associated with the peaks, but they appear to be polymeric in nature.

If liquid sulfur at high temperatures contain some of these species, the question arises why it does not show color except yellow and red. An examination of Figure 5d gives the answer. Absorption is very high in the visible region for the liquid film so that the presence of absorption bands would not be observed visually. The color would be decided solely by the absorption edge. Hence liquid sulfur appears deeper red with increase in temperature.

The region 2600 - 2800 Å is of special interest. It has been shown by vapor phase studies that at 800°C and low vapor pressures sulfur vapor consists almost 100 per cent S_2 (50). It was not, however, possible to detect S_2 by UV spectrum for a deposit at 77°K. ESR studies have shown the presence of diradicals in the deposit (55). The only conclusive evidence for S_2 molecules in the deposit at 77°K comes from infrared spectrum where the forbidden band at 668 cm^{-1} has been shown to be due to S_2 (54). The proportion of S_2 must be very small in the deposit. Two reasons for not

observing S_2 are (53): first, the composition of sulfur vapor changes as a complex function of temperature and pressure, and second, hot S_2 molecules striking a cold target can react with each other and with their reaction product to give a variety of new sulfur molecules. Trapping inert gas matrices at lower temperature is the only effective method known. The disappearance of S_2 bands in the UV region has been observed during warm-up of trapped S_2 species (53). In view of these observations it is not surprising that S_2 could not be identified in the UV spectrum of the deposit.

Summary

Colored allotropes of sulfur were formed on a cold target according to the method used by previous workers, viz., condensing hot sulfur vapor. Optical spectrum of the deposit was recorded at 76°K; the spectrum showed several absorption peaks some of which were observed in the spectrum of sulfur vapor over liquid sulfur. This suggests that the colored species can at least partly be identical to species in hot liquid sulfur. The deposit was purple at 76°K but changed to green on warming up and finally became yellow. Peaks in the visible region disappeared at room temperature. This indicated a conversion to the more stable (orthorhombic) form. The change was irreversible. Evidently the colored species are

metastable.

Further Work Suggested

It will be useful to find correlations between the temperature and pressure of the vapor, and the absorption bands. The present work is considered a step in this direction. Identification of the peaks with definite molecular species is not expected from such studies until the composition of the mixture is known. For this the spectra of various sulfur vapor mixtures in low temperature matrices should be studied.

CHAPTER IV

A STUDY OF SULFUR VAPOR

Introduction

A. General

Sulfur vapor has been studied extensively by a variety of physical methods (56). The vapor phase, like the liquid, was found to be very complex but the nature of the complexity was different. At least two factors contribute to the complexity of the vapor (56)

1. The vapor contains several molecular species.
2. The proportions of these species vary with temperature and pressure

For the study of spectra a third factor is also important. Traces of impurity can modify the spectra considerably. A discussion of this aspect is given in a later part of this chapter.

B. Previous work on UV-VIS spectra

Spectroscopic studies of the vapor have been conducted by several workers (57). Above 7000°C, the spectrum is essentially due to S_2. This molecule has also been observed spectroscopically at lower temperatures. Bass, 1953 (57) reported that below 250°C, the spectrum of saturated sulfur vapor

consisted of a broad, continuous absorption band with maxima at 2100 Å, 2650 Å and 2850 Å. These were attributed to cyclo-S_8 species in the vapor. The peaks broadened with rise in temperature, showing a decrease in S_8 molecules. Above 250°C, S_8 bands could be observed.

C. Purpose of the present work

A re-investigation of the vapor spectra at lower temperatures (140 - 500°C) was considered useful for the following reasons:

(i) The proportion of S_2 in the vapor has been found to be higher at lower vapor pressures (58) than at higher vapor pressures. It was assumed that S_2 species could be identified from the spectra at temperatures below 250°C if vapor pressure is reduced.

(ii) Hot sulfur reacts with air to form SO_2; hence this compound should be expected in the products. It is not known whether the concentration of SO_2 in a normal sample is sufficient to give a spectrum. If impurities are present in sulfur or in the air, other species may also be expected in the vapor. The influence of these impurities on the spectrum has not been studied.

Experimental

a. Vapor cell

This is illustrated in Figure 21. It consists of an optical cell (6 cm long) with quartz windows, and a side arm, (7 cm long) serving as the sulfur reservoir. Separate heaters and thermocouple devices are provided for the cell and side arm.

To prepare the cell for the study, about 1 g. of high purity sulfur (99.999%) was introduced into the cell through the side-arm. The latter was connected to a vacuum system and the air was pumped off till the pressure reached about 1 micron. The tubing was sealed off at the free end. By tilting the cell, the sulfur was brought into the side tube.

b. Study of spectra at different temperatures and pressures

The cell was placed in the optical path of a Cary 14 H spectrophotometer, with the side arm pointing downwards. A spectrum was taken at room temperature. The temperature of the cell was raised to about 140°C while that of the side arm to about 120°C. The cell had always to be at a higher temperature because otherwise sulfur would condense on the cell windows. The pressure of the vapor was determined by the temperature of the sulfur reservoir. It was found that a

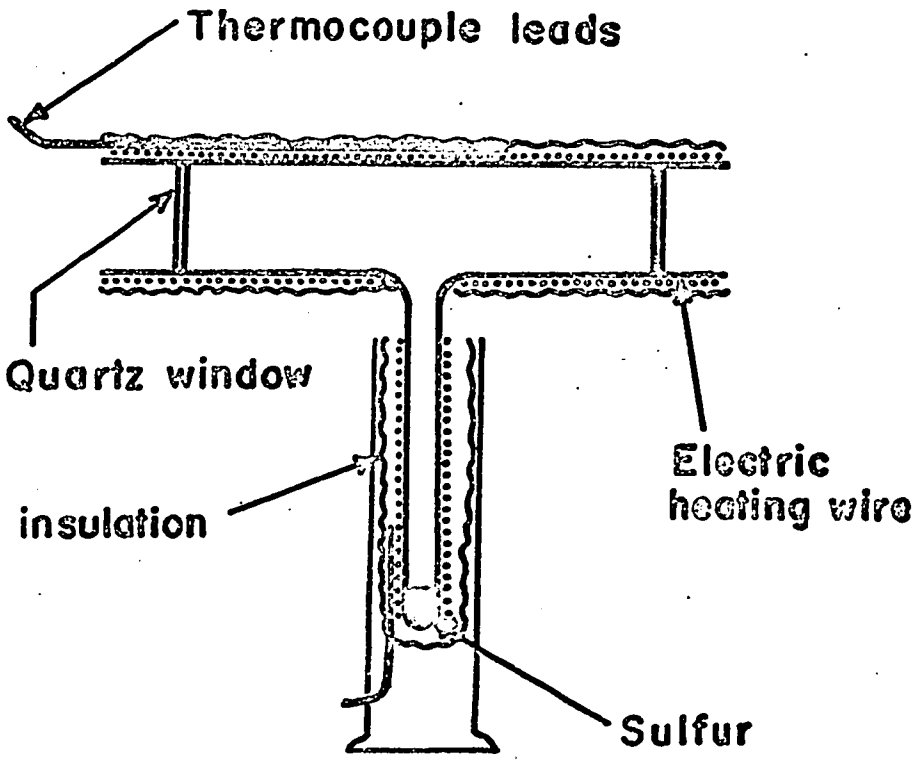


Figure 21. Cell for the Study of Sulfur Vapor

vapor pressure of 0.04 torr, corresponding to 120°C (59), was insufficient for recording spectra. At least 0.1 torr pressure (corresponding to 160°) was necessary.

Two sets of experiments were done: first, the vapor was studied at different temperatures for a given vapor pressure; secondly, at different vapor pressures for a given temperature. The highest temperature used was 500°C.

These experiments were repeated for the following situations: (1) a less evacuated cell (about 25 micron pressure), (2) lower grade sulfur (99.96%)

At the end of the experiments, when the cell was cooled to room temperature, another spectrum was taken (all spectra were taken in the range 1900 - 7000 Å).

Results

1. General

Absorption was low at vapor pressures less than 0.1 torr and the spectrum was broad and continuous with unresolved maximum in 2600 - 2800 Å and another in 1900 - 2100 Å region as observed by Bass (57); it increased with increase in vapor pressure for a given temperature of the vapor; for a given vapor pressure, increase in absorption was not appreciable with rise in temperature.

2. Specific absorption bands

Discrete and well-resolved vibrational band systems were seen in the 1900 - 2500 Å and 2500 - 3000 Å regions, the former, at temperatures as low as 130°C and the latter, above 185°C (Figure 22). On cooling the sample to room temperature the former bands persisted while the latter disappeared. A new set of bands appeared in the 2800 - 3100 Å region which persisted on reheating but did not increase in intensity (Figure 23). These were more intense for the less evacuated cell; the 2000 Å bands were more intense for the lower purity sulfur samples. At temperatures above 400°C and a vapor pressure of about 340 torr, another set of bands appeared in the 2000 Å region, while the 2500 - 3000 Å bands became exceedingly intense.

3. Identification of the bands

a. 2500 - 3000 Å bands

These were easily identified as due to S_2. All the band positions agreed with previous data (60) of Rosen and Desirant. The lowest temperature at which S_2 could be identified was 185°C, at a vapor pressure of 0.43 torr. This is the first spectroscopic demonstration of the presence of S_2 at temperatures below 200°C. The S_2 peaks remained at low intensity below 250°C, and above 250°C they were quite intense.

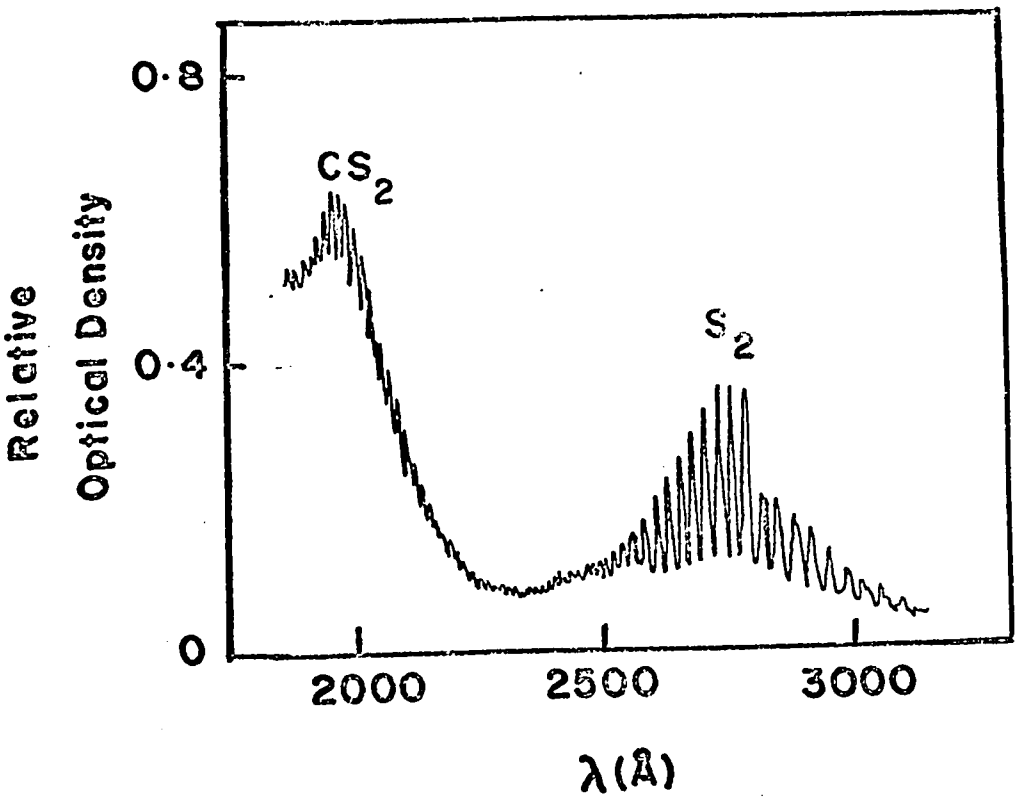


Figure 22. Spectra of S_2 and CS_2 in Sulfur Vapor at 370°C and 8.7 torr.

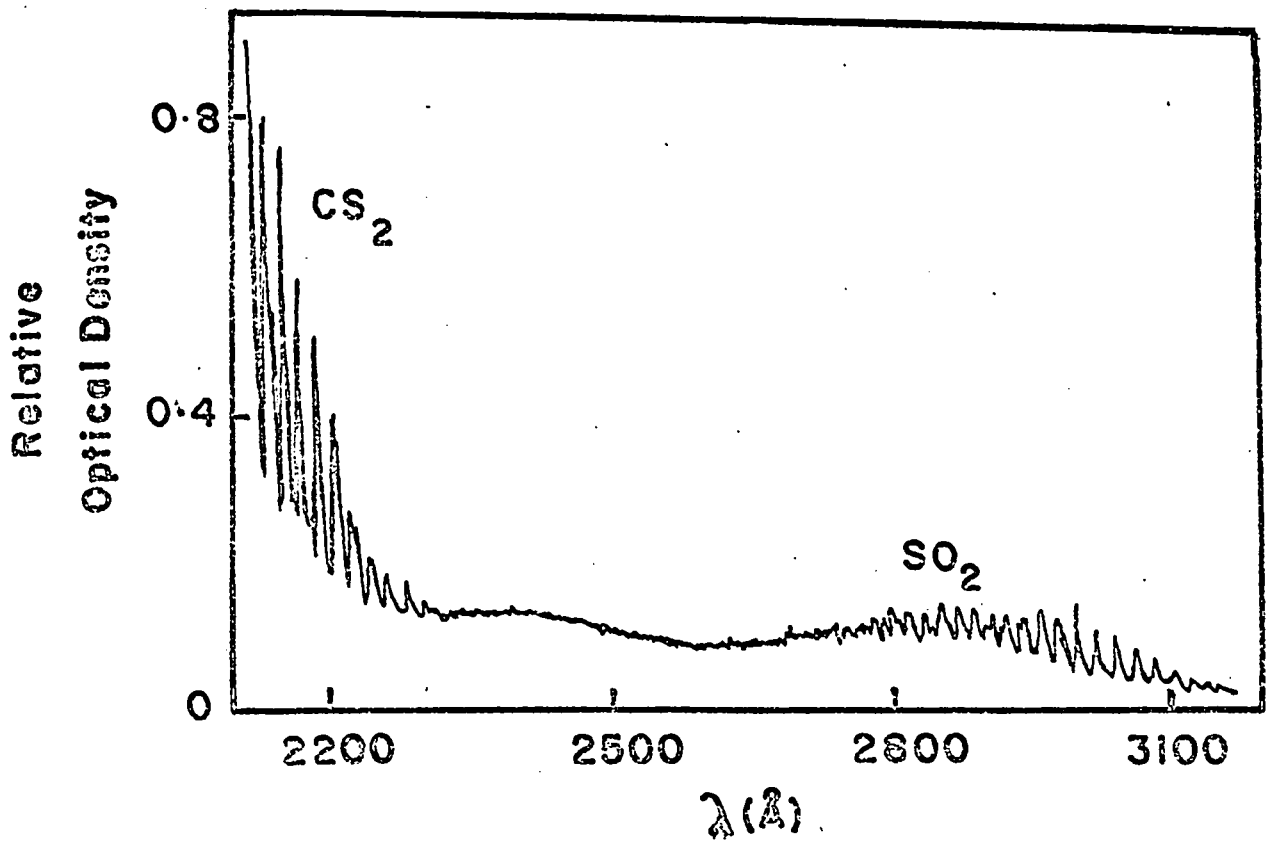


Figure 23. Spectra of CS_2 and SO_2 in Sulfur Vapor: Preheated Specimen at 25°C.

On cooling to room temperature, the S_2 molecules were converted to orthorhombic sulfur.

b. 2800 - 3100 Å bands

In spite of their low intensity, they could be identified as due to SO_2, by comparison with data already available (61). The reason why they could not be observed at higher temperatures is that S_2 bands were much stronger and masked the SO_2 bands. Apparently, SO_2 was formed by reaction of sulfur with oxygen at about 250°C or above.

The presence of SO_2 bands is no problem in the identification of the S_2 bands as long as the former are weak. This emphasizes the necessity for reasonably good vacuum (ca. 1 micron) in experiments with the vapor.

c. 1900 - 2100 Å bands

At least two substances were suspected responsible for these bands because two sets of bands were observed in this region. One set of bands could not be observed below 250°C; the other set was observed at about 130°C but they persisted even on cooling to room temperature.

The high temperature bands were identified as S_2 by comparison with standard data (62). Their disappearance at lower temperatures is explained in the same way as done for the 2800 - 3100 Å bands.

The other set of bands was found to be due to CS_2. This was verified in two ways:

1. Comparison of the bands with known CS_2 bands in this region (63).
2. Obtaining the spectrum of pure CS_2 on the same instrument (Figure 24).

The second procedure was necessary because CS_2 was not expected in the vapor in appreciable quantities. The well-known CS_2 bands in 3000 - 3400 Å region (Figure 24), obtained for saturated CS_2 vapor, were not observed in the present spectrum. The vapor had to be diluted several times to obtain the 2000 Å bands of CS_2 and at the dilution when they appeared (about 1/2500 saturation) the 3000 - 3400 Å bands were totally absent or unidentifiable.

The 2000 Å bands of CS_2 could also be observed in the spectrum of liquid sulfur whenever a bubble of vapor was present. This fact had been omitted in the discussion of liquid sulfur spectra.

Further confirmation of the presence of CS_2 was obtained from mass spectrum. A specimen of high purity sulfur (99.999%) in a nearly evacuated tube was heated to about 300°C and cooled to room temperature. The mass spectrum of the gaseous products in the tube showed parent peaks due to CS_2 and SO_2. The presence of fragments of these molecules were also observed. Other compounds found in the vapor were

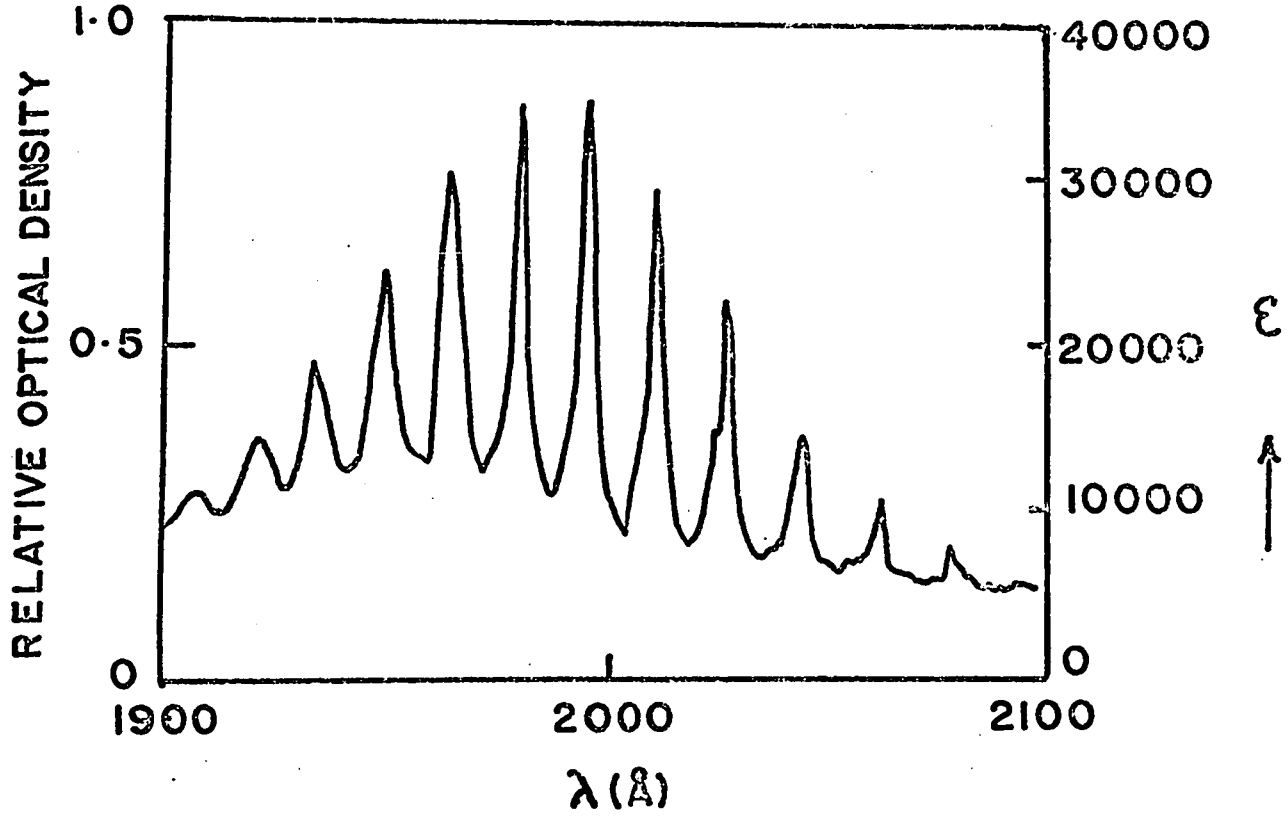


Figure 24a. Spectrum of CS_2 in Far UV region.

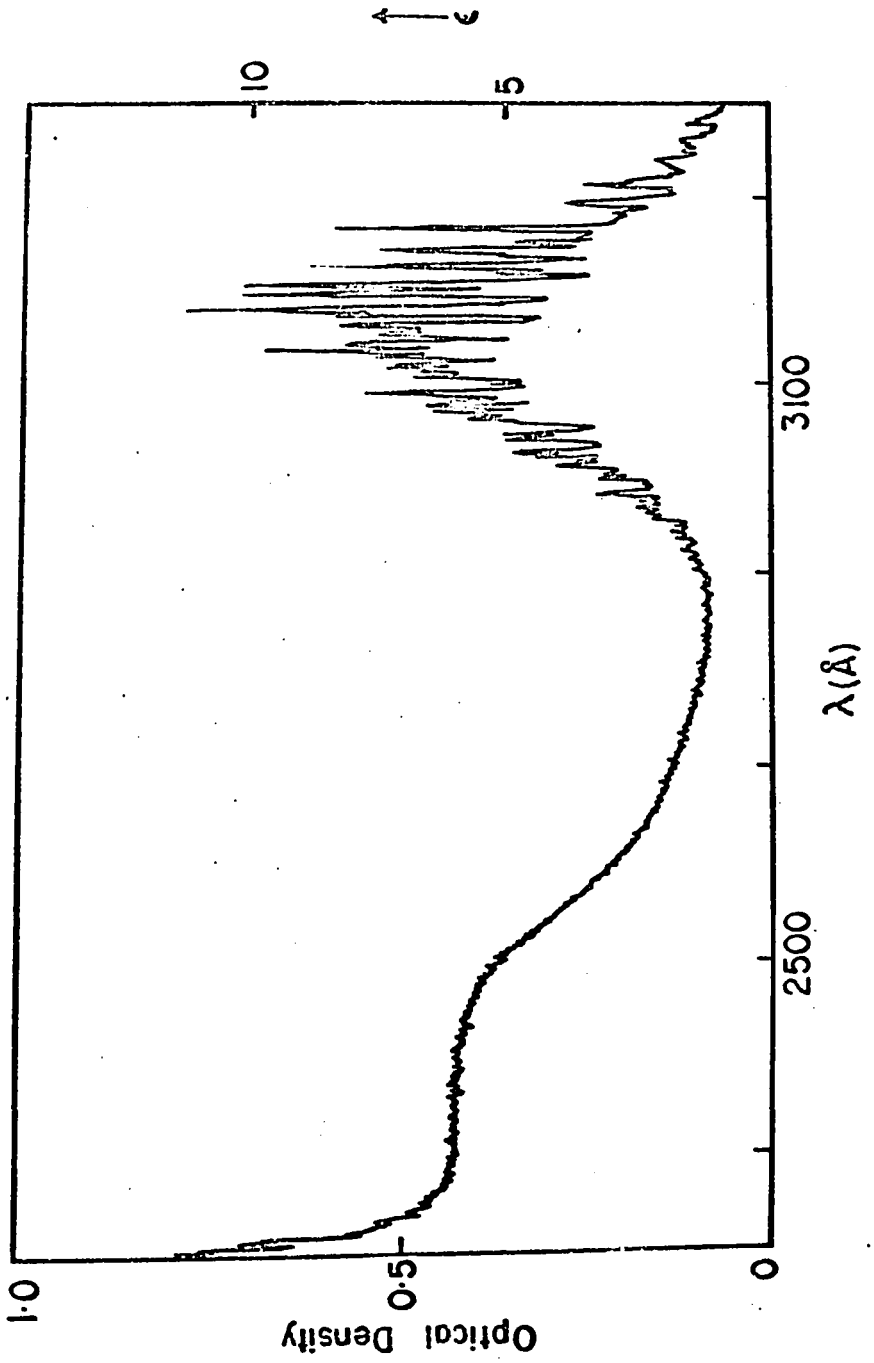


Figure 24b. Spectrum of CS_2 in near UV Region

CO, CO_2, O_2 and N_2; CO may be a secondary reaction product; the others were present in the background.

d. Other band systems

It is necessary to point out that at high vapor pressure (475 torr) and a temperature of 475°C, a weak, broad, absorption band with a maximum at about 3925 Å appeared in the region 3500 - 4500 Å region. Although about 20 small band heads could be identified with S_2, many of the stronger band heads were not identified. Whether this absorption is due to another species of sulfur in the vapor remains to be proven. Berkowitz (18) suggested the existence of several cyclic species, S_4 through S_{11} in the vapor. Small catena species may also be suspected in the vapor. This possibility has been described in Chapter I.

A Discussion on the Purity of Sulfur

This study showed that even 99.999 per cent pure sulfur was not satisfactory for spectroscopic investigation of sulfur vapor at lower temperatures. It is especially unsuitable for investigation in the 2000 Å region due to the strong bands of CS_2.

The origin of CS_2 in the vapor may be traced to two sources

1. Trapped CS_2 solvent in sulfur crystals.

2. CS_2 formed by reaction of sulfur with carbon or other organic impurities.

Both possibilities need be considered. It was observed earlier (Chapter II) that even after prolonged degassing, complete removal of CS_2 from a sulfur crystal was not possible. This fact, combined with the high solubility of sulfur in CS_2 suggests that CS_2 is either enclosed in or complexed with S_8 species. When the crystals break up the CS_2 escapes into the vapor phase. But it was found that the amount of CS_2 produced this way was too small to give a distinct UV spectrum. The second possibility, reaction of carbon with hot sulfur is more significant. It appears that sulfur in molten state reacts with carbon particles or organic impurities to form CS_2. Heating followed by pumping off the CS_2 reduced the carbon content in the liquid but complete removal was not achieved even after repeated procedure.

A very sensitive method of estimating carbon impurity in sulfur samples is provided by these experiments. The following calculations illustrate this fact.

Experimentally, a 1 cm cell containing pure CS_2 at 1/2500 saturation gave an intense spectrum (O.D. = 1.0) in 1900 - 2100 Å region (Figure 24). The vapor in this cell contained about 8×10^{-7} moles of CS , i.e., 6×10^{-5} g of CS_2, since the vapor pressure of CS_2 at 25°C is 360 torr. This corresponds to about 10^{-5} g of carbon. It was found that

the CS_2 from 1 g. of sulfur sample gave an identical spectrum. Hence 1 g. of sulfur contained at least 10^{-5} g. carbon. The purity of the sample would therefore be 99.999 per cent. This agrees very well with the labelled purity.

Even if the carbon content in 1 g. of sulfur had been 10^{-6} g. or less, the spectral peaks could be sufficiently intense for identification. Hence a purity of 99.9999 per cent or slightly higher could be estimated by this method.

It appeared that the purity labelled on the sample used (99.999%) was higher than it actually was. The present method of estimation of carbon impurity is by converting it to CO_2 (64). The reliability of this method for testing very small quantities of carbon is questioned in view of the observations described.

Summary

Spectrum of sulfur vapor was studied at temperatures 140 - 500 and vapor pressures 0.1 torr to 350 torr. The presence of S_2, SO_2 and CS_2 in the vapor was established, and S_8 was indicated. S_2 was observed above 185°C. SO_2 and CS_2 were reaction products. Mass spectrum confirmed the formation of these products. A spectroscopic method of estimation of carbon impurity in sulfur is suggested.

Scope for Further Work

The variation in proportion of S_2 in the vapor at different temperatures may be estimated from the spectrum. Vapor pressure must be kept constant for such measurements. Estimates made in this way may be compared with standard data.

Evidence for absorption in the visible region may also be looked for because at high temperatures absorption bands are expected in this region, due to colored allotropes as indicated by the experiments of Braune and Steinbacher (20) discussed in Chapter I.

CHAPTER V

SULFUR IN SOLUTION AND GLASS

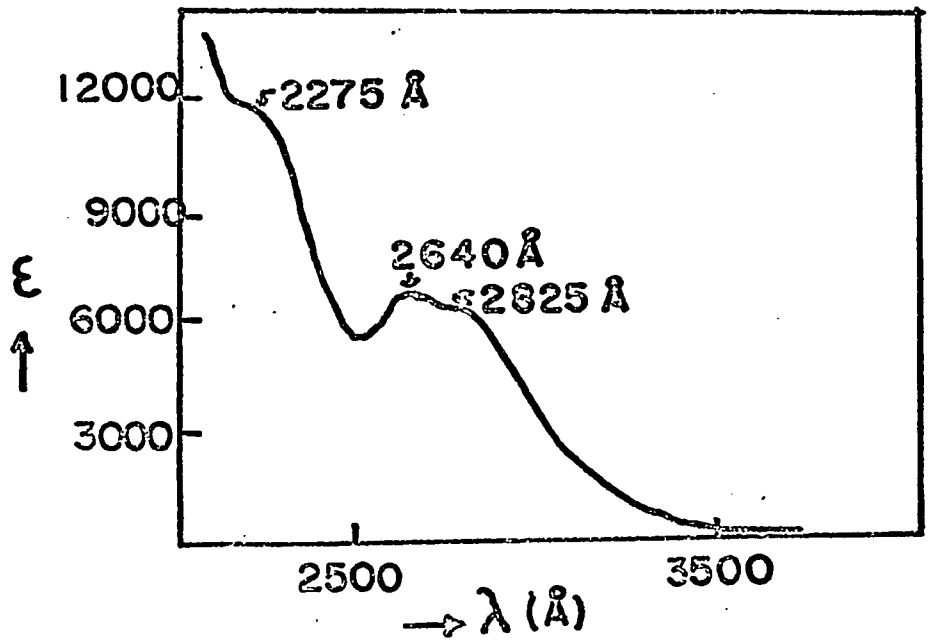
Introduction

The spectrum of sulfur in various solvents has been examined at room temperature by several investigators, the earliest reported result being by Baer and Carmack (65) and by Koch (66), both in 1949. The general appearance of the spectrum is shown in Figure 25a. The peaks at 2275 Å, 2640 Å and 2825 Å have been ascribed to cyclo-S_8 molecule, and the peaks at 2640 Å and 2825 Å, to the first electronic transition, Figure 25b (17). The solution was shown to consist of S_8 molecules by molecular weight determination and Raman spectroscopy (67). David et al., (68) measured the extinction coefficients at various wavelengths and found that for a given wavelength extinction coefficient ε, and the refractive index of the solvent are related by

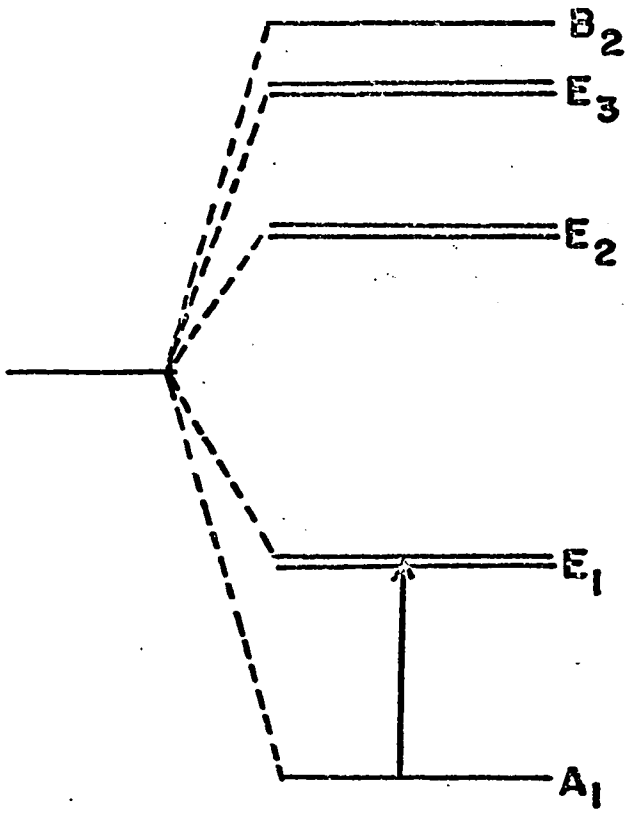
$$\varepsilon = c(n^3 + 4n + 4/n)$$

where c is a constant and n, the refractive index. The variation in extinction coefficients due to this factor is not appreciable.

Spectrum of sulfur solutions below or above room temperature has not been reported although David (68) has briefly



a



b

Figure 25. a. Spectrum of sulfur in absolute methanol, 25°C
b. Energy levels in cyclo-S_8 molecule(D_{4d}), Ref.(17)

remarked on an examination of the peaks at 130°K. Absorption bands sharpen and intensify with decrease in temperature. Bands which appear as shoulders at ordinary temperature are changed to full peaks and sometimes new peaks appear. In the present study it was intended to carry out the investigation at temperatures as low as that of liquid nitrogen (76°K) and to record the spectrum. It was also planned to study the spectrum above room temperature. The study of liquid sulfur has indicated that changes in molecular composition take place above 160°. It is logical to assume that similar changes take place in solution also. The advantage of the solution is that absorption is much lower than that of the pure liquid. For convenience of discussion, the study at low and high temperatures are described in sections A and B respectively.

A. Sulfur in Glass at Low Temperature (76°K)

One serious objection to the use of solvents at very low temperatures such as liquid nitrogen temperature (76°K) is that most of the solvents freeze before the desired temperature is reached. A solution may freeze into more than one phase. Internal strains often appear, making the solvent unfit for spectroscopic work.

The problem has been partly solved by the use of certain solvents or solvent mixtures which form transparent

glasses with the solute. Data on such solvents are available in the literature (69). No previous work has been reported on glasses containing sulfur. The purpose of the present work was therefore to find out a suitable glass for sulfur and study the spectrum.

Experimental

Materials:

Sulfur. Spectroscopic grade, as in the previous experiments.

Solvent. From the available data on solvents useful for making glasses (69), those which were suitable around 76°K and which do not react with sulfur were chosen. Two types of solvents seemed to fit the requirements: alcoholic and hydrocarbon. From the former category, ethanol/methanol mixture and from the latter, isopentane/methyl cyclohexane mixture were selected. Recommended combinations of these solvents are:

ethanol/methanol: ratio 4/1, 5/2, 1/9

Isopentane/methyl cyclohexane: ratio 1/4 to 6/4

The alcoholic mixture did not yield a transparent glass with sulfur. The hydrocarbon mixture formed clear glasses for all the above proportions. The ratio 1:2 was found to yield

the best results. This glass is transparent at liquid nigrogen temperature and is considered to be relatively strain-free.

Spectroquality solvents (MC&B) were used in all the experiments. The UV cut-off for the mixture is at about 2100 Å but with sulfur as solute, the cut-off was found to be ca. 2400 Å.

Low temperature cell

An optical cell was built into a Dewar as shown in Figure 26. Since liquid nitrogen was used as the coolant no provision was made for measuring the temperature. The cell had a path of 3 cm and a capacity of ca. 10 ml up to the neck.

Procedure:

About 15 ml of a solution of sulfur in the 1:2 solvent mixture containing 10 μg/ml of sulfur at room temperature was placed in the cell. A larger amount of solution than the cell capacity is required since the solution shrinks on cooling. Liquid nitrogen was poured into the outer jacket, a few milliliters at a time. The slow addition was to ensure a gradual cooling of the contents. This was found essential for the formation of a clear glass. As the solution started to cool down, the space above the liquid was slowly evacuated and as the glass was about to form, the tube was closed. The necessity for the evacuation is that oxygen may condense in

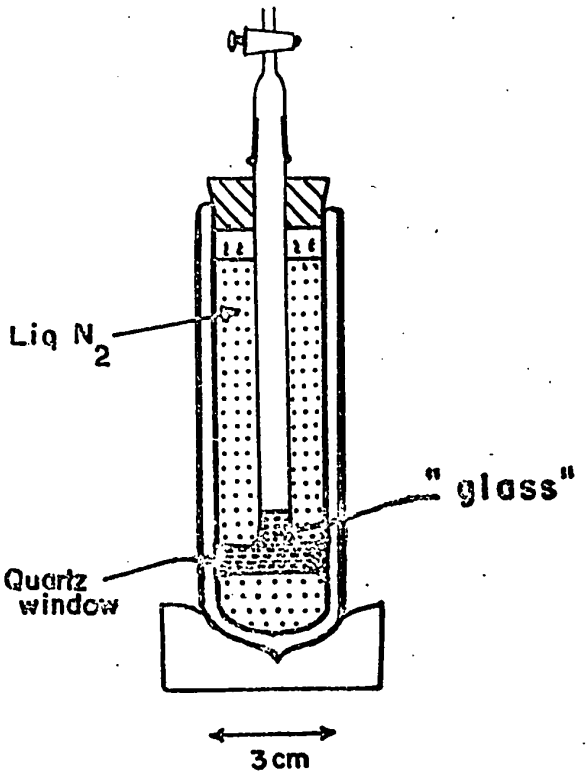


Figure 26. Low Temperature Cell Equipment

the tube and its presence is a source of contamination and hazard. The formation of the glass could be seen from the depression of the meniscus of the liquid. When the glass was finally formed, the meniscus appeared as a cone. Due to shrinkage of the solution the menisus was considerably lowered but the level was still above the neck of the cell. From the decrease in the height of the meniscus, the contraction in volume was estimated to be ca. 25 per cent of the original volume.

The spectrum was scanned with a Cary 14 H Model spectrophotometer provided with an open sample/reference compartment. With the glass the cut-off in the UV region was at about 2400 Å. To apply correction for solvent absorption a blank was run with the solvent at 25°C and another at 76°K. Correction for solvent contraction was made as follows: since the solution contracted in volume by 25 per cent, the glass was more concentrated than the original solution by the same percentage. The observed absorption would therefore be 25 per cent higher than the absorption for a glass of the same concentration as the solution.

Results and conclusion

Figure 27 is the spectrum of sulfur in glass at 76°K The essential differences shown by this spectrum from the room

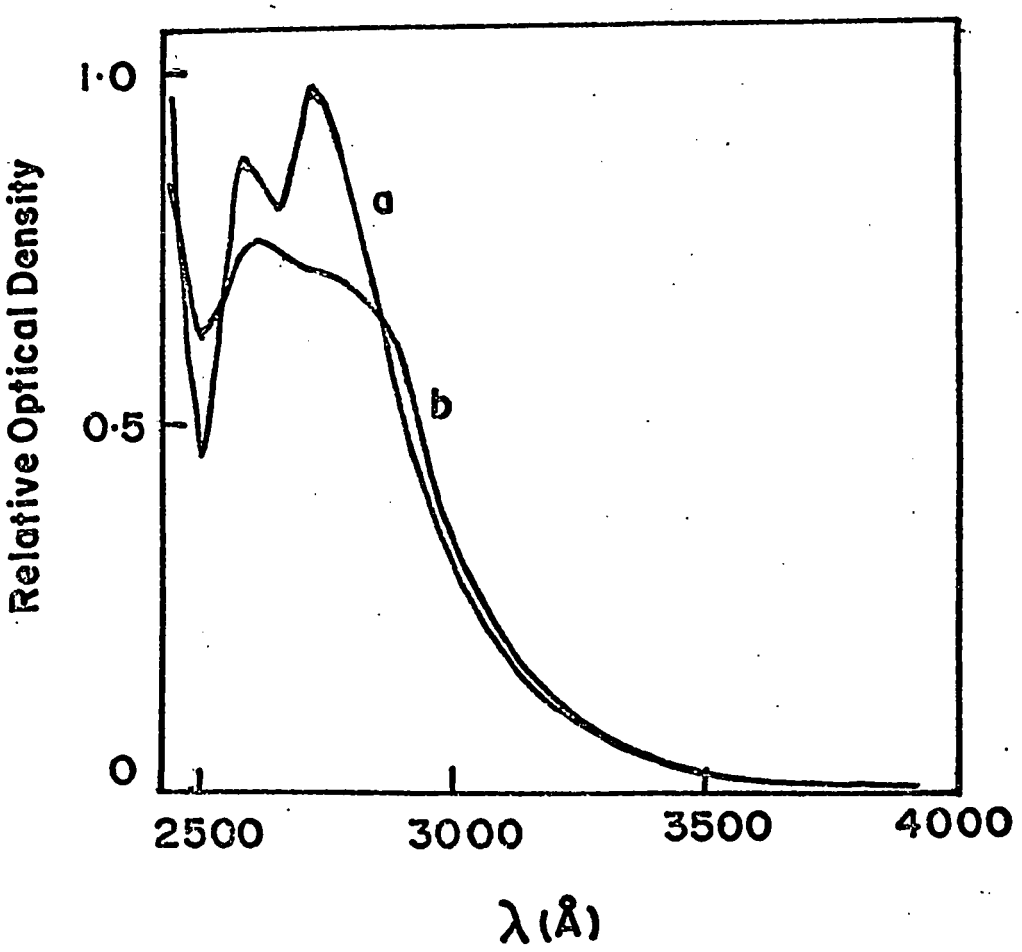


Figure 27. Spectrum of sulfur. a. in Glass, 76°K. b. in solution , room temperature

temperature spectrum are summarized as:

1. The spectrum is sharper in the region of the peaks in the 2600 Å - 2850 A region.

2. The peaks are more intense but the minimum at 2500 Å is lowered.

3. The peaks are much better resolved but the resolution is not high enough to elucidate the fine structure of the peaks.

4. The peaks are slightly shifted to shorter wavelengths the 2640 Å peak to 2620 Å and the 2825 Å to 2775 Å positions. This corresponds to a shift of 1.3 $cm^{-1}/°K$.

5. The 2775 Å peak is more intense than the 2620 Å peak.

6. The absorption edge shifted by about 2.3 $cm^{-1}/°K$.

These observations are anticipated, at least in a qualitative fashion, from the dependence of absorption upon temperature discussed in Chapter I. A change in temperature brings about a redistribution in vibrational energy levels of the molecules. Since the total number of absorbers (molecules, in this case) must remain the same, the integrated absorption must be unaltered. At very low temperatures the lowest vibrational level is almost exclusively populated and transitions to various levels in the upper electronic state take place when energy is absorbed. The resulting absorption pattern has a sharp maximum corresponding to each electronic transition. At 76°K this is nearly the case. At room temperature, higher vibrational levels in the ground state are populated although the fraction of molecules in higher levels

is still very low compared with the total number of molecules. However, we should still anticipate a corresponding change in the absorption pattern. The spectrum will be broader and the peaks less intense than the low temperature spectrum. Quantitative analysis of the shift in intensity was not achieved in the present case because there is some overlap from the absorption peaks below 2400 Å and the extent of overlap is not known. It is possible that solvent interaction is responsible for the slight shift in peak maxima.

Suggestions for further study

This work has demonstrated the possibility of study of sulfur in solution at very low temperature. Further work may be done using other glasses. It is known (71) that glasses meta-stable at liquid hydrogen temperature or below can be prepared. Study at these temperatures should be still more profitable. Absorption studies at several temperatures may also be done to elucidate the temperature dependence. Such studies may lead to the discovery of structural changes taking place at low temperatures.

It is also suggested that other molecular species such as cyclo-hexa sulfur be examined in solution at low temperatures. The spectrum of cyclo-S_6(70) in Figure 28 shows a broad peak. At low temperatures, better resolution is

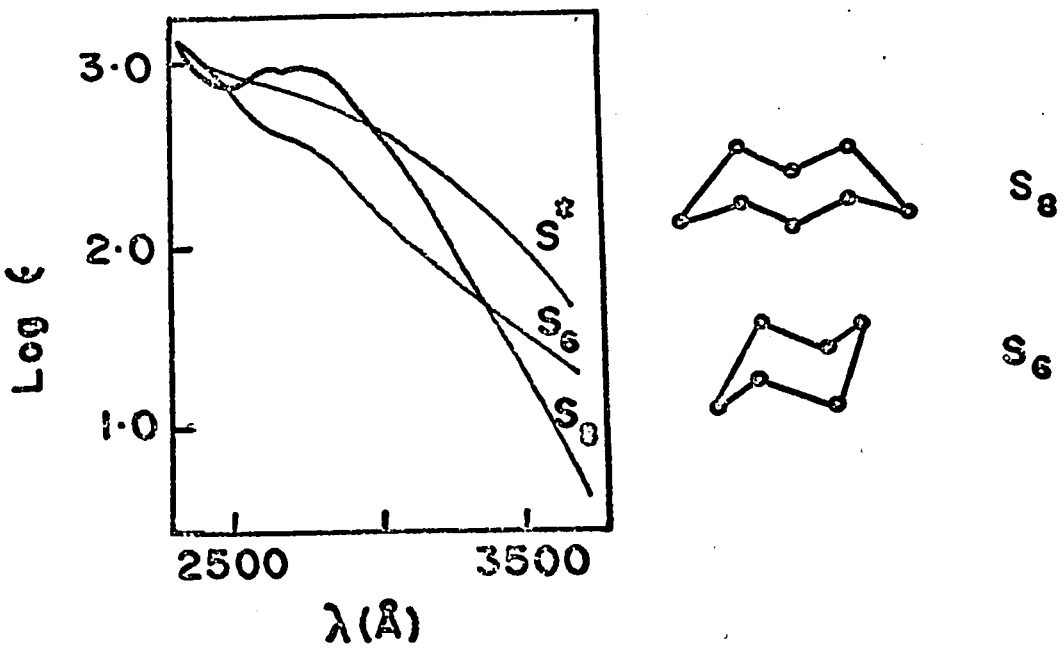


Figure 28. Spectra of S_8, S_6 and Irradiated Sulfur (Solution: Triethylamine) Ref. (70)

expected.

Molecular weight determinations on sulfur have not been carried out below - 75°C. By selecting solvents which freeze at very low temperatures, such as the hydrocarbon mixture used in the experiment, investigation at lower temperatures can be carried out.

A final suggestion is that this technique may be applied to detect traces of impurities in sulfur because at lower temperatures absorption peaks are sharper and therefore better identified.

B. Sulfur Solution Above Room Temperature

Introduction

This study is an extension of the work described in the preceding section. No previous work has been reported on sulfur solutions at higher temperatures for spectroscopic studies. Most of the solvents for sulfur are highly volatile and are therefore unfit for the purpose. Sulfur undergoes a variety of structural changes on heating and it should therefore be possible to follow these changes in solution phase. Since these changes take place above ca. 160°C (Chapter I), the solvent must have a high boiling point.

It is not difficult to find a few solvents that can be used up to 200°. Glycerol is an example, its boiling

point being 290°. It can be used up to about 175° because the vapor pressure is not appreciably changed in this range. Solid hydrocarbons and their derivatives are also suitable. It is important to ensure that the solvent is free of absorption in the desired wavelength range and that it does not react with sulfur in the temperature range.

Since the spectral properties of glycerol were known, this solvent was selected for the present study.

Experimental

Materials

Sulfur. Spectroscopic grade, as in the previous experiments.

Glycerol. U.S.P. grade available from Mallinkrodt Chemical works, St. Louis. This grade was found satisfactory for spectroscopic work. The cut-off in the UV region is at ca. 2300 Å and with sulfur may be used up to 2400 Å.

Cell and heating equipment

The heating equipment was primarily designed for Infrared work (Chapter I) but was found suitable for the present purpose. A quartz cell, 2" dia. and 0.5 cm path thickness replaced the infrared cell. The quartz used was Suprasil grade, having a transparency of 100 per cent up to ca 2300 Å,

supplied by Amersil quartz division, New Jersey. 1/16" thick plates were used in the construction. The stem of the cell was 4" long.

UV-VIS spectra

A Cary 14 H Model Spectrophotometer designed for high temperature work was used. The spectrum was scanned from 2400 Å to 7000 Å at a scan speed of 5 Å/sec and chart speed of 2"/min. to obtain a spectral display of 50 Å/div.

Sufficient time was allowed to attain a steady temperature. The spectrum was recorded at temperatures in the range 85°-175°C and at 25°C after the solution was cooled to room temperature. Above 175°C the solution started fuming and higher temperatures were not used.

Results and conclusion

The spectral displays are shown in Figure 29. The characteristic S_8 peaks are not resolved and the spectrum broadens with increase in temperature. This is a general result expected at high temperatures, as already explained in section B. The rise in absorption intensities of the peaks with increase in temperature may appear to violate the general rule. There is, however, no contradiction if we examine the curves more carefully. As a result of the broadening of the

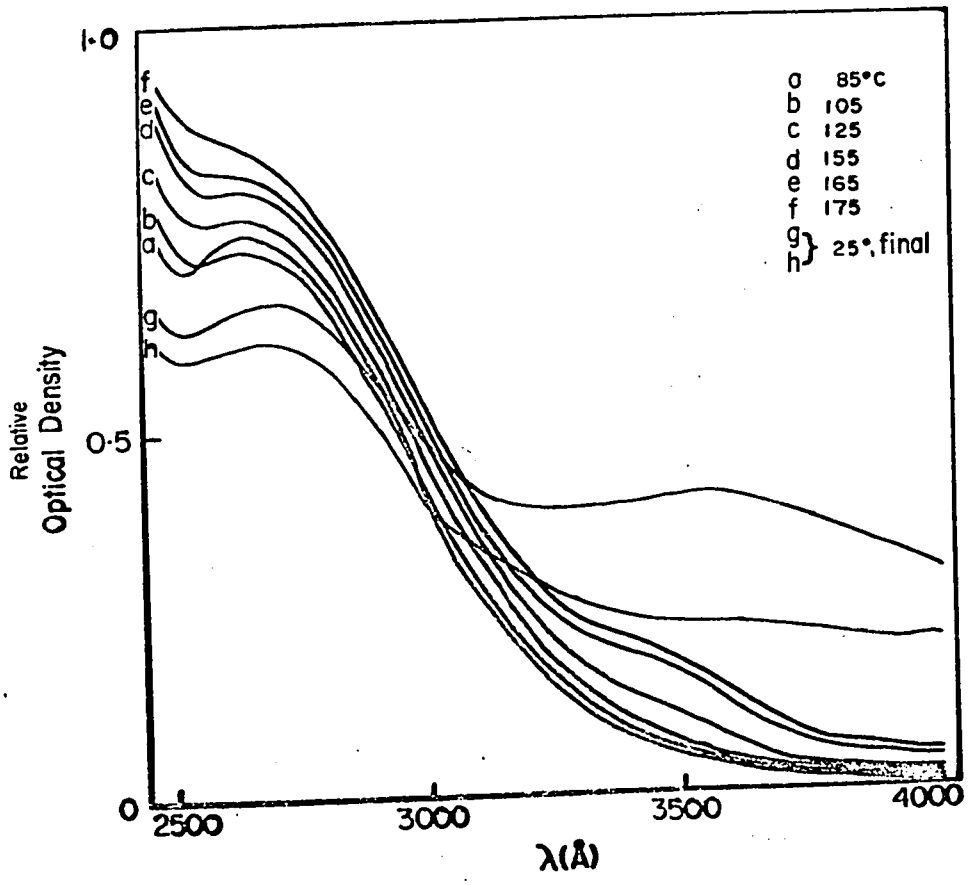


Figure 29. Spectrum of Sulfur in Glycerine

spectrum, we should expect a shift in the absorption edge, towards the red. But there are other absorption peaks beyond 2400 Å whose edges shift likewise. The overall result is that the absorption increases. If one had examined the entire range of the spectrum, there should be regions where the absorption decreases as expected.

The most noteworthy aspect of the spectrum is the appearance of a broad maximum in the 3500 Å region between 155° and 165°C. The solution at this stage was pale yellow although at lower temperatures it was colorless. On cooling the solution back to room temperature the solution became turbid with yellow particles of sulfur suspended in a pale yellow solution. On long standing the solution assumed a milky appearance. Figure 29h illustrates the spectrum in this situation.

To provide an explanation for the above observation, it is suggested here that the appearance of the broad maximum is associated with the appearance of a new species in the solution. From studies with liquid sulfur (Chapter I) it is established that sulfur chains are formed above 160° as a result of the rupture of S_8 rings; below 160°, liquid sulfur consists below that mostly of cyclo-S_8. The new species must be deeper yellow than rhomic sulfur. On cooling, the re-conversion to S_8 species

does not seem to take place immediately. This could be the reason for the shoulder in the spectrum of the cooled sample. The high optical densities in the 3000 Å - 4000 Å region for the last two spectra do not mean that the new species increase in concentration on cooling. This is a result of the light scattering effect caused by the suspended particles. The broad band disappears on standing, evidently a result of the conversion to normal species. Since sulfur is very slowly dissolved by glycerol unlike other solvents, it is retained as a suspension for a long time, even though the concentration is well below the saturation limit.

Even below 160°C the region around 3500 Å shows a slight but perceptible maximum. This might imply that traces of the new species are formed at lower temperatures. However, the major change is supposed to take place at ca. 160°. A more detailed discussion was given earlier (Chapter I).

Summary

From a study of the solution spectrum of sulfur at various temperatures, at least two observations can be made: (1) at temperatures below 160°, the shift in the spectrum appears to be a temperature effect on absorption; (2) above 160°, a structural change involving the formation of new species is also assumed. These observations are in agreement with those made in Chapter I on liquid sulfur.

CHAPTER VI

POLYSULFIDE SPECTRA

Introduction

Polymeric sulfur species were discussed in Chapter I. The complexity of spectrum of liquid sulfur results partly from the presence of such species. Sulfur chains in liquid sulfur can be exceedingly large, containing up to 10^6 sulfur atoms (72).

A simpler approach to the study of polymeric sulfur chains would be the spectral investigation of compounds containing polysulfide chains. Basically, they are derived from sulfanes, H_2S_x where x = 2 to 10, generally. Examples of such compounds are found in polysulfides and polythionates. In the former, a metal or an organic radical takes the place of hydrogen in H_2S_x and in the latter, SO_3^{2-} groups replace the hydrogen.

UV absorption spectra of a few polysulfides and polythionates have been studied (73,74). The latter are colorless whereas the former are yellow to red. Organic polysulfides and alkali polythionates show absorption bands at wavelength lower than 3300 Å; hence they are of little help in understanding the spectrum of polymeric sulfur. On the other hand, alkali

polysulfides and other ionic polysulfides are deeply colored and give absorption bands at higher wavelengths. Schwarzenbach and Fischer, 1960, (75) observed two peaks, at 2900 Å and 3750 Å, in the spectrum of sodium and potassium polysulfides M_2S_x, x = 2 to 5. They had used aqueous solutions for the study. From analytical methods they concluded that solutions of di, tri and tetra sulfides contained S_4^{2-} ions while solutions of penta sulfide contained S_5^{2-} ions. S_2^{2-} and S_3^{2-} ions were not observed. The observed spectra were attributed to S_4^{2-} and S_5^{2-} species. Peak positions were the same for both ions but S_5^{2-} peaks had higher extinction coefficients.

There was some conflict in the absorption pattern of sulfur chains of the same length, obtained from different sources. The agreement between polythionates and organic polysulfides is fairly good (75) but ionic polysulfides show considerable deviation, as explained in the previous paragraph. This caused difficulty in assigning absorption peaks to definite species.

The purpose of this study was to re-examine the optical spectra of alkali polysulfides in other solvents such as alcohol. This, it was hoped, would show whether the absorption peaks reported had real significance in relation to the spectrum of polymeric sulfur. An nmr characterization of the

polysulfides was also planned because this would give an idea of the relative abundance of the various species in solution.

Experimental

The experimental part consisted of 3 stages:

1. Preparation of polysulfides
2. Characterization by NMR
3. Optical spectra

Details

1. Preparation of sodium polysulfides

The known sodium polysulfides are:

Disodium disulfane, Na_2S_2

Disodium tetrasulfane, Na_2S_4

Disodium pentasulfane, Na_2S_5

Samples of these polysulfides, prepared by the methods due to Feher (76) were available. The preparation methods are outlined below

Na_2S_2

$$Na_2S_4 + 2\ Na = 2\ Na_2S_2$$

A solution of Na_2S_4 (see preparation, later) in absolute alcohol (6 g in 50 ml) is prepared. While the solution is kept warm and a continuous stream of N_2 gas is passed through, 4 g. of shining Na, cut into fairly large pieces, is introduced rapidly one after another, by briefly

removing the reflux condenser. The solution is then heated for about 30 minutes at 80°C. The light yellow Na_2S_2 precipitate was rapidly suction-filtered through a glass frit in vigorous N_2 stream. It is thoroughly washed several times with absolute alcohol in order to remove occluded Na_2S_4 and adhering mother liquor. It is then allowed to stand in a vacuum desiccator over P_2O_5. The yield is about 7 - 8 g. of Na_2S_4. The product is microcrystalline and light yellow.

$\underline{Na_2S_4}$

$$2\ NaHS + 3\ S = Na_2S_4 + H_2S$$
$$112.14 \quad 96.20 \quad 174.25 \quad 34.09$$

A mixture of 50 ml of absolute and about 2 g. of fairly small pieces of shining Na is prepared in a 150 ml flask equipped with a reflux condenser and an (initially closed) side arm for holding a gas inlet tube. A drying tube on the condenser prevents contact with atmospheric moisture. After all the Na has dissolved to the ethoxide, a glass tube extending to the bottom of the flask is introduced through the side arm. It is sealed tightly in place, and pure, carefully dried H_2S is passed through it to saturate the solution. Then the stoichiometric quantity of pure, very finely powdered S (2.00 g. of Na corresponds to 4.17 g. of S) is added and the reaction mixture boiled for one hour on a steam bath while a vigorous stream of oxygen-free, dry N_2 is passed through.

A dark-red solution of Na_2S_4 is formed. This is evaporated to 5 ml in vacuum at about 40°C, causing a dense, yellow precipitate of Na_2S_4 to separate. The product is rinsed out onto a fritted filter with some absolute alcohol, quickly suction-filtered in a vigorous N_2 stream and washed with some alcohol. It is kept in a vacuum desiccator over P_2O_5 to remove the alcohol. Orange yellow crystalline powder results. The yield is 5 - 6 g.

Na_2S_5

$$Na_2S + 4\ S = Na_2S_5$$
$$78.06 \quad 128.26 \quad 206.32$$

About 2.5 g of Na_2S and the stoichiometric quantity of S are placed in a Pyrex tube in a vigorous stream of dry, oxygen-free N_2. After the tube has been sealed off in high vacuum, the reactants are fused at 500°C in an electric furnace until completely homogenized (about 45 minutes are required). The melt solidifies on cooling to a hard, grayish yellow cake of Na_2S_5.

2. Characterization of Polysulfides by nmr

In this method, polysulfides were converted to hydrogen polysulfides (sulfanes) and analyzed by proton nmr. The nmr signals for sulfanes have been interpreted by previous workers (77).

To apply this technique, the polysulfides were dissolved in water (1 g in 5 ml). 1 ml of each solution was added to 10 ml of conc. HCl in an ice bath (-10°C) while being stirred by a magnetic stirrer. The contents were allowed to stand for some time. An oily layer, containing the sulfanes, separated at the top. This was dissolved in CS_2 and a proton nmr spectrum was taken at room temperature, as quickly as possible. A Varian A - 6 model NMR spectrometer was used in these investigations. The sweeptime was 250 sec. and the sweepwidth, 500 cycles in all the experiments. Since CS_2 has been found to show a solvent shift of about 47±3 cps when compared with TMS standard, the positions of the signal could be adjusted to standard values (78).

In another set of experiments, a few organic acids such as CF_3COOH and HCOOH were used instead of HCl to obtain the sulfanes.

3. UV-Visible Spectra (2400-7000 Å)

Solutions of the various polysulfides were prepared in water and absolute ethanol and the spectra were scanned as quickly as possible with a Cary 14 model spectrophotometer. The aqueous solution coagulated in a few minutes when exposed to radiation. The ethanol solution, on the other hand, became colorless after some time.

Results and Discussion

1. Composition of the sulfanes from polysulfides

Figure 30 shows a typical nmr spectrum obtained for the sulfane mixture. The four peaks found in all spectra have been assigned to H_2S_6, H_2S_5, H_2S_4 and H_2S_3 (77). The H_2S_2 peak is very weak in sulfane spectra. This was verified from the present study too.

Table V summarizes the data on composition of the sulfane mixtures obtained by conversion of polysulfides under different conditions. The percentages were worked out on a relative basis, from the area under each peak.

Though a mixture of sulfanes resulted from the polysulfides, the predominant species corresponded to the parent compound, except for Na_2S_2 (H_2S_4 was the largest proportion). The conversion of polysulfides into sulfanes is responsible for the mixture. It appeared that S_4^{2-} species might be the most stable ion in solutions of Na_2S_4 and lower polysulfides. The same observation has been made from titrimetric estimations of polysulfide solutions (75).

It is seen from Table V that when organic acids are used, the compositions are different for the sulfane mixtures. More of the parent type species resulted (except for Na_2S_2). This might mean that strong acids like HCl bring about

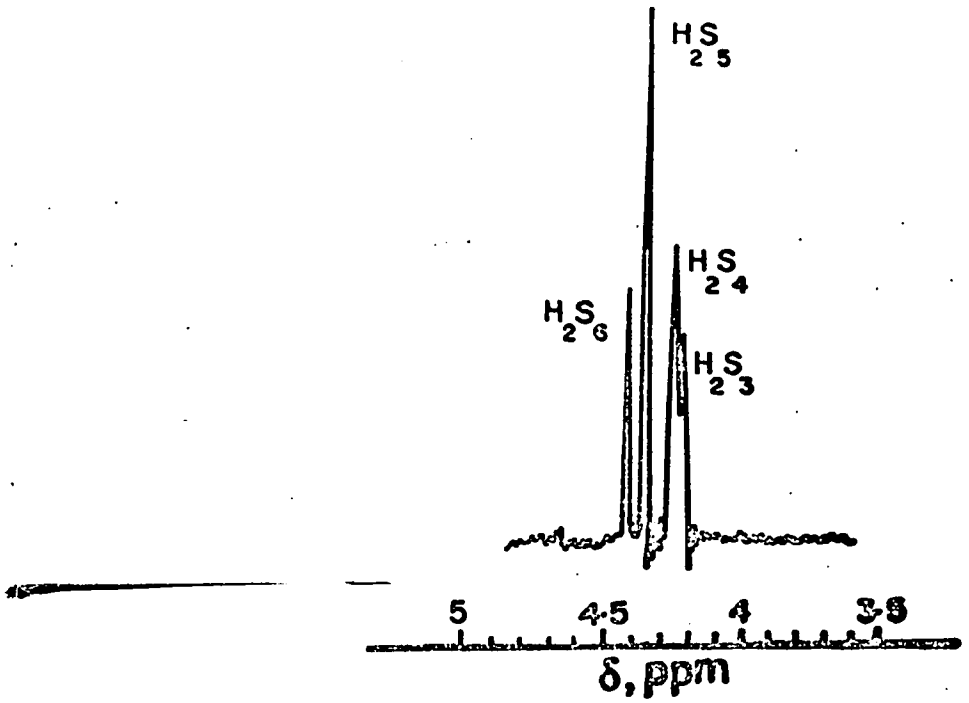


Figure 30. Typical NMR Spectrum of Sulfanes from Sodium Polysulfides

TABLE V

COMPOSITION OF SULFANES FROM POLYSULFIDES

Polysulfide	Acid	Per cent Composition of Sulfanes (Relative)			
		H_2S_6	H_2S_5	H_2S_4	H_2S_3
Na_2S_2	HCl(aq)	18	15	50	17
Na_2S_2	CF_3COOH	3	5	79	13
Na_2S_4	HCl(aq)	32	20	42	6
Na_2S_4	HCOOH	13	15	59	13
Na_2S_4	CF_3COOH	16	17	56	11
Na_2S_5	HCOOH	24	44	29	4
Na_2S_5	CF_3COOH	20	48	28	3

considerable decomposition of the sulfanes. The results obtained with formic acid and trifluoro acetic acid were consistent.

2. Spectral features

Figure 31 shows the spectra of polysulfides in aqueous and alcoholic solutions. All the alkali polysulfides gave the same type of spectrum for a given solvent. For aqueous solutions, the peaks were at 2950 Å and 3750 Å and the spectrum agreed with that obtained by Schwarzenbach (75). For alcoholic solutions, a strong peak at 4100 Å and a shoulder at ca. 3250 Å were observed. In a few minutes the peaks faded and the typical S_8 peaks in 2600 - 2800 Å region (Figure 25a) resulted. The aqueous solution, on the other hand, turned cloudy and all peaks disappeared. The spectrum became broad and resembled the spectrum of sulfur in solid and liquid states. The conclusion was that in both cases elemental sulfur was present. In alcoholic medium the sulfur dissolved but in water it remained as suspended particles.

The shift in peak positions with change of solvent is not easily explained. Two possible causes are suggested: (1) the species are different in different solvents, (2) the same species are present but their absorption bands are shifted due to solvent interaction. A decision cannot be made until

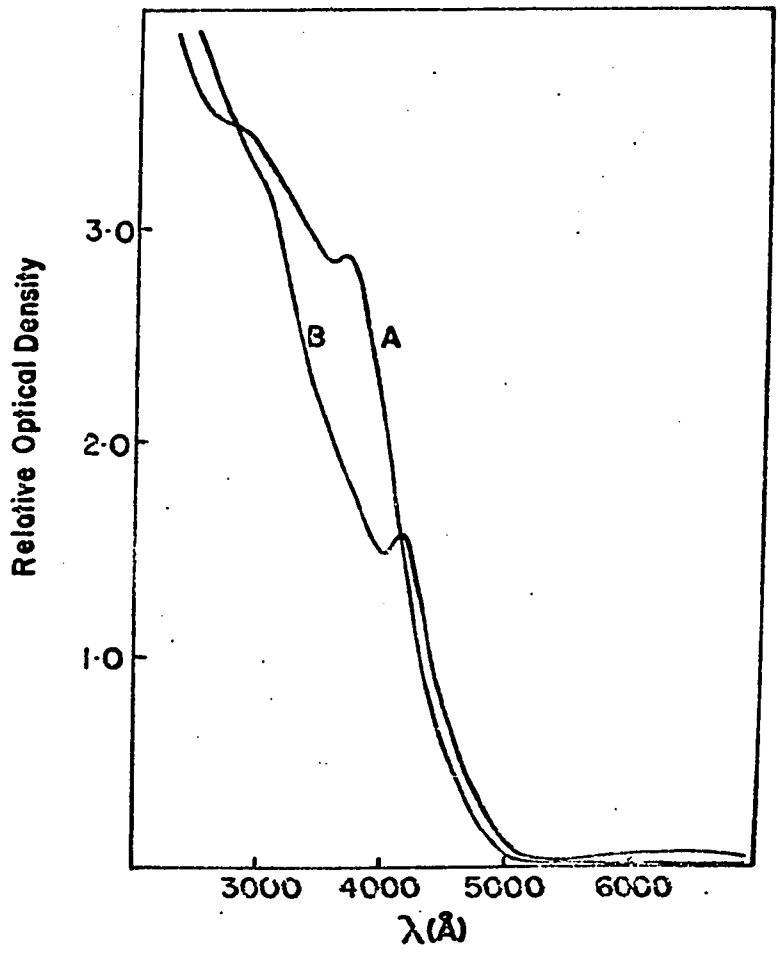


Figure 31. Optical Spectrum of Na_2S_5 a. in Water. b. in Absolute Ethanol

the alcoholic solution is analyzed for species present.

The peaks observed for aqueous solutions were attributed by Schwarzenbach and Fischer to S_4^{2-} and S_5^{2-} ions (75). Both species were found to give the same peaks. For solutions of Na_2S_2, and Na_2S_4, the predominant polymeric species was S_4^{2-} whereas for Na_2S_5, the S_5^{2-} ion had the largest concentration. NMR analysis reported in the previous section leads to the same conclusion. The reactions in aqueous solutions are represented by (75):

$$3\ S_2^{2-} + 2\ H_2O \longrightarrow 2\ HS^- + 2\ OH^- + S_4^{2-}$$

$$4\ S_4^{2-} + H_2O \rightleftharpoons OH^- + SH^- + 3\ S_5^{2-}$$

$$S_5^{2-} + H_2O \rightleftharpoons OH + HS_5^- \overset{H_2O}{\rightleftharpoons} OH^- + H_2S_5$$

An interesting observation from the spectra of organic polysulfides is the intensification of absorption with increase in chain length, with a change in peak positions (Figure 9b, Chapter I). If this result is applied to liquid sulfur, one should expect the absorption to increase with increase in temperature, up to 200°C and then decrease with further rise in temperature because this is the pattern for sulfur chain-length in liquid sulfur. This is contrary to the observed result in liquid sulfur.

It was mentioned in the Introduction that the spectra of polysulfide ions were different from the spectra of

polythionates and organic polysulfides. The latter showed good agreement among themselves. For a chain of four sulfur atoms, a peak is found at ca. 3000 Å and for 6 sulfur atoms, at 3250 Å (73). These differ greatly from the peaks at 3750 Å and 4100 Å shown in Figure 31 and attributed to S_4^{2-} ion.

The lack of correlation may be due to the nature of the sulfur chain in these compounds. In organic polysulfides and polythionates the sulfur chain is attached to terminal groups. Ionic polysulfides, on the other hand, dissociate giving polysulfide ions. The sulfur bonds in these free chains may have more double bond character than those in organic polysulfides; hence they may be expected to show transitions at longer wavelengths.

Summary

Sodium polysulfides Na_2S_4, Na_2S_4 and Na_2S_5 prepared by the methods suggested by Feher, were used in this study.

NMR analysis showed that H_2S_6, H_2S_5, H_2S_4 and H_2S_3 were formed from the polysulfides. Na_2S_4 and Na_2S_5 showed a larger proportion of H_2S_4 than of H_2S_2 and H_2S_3. The results obtained with organic acids were consistent but different from those obtained with HCl. Weak acids are considered to give better results.

UV-VIS spectra of various alkali polysulfide ions were

similar for a given solvent. Peak positions were found to shift with change in solvent.

Polysulfide ions absorb light of longer wavelength than do organic polysulfides. This may be due to the difference in bonding in sulfur chains in the two cases.

This study did not give definite correlations between spectra of polymeric sulfur and polysulfide spectra since polysulfide ions gave absorption bands in the visible spectrum, it seems possible that certain short chain polymers of sulfur may also absorb in the visible.

Further Work Suggested

Analytical methods of investigation are necessary to identify the species present in alcoholic solutions of polysulfides. This might enable a better understanding of the spectra of alcoholic solutions.

Solvents other than alcohol may also be used. A preliminary study showed that in acetone solution, alkali polysulfides show a transient blue-green color. Two absorption bands at 6500 Å and 4100 Å were observed. When the solution became colorless, spectrum of S_8 in solution was obtained. It is known (79) that aldehydes, ketones and some alkaloids form additional compounds with sulfanes. Further investigation would be useful.

CHAPTER VII

SULFUR-IODINE SYSTEM

Introduction

In Chapter V, where the solution spectrum of sulfur was discussed, it was seen that sulfur (S_8 molecules) has characteristic absorption bands in 2600 - 2800 Å region. If other species besides sulfur are present in solution, and if they do not interact, the spectra of the various species should be additive. On the other hand, if new compounds are formed, new absorption bands can be expected.

In this chapter spectroscopic study of solutions containing sulfur and iodine will be described. The main purpose is to examine whether any compound is formed between the two elements.

So far no definite evidence is available for the existence of a sulfur-iodine compound. Many attempts to effect combination have been unfruitful (80). This aspect will be examined in greater detail under discussion of results.

A few authors, however, think that they have obtained some evidence of sulfur-iodine compounds existing in solution or in the solid state. Linebarger, 1895 (81) concluded from cryoscopic studies the existence of S_2I_2. Recently, Feher

and Munzner, 1963 (82), and Jander and Turk, 1964 (83) claimed the existence of several sulfur-iodine compounds. Feher and Munzner conducted a spectroscopic study of sulfur-iodine system in cyclohexane and observed a weak band at ca. 3000 Å which they ascribed to iodosulfanes, S_xI_2, x = 2 to 6. The characteristic S_8 bands were not found in 2600 - 2800 Å region. This would suggest strong compound formation. Jander and Turk studied the solubilities of sulfur-iodine systems in dichloromethane and analyzed products obtained on freezing the solutions. They concluded that a compound, S_8I_2 existed as a solid at low temperature (- 50°C).

In view of the inconclusive evidence for sulfur-iodine compounds, it was thought desirable to re-examine the above results. The absence of S_8 peaks in the spectra of S - I system could not be explained on the grounds of the extremely weak bond between sulfur and iodine. It was suspected that some other factor was responsible for the observed spectra. In the case of the work of Jander and Turk where a compound was reported at low temperatures, the possibility of compound formation seemed real; hence a low-temperature study of sulfur-iodine system was also planned.

This chapter also describes the spectrum of iodine in several solvents, because it was found necessary to analyze the spectral behavior of each component at lower temperatures.

Low temperature spectra of sulfur solutions have already been studied but such studies have not been done on iodine solutions.

In these studies the same solvents as used by earlier workers (82) were selected. However, other solvents were also used to give comparable results.

Experimental

A. Study at room temperature

Materials: Sulfur: 99.999% pure, as before.

Iodine: A.R. Grade (sublimed): suppliedby Mallinckrodt Chemicals.

Solvents:

1. 2 - Methyl butane (Isopentane), Spectroscopic grade (M C & B)

2. Cyclohexane, Spectroscopic grade, (M C & B.)

Standard solutions of sulfur and iodine were prepared in each solvent. Two methods were employed to obtain mixtures of varying proportions:

1. The stock solutions were diluted to obtain solutions containing the same atomic concentration of sulfur and iodine in each solution. They were mixed in varying proportions so that the total volume was the same in each case. This method was used with isopentane. This mixtures contained sulfur and iodine in ratios in which compound formation could be expected to take place.

2. The concentration of sulfur was kept constant while the concentration of iodine was changed thereby giving various ratios of sulfur and iodine. The solvent used was cyclohaxane in this case.

Spectra

A Cary 14 Model Spectrophotometer was used. Spectra were scanned from 7000 Å to 2400 Å.

In addition to obtaining the spectra of the mixtures and pure substances, the individual solutions were placed in a line one behind the other in two cells and spectra were recorded. This served as a check of the additivity of spectral absorption for a pure mixture.

B. Sulfur-iodine system at low temperatures

Since most solutions freeze above 77°K, solvents which gave transparent glasses had to be chosen for study at very low temperatures. The glass used in earlier studies (Chapter V) was found suitable for the present study.

Materials: sulfur and iodine: as before

Solvents: 2:1 mixture of methyl cyclohexane and 2 - Methyl butane (spectroscopic grade, M C & B)

Low temperature cell: same as described in Chapter V, Section A.

Procedure: the following temperatures were used in the study:

Temperature	Bath
- 78.5°C	Dry ice - acetone
- 126°C	Methyl cyclohexane slush with liquid nitrogen
- 196°C	Liquid nitrogen

A 1:1 atomic ratio solution of sulfur and iodine was prepared. About 15 ml of it were placed in the low temperature cell (Figure 26). Using the various baths, the solution was cooled to - 78.5°C, - 126° and - 196° and the spectra were obtained. Details of experimental procedure are given elsewhere (Chapter V).

The study was repeated using a pure iodine solution (in the same solvent mixture).

Results

A. Room temperature study

Figures 32 & 33 show the spectra of sulfur-iodine mixtures. An examination of these spectra revealed that for all mixtures only two peaks were present. In the 2600 Å region, the characteristic S_8 peaks were found. The peak at 5200 Å was due to iodine because the pure iodine solution (Figure 32a) showed the same peak. The spectra were merely the sum of the individual spectra of sulfur and iodine. This was confirmed by obtaining identical spectra for the separate solutions placed together in the optical path.

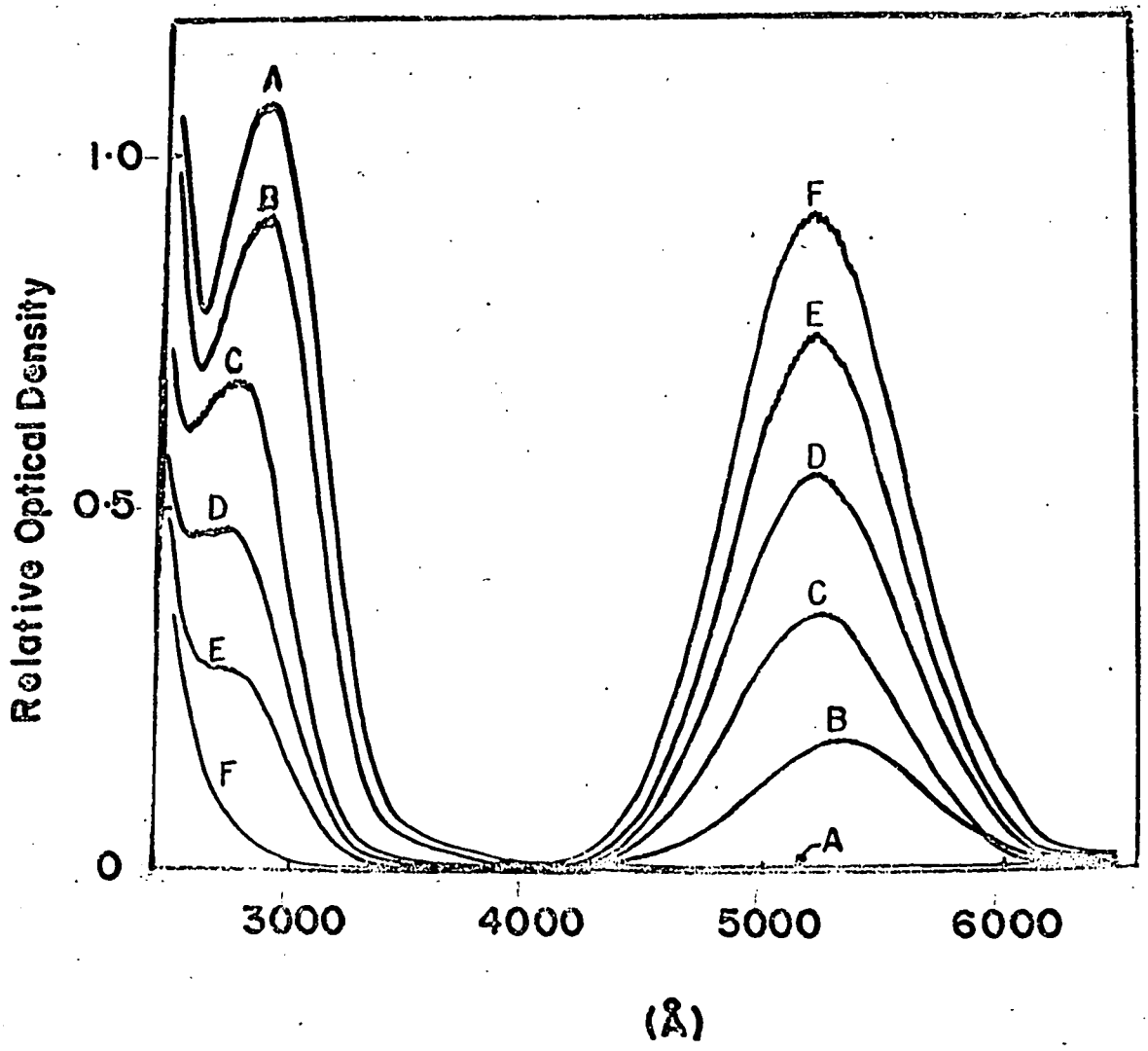


Figure 32. Spectrum of Sulfur-Iodine Mixture in Isopentane. A. Sulfur Solution; B.C.D.E.: Ratios Corresponding to S_8I_2, S_4I_2, SI_2, SI_4 Respectively. F. Pure Iodine Solution

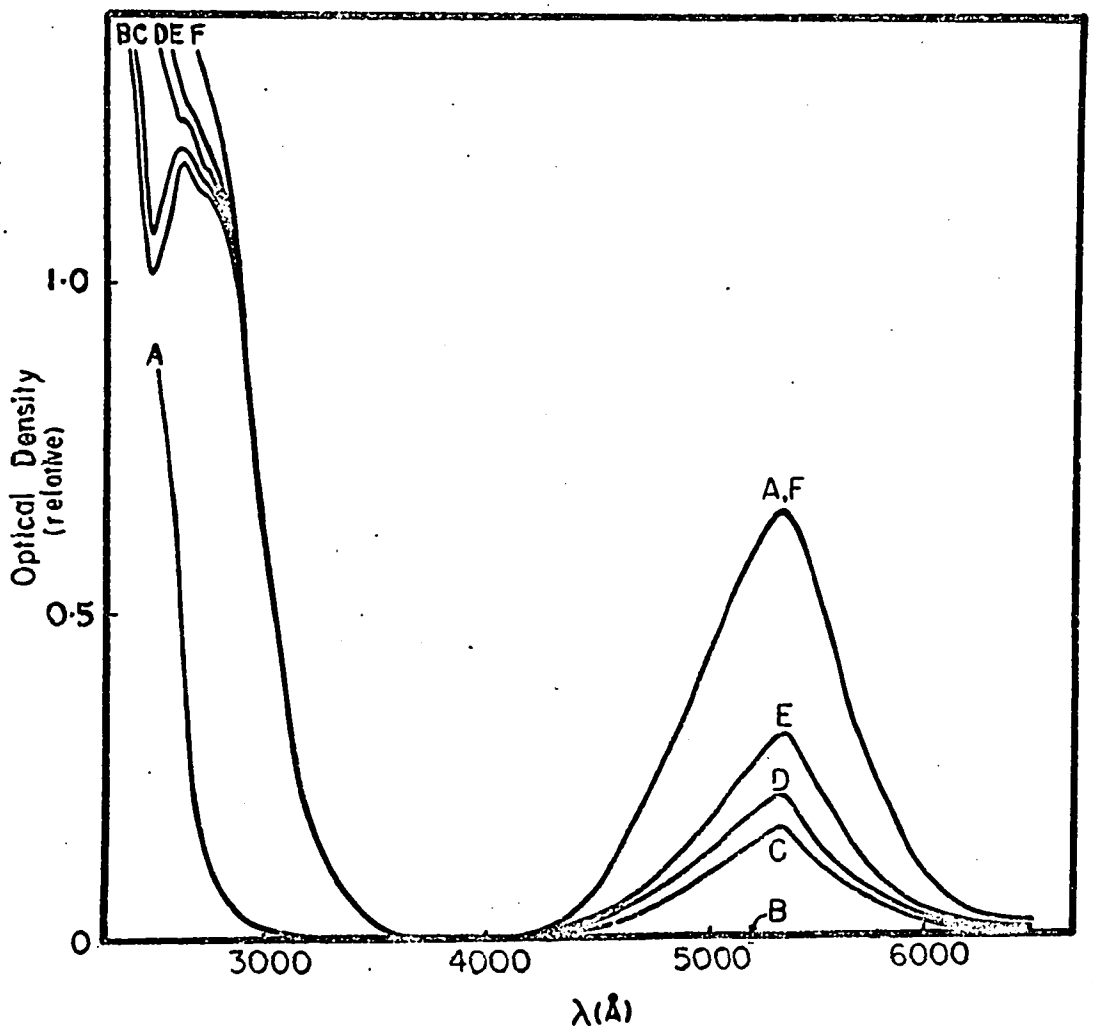


Figure 33. Spectrum of Sulfur-Iodine Mixture in Cyclohexane. A. Iodine Solution; B. Sulfur Solution C,D,E,F,: Ratios Represented by S_8I_2, S_6I_2, S_4I_2 and S_2I_2 respectively

B. Low temperature study

Figure 34a shows spectrum of sulfur-iodine mixture at - 196°. Comparison with Figure 34b, the spectrum of iodine at - 196° revealed that even though peak positions were different from those at room temperature, the shift was due to iodine. The new peak positions were at 4600 Å and 3200 Å. The S_8 peaks were not displaced. At - 78.5°C, the peak positions were as at room temperature, but at - 126°, the spectrum was similar to that at - 196°.

Discussion of Results: Sulfur-iodine System

There was no indication of a reaction product of sulfur and iodine at room temperature or at low temperatures. The solution behaved as a mixture. The same conclusion was reached by other workers: (1) The variation in density of a sulfur-iodine solution was found to be linear (84). (2) Cryoscopic studies (85) on the molten mixture revealed existence of S_8 and I_2 species exclusively in the mixture. (3) Ebullioscopic methods (86) also gave the same result. (4) The phase equilibrium diagram of S - I system (87) showed that it is a simple eutectic system, the eutectic mixture containing about 51 to 54 per cent S, at 66°C. (5) The heat of solution of a sulfur-iodine mixture in CS_2 was found to be the sum of the individual heat of solution (88). (6) The rule of additivity,

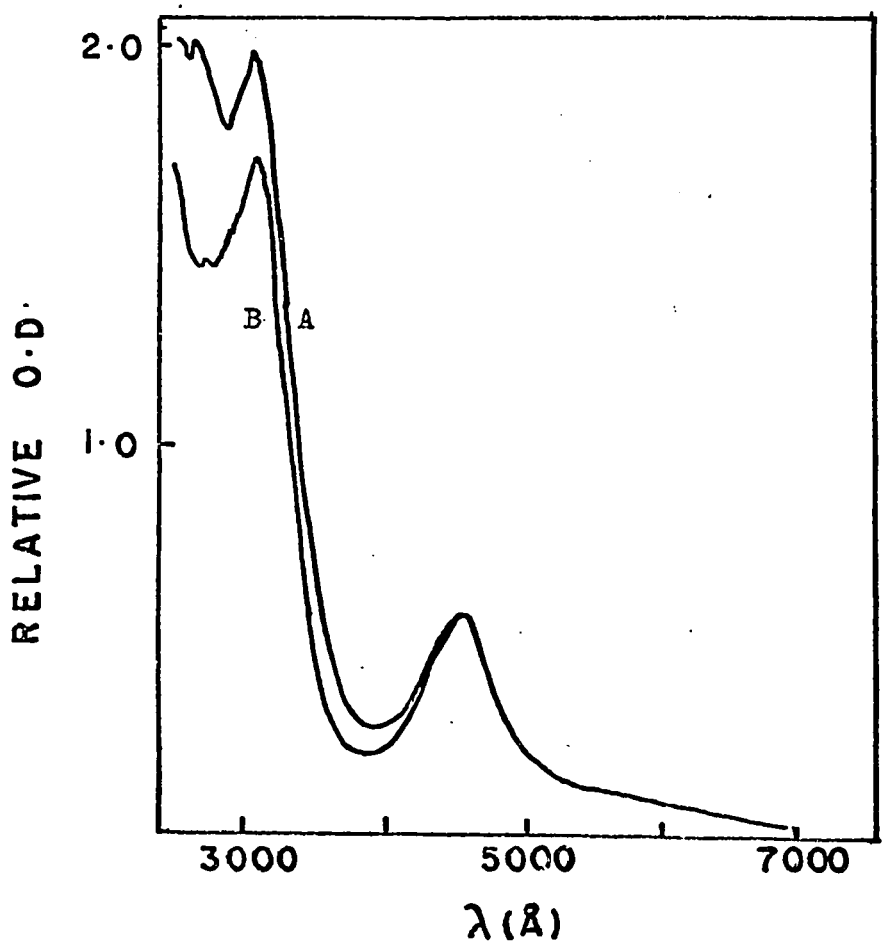


Figure 34. Spectrum of Sulfur-Iodine System at 76°K in Glass. A. 1:1 Atomic Ratio; B. Pure Iodine Solution

true for mixtures, was found to be valid for sulfur-iodine system when magnetic susceptibility measurements were carried out (89). The same was not true for other sulfur-halogen systems in which chemical reaction occurs.

Stability factors derived from heats of dissociation show that the sulfur-iodine bond must be weak, e.g., heats of dissociation of dihalides (80)

S_2Cl_2	14.3 kcals
S_2Br_2	4.0 kcals
S_2I_2	(zero)

The observation of a peak at 3000 Å by Feher and Munzner for solutions of sulfur-iodine in cyclohexane could not be substantiated by the present study. It is suspected that some impurity might have been responsible for the peak. The observed absence of S_8 peaks must also have been erroneous or due to presence of impurities.

The conclusion, therefore, is that sulfur and iodine do not combine chemically under the conditions described.

Iodine Solutions: Charge Transfer Phenomenon

A few significant observations on this aspect could be made during this study. It is well-known that iodine solutions in different solvents have different colors. In aliphatic hydrocarbon solvents, CS_2, CCl_4 etc., it has a

violet color. The spectrum in such solvents is shown in Figure 32a. In aromatic, basic (electron donor) and polar solvents, the color varies from red to brown to pale yellow. In alkalies, it is colorless. Figure 3.5 shows the spectrum of iodine in several solvents (90).

In the present study, inert solvents were used. At room temperature, the solutions were violet and the familiar iodine peak at 5200 Å was observed. In vapor phase the spectrum is similar and shows the 5200 Å peak (91).

On cooling the solution to - 126° or below, it was observed that the peak suddenly shifted to 4600 Å; a new peak at 3200 Å was also seen. At first it would appear that this is a result of temperature effect on spectral shifts, discussed elsewhere. On closer scrutiny, however, one finds that such a view is untenable. There was no shift in peak position from room temperature to - 78.5°C. The observed shift at - 126° and below was exceedingly high (ca. 600 Å). The appearance of the new peak is also not explained.

If, however, we consider the shift as due to a phenomenon similar to that in donor solvents, the spectrum could be understood more clearly. Comparison of spectrum of iodine in various solvents reveals some correspondence. The absorption peak at 5200 Å is shifted to 4500 - 4600 Å in toluene, ethanol and water. Another peak at 3200 Å is found

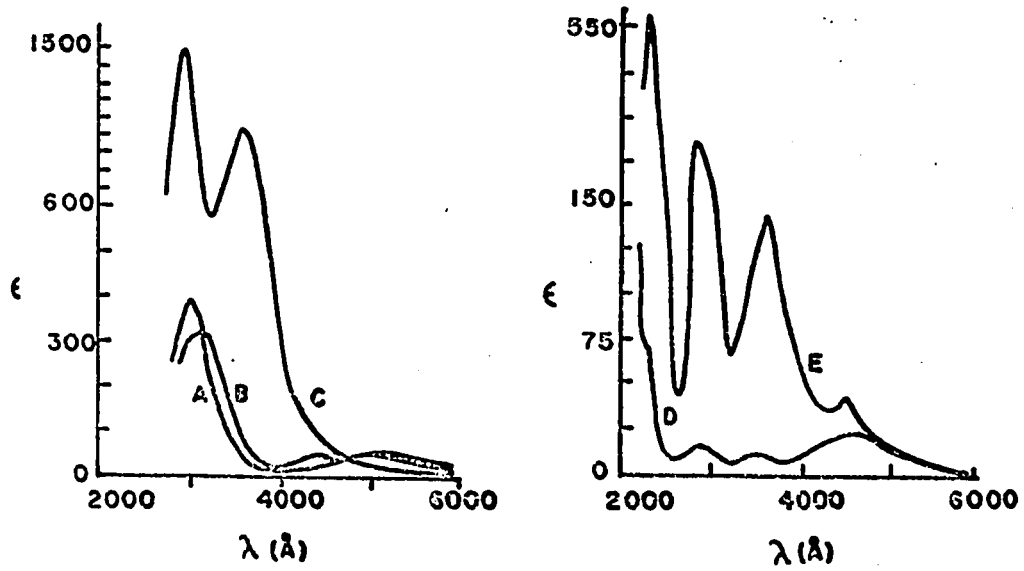


Figure 35. Spectrum of Iodine in Solvents. A Benzene, B. Toluene, C. 5% KI, D. Water, E. Ethanol.

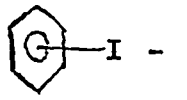
for toluene solution. In some other solvents another peak at 3500 Å is seen.

The new peaks and the shift in the 5200 Å peak are ascribed to a charge-transfer type of complex formed between iodine and the solvent, represented by

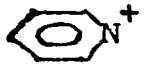
$$X_2 + \text{solvent(s)} \longleftrightarrow X_2^- \text{--- S}$$

The exact mechanism of charge-transfer phenomenon is not yet understood (92). Recent workers (93) include factors such as electrostatic attraction and repulsion terms in the wave function describing these systems, to explain the results. The interaction of iodine with solvents increases with the donor properties of the latter, as illustrated below: (84)

$I_2 + CCl_4 \longrightarrow$ no change (violet color)

$I_2 + C_6H_6 \longrightarrow$  (red)

$I_2 + (C_2H_5)_2O \longrightarrow (C_2H_5)_2O: I = I$ (brown)

$I_2 +$  $\longrightarrow$  $\underbrace{I - I = I}_{I_3^-}$ (Brown solution, solvolysis)

$I_2 + OH^-$ (alkali) $\rightleftharpoons$ H:O:I + I^- (colorless)

$\Downarrow$ heat

$IO_3^- + I^- + H_2O$

It has been observed that (95) temperature is a deciding factor in the stability of these complexes. The lower the temperature, greater the stability. If this rule is

extended to the so-called inert solvents (CS_2, CCl_4, aliphatic hydrocarbons etc.), we might expect stable charge-transfer complexes at sufficiently low temperatures. In the present case, we may suppose that stable complexes were formed at - 126° and below.

Summary

In this chapter, the spectra of sulfur-iodine and iodine were discussed. The observed spectra indicated that in solution and in the frozen solid state, sulfur and iodine do not form any new chemical compound. The stability of S-I bond is very small and thermodynamic measurements support the present observation that the system is best described as a mixture.

The spectrum of iodine in inert solvents at room temperature was similar to the vapor phase spectrum and revealed little interaction of iodine with solvent. At very low temperatures, the spectrum resembled that given by solutions of donor solvents. It was assumed that even the "inert" solvents such as CS_2, CCl_4, aliphate hydrocarbons, etc. would form complexes with iodine at sufficiently low temperatures.

Further Work Suggested

It is useful to conduct an extensive study of band shifts for various "inert solvents" and find out the transition

temperatures. This would reflect the donor ability of each solvent and the strength of the charge-transfer complex.

PART II

PREPARATION OF FLUOROSULFANES FROM ELEMENTAL SULFUR

PART II

PREPARATION OF FLUOROSULFANES FROM ELEMENTAL SULFUR

CHAPTER VIII

PREPARATION OF FLUOROSULFANES FROM ELEMENTAL SULFUR

Introduction

Fluorosulfanes are divalent sulfur fluorides of the general formula, S_xF_2 where x = 1,2,3, etc. Only one member of this series has been prepared with certainty. This is disulfur difluoride, F-S-S-F, (1) one of the two isomers of S_2F_2. It is an unstable compound that melts at -133°C and boils at +15°C. The other isomer is thio-thionyl fluoride, SSF_2 (2) (m pt. -165°, b. pt. -10.6°), evidently not a fluorosulfane. F-S-S-F slowly isomerizes to SSF_2 at room temperature. Both isomers are formed by the reaction of AgF with elemental sulfur (3) but the proportion of each isomer is dependent on temperature. If the reaction is carried out at 120°, S_2F_2 formed contains at least 50 per cent of the F-S-S-F isomer; at higher temperatures more of SSF_2 is formed. The preparation of the first member of the fluorosulfanes, SF_2, has been claimed by several workers (45) but the available evidence, even the ^{19}F-NMR and mass spectra obtained by Seel (4), still leaves room for doubt.

This NMR spectrum reported by Seel (4) was obtained

from a sample of volatile products of the reaction of AgF with sulfur. The spectrum consisted of 11 peaks varying in chemical shift from -90 to +215 ppm (with respect to $CFCl_3$). SSF_2, F-S-S-F and SF_4 were identified by their known chemical shifts. A peak with $\delta = 71$ ppm was assigned to SF_2 by analogy with the peak position of SSF_2 and OSF_2. Six remaining peaks with values -52 to +215 ppm could not be assigned to any known compounds. These peaks were tentatively assigned to higher members of the fluorosulfane series.

The purpose of the present study was to repeat earlier experiments with a view to isolating fluorosulfanes believed formed in the reaction between AgF and S, and to characterize them. Direct characterization by ^{19}F NMR is clearly impossible because the fluorosulfanes have not previously been isolated. If, however, fluorosulfanes react with H_2S to form sulfanes as do chlorosulfanes (6) proton NMR could be used indirectly to characterize the fluorosulfanes. Other reactions of fluorosulfanes, for example, reaction with CF_3 - SH, may be used to confirm the nature of the species, and ultimately, the F-NMR can be measured and assigned. The study of proton-NMR and ^{19}F-NMR spectra will be described in sections A and B respectively.

A. Proton-NMR Study

Experimental

Earlier workers warned that the isomers of S_2F_2 react rapidly with glass, so that the more recent studies have used

Monel metal, Teflon and Kel-F apparatus (7). However, it is well established that many such warnings in fluorine chemistry are based on experiences with glassware that has not been scrupulously dried; so it was decided to begin the present work in borosilocate glass.

Materials: AgF: available from ALFA Inorg. Inc. Beverly, Mass. Approximately 1 g. of the material was transferred to a glass ampoule (about 50 ml. capacity) in a dry bag. It was then dried by heating to 200° for 6 hours under vacuum, and sealed. The ampoule was provided with a break seal.

Sulfur: 99.999 per cent purity, supplied by American Smelting and Refining Co. New Jersey. About 6 g. were transferred to a similar ampoule, degassed under vacuum after melting and the gaseous products pumped out.

H_2S: C.P. Grade: obtained in a cylinder from Matheson Chemical Company.

Procedure

The apparatus, made of Pyrex glass, is shown in Figure 1. It consisted of the two ampoules containing the reactants and two traps A and B. The two break seals separated the reactants prior to experiment. The apparatus was flamed out several times while pumping, before commencing the experiment.

The break seals were broken and the silver fluoride was allowed to fall into the lower ampoule. The magnetic breaker and the empty AgF ampoule were then sealed off and removed.

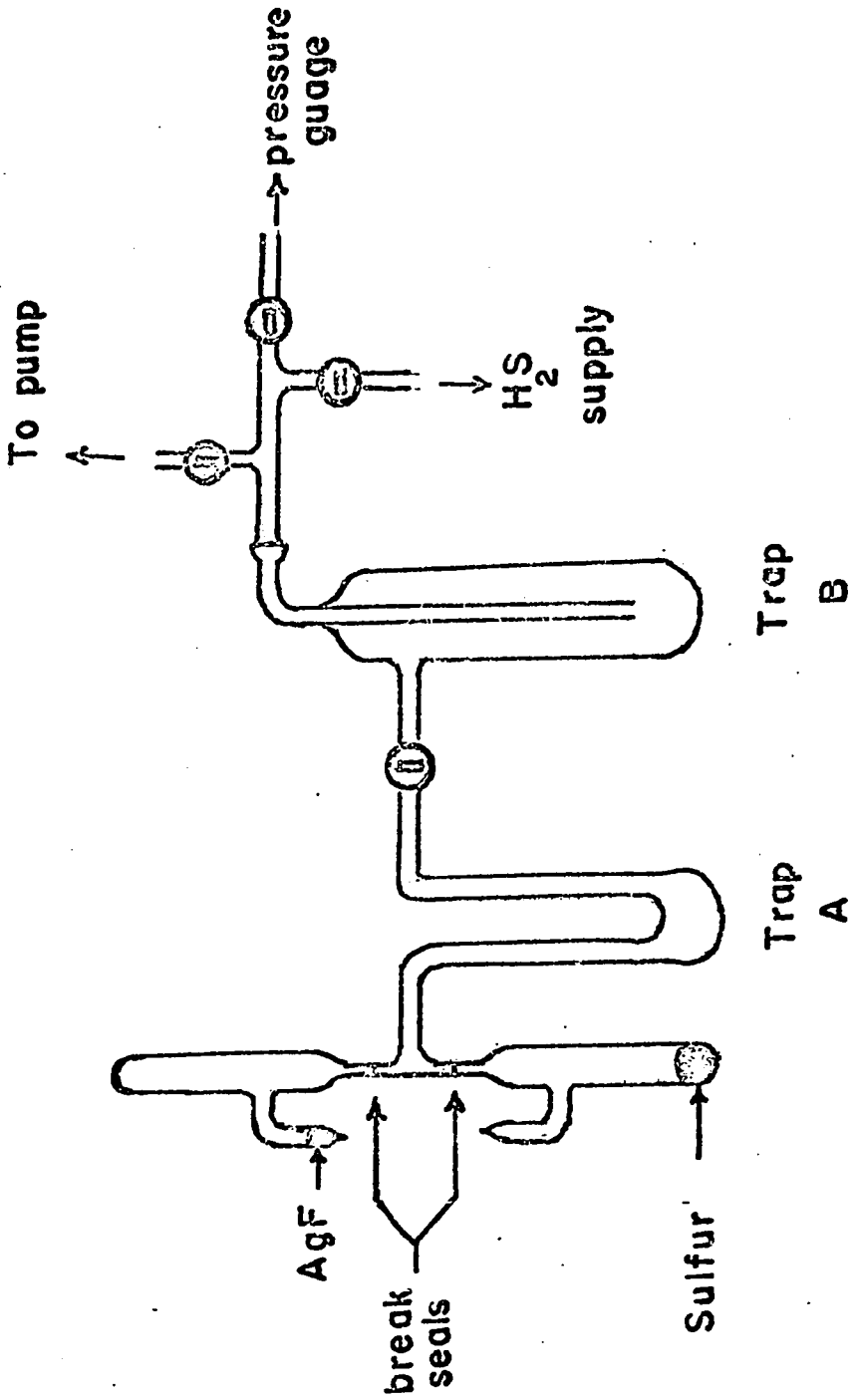


Figure 1. Apparatus for the Study of AgF/S Reaction

The ampoule containing the mixed reagents was heated in an oil bath to 120°, trap A being immersed in liquid nitrogen. The AgF/S mixture bubbled vigorously and slowly darkened; a pale yellow solid collected in trap A. A yellow solid condensed on the upper part of the ampoule which could be melted down by a heat gun.

After about 2 hours very little further material was condensing in the trap (A). Heating was stopped and a large excess of H_2S was distilled into the liquid N_2 trap (A) which was then warmed slowly. The products melted and turned yellow, and at about -80°, orange. A sudden increase in pressure (of H_2S) resulted in the disappearance of the orange color, leaving liquid H_2S with some yellow solid in the trap. This was then cooled to -196°.

The reaction part of the apparatus, which had been at room temperature since the H_2S was introduced, was now sealed off and set aside. The trap (A) containing the products and H_2S was warmed to room temperature and the evolved compounds were trapped out in another part of the vacuum line and subsequently destroyed by hydrolysis. These procedures left a dark, greenish-yellow oil in the trap (A). This part of the line was opened to air and the non-volatile residue extracted with cold CCl_4. A pale yellow oil and a dark green residue resulted. After decanting the CCl_4 solution, the residue was

found to be soluble in CS_2, giving a dark green oil.

Proton NMR spectrum of the yellow and green oils were taken on a T-60 model NMR spectrometer.

Results and Discussion

Figures 2 and 3 show the NMR spectra of the yellow and green oily products. Both spectra contained peaks which could be assigned to sulfanes, H_2S_x (8). Hence it was evident that sulfanes were formed by the reaction of H_2S with the products of AgF/S reaction. The CCl_4-soluble part of the sulfane mixture gave rise to strong peaks corresponding to H_2S_6, H_2S_5 and H_2S_4, the concentration of these species being in the order $H_2S_6 > H_2S_4 > H_2S_5$. In the CS_2 solution, the order was the same but the proportion of H_2S_6 was much greater. A shoulder was seen on the peak due to H_2S_6 and could not be identified. It could be due to a partially fluorinated sulfane. A very weak peak corresponding to H_2S_3 was found in both spectra.

Assuming a simple exchange reaction between H_2S and fluorosulfanes, formation of the various sulfanes can be represented by

$$H\text{-}S\text{-}\boxed{H + F} - S_x - \boxed{F + H} - S - H = H - S - S_x - S - H + 2\,HF$$

and generally by

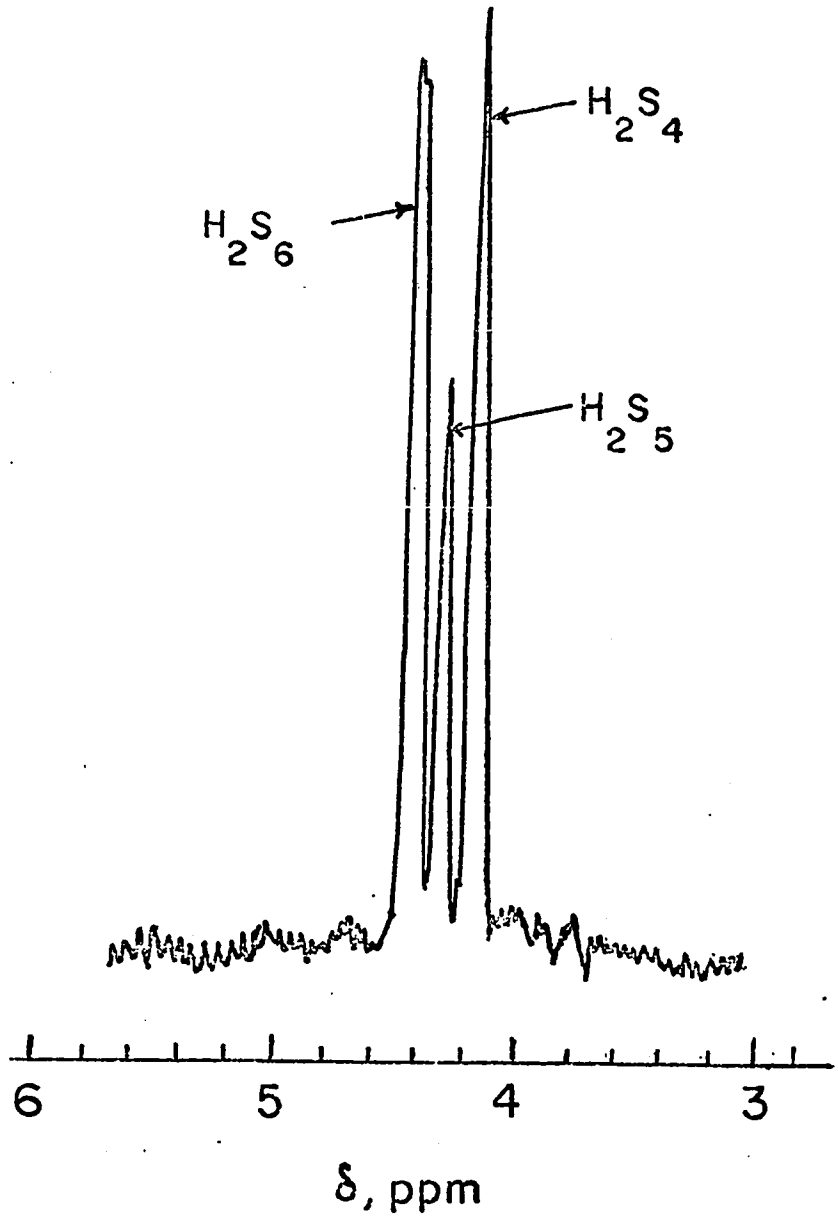


Figure 2. Proton NMR Spectrum of Sulfanes from Reaction Products. Solvent: CCl_4

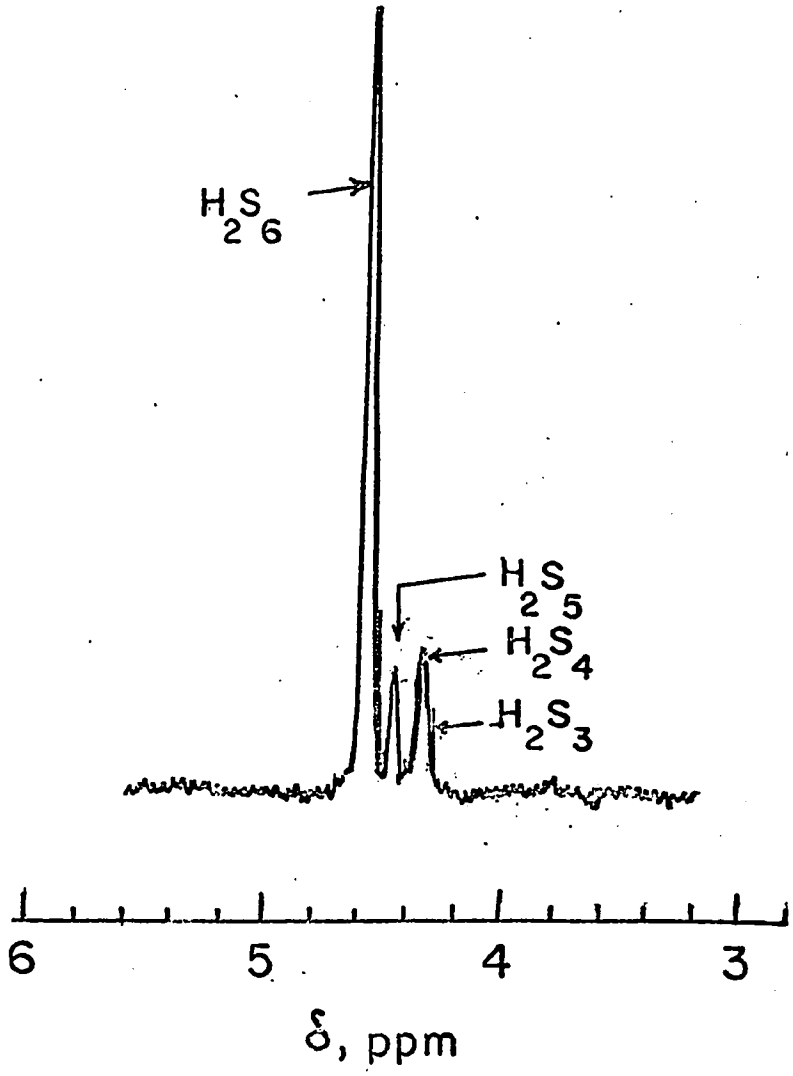
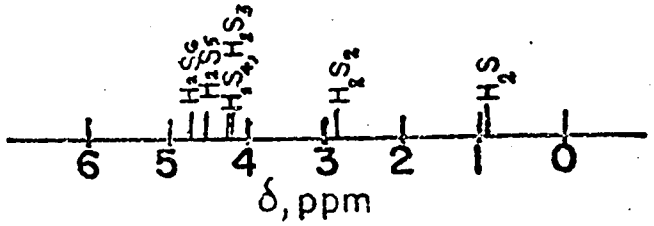


Figure 3. Proton NMR Spectrum of Sulfanes from Reaction Products. Solvents CS_2; below: relative positions of sulfanes.



$$S_yX_2 + H_2S\ (liq)\ (excess) \longrightarrow S_{y+2}H_2 + H_2S + 2HX$$

where H_2S is both a solvent and reactant.

The correlation between the sulfanes observed and the fluorosulfanes believed formed by the original reaction of H_2S and fluorosulfane is valid only if the reaction with H_2S leads quantitatively and reproducibly to only one sulfane and second, the resulting sulfane is stable.

The reaction between S_xF_2 and H_2S can be assumed to be similar to that of S_xCl_2 and S_xBr_2. The reaction of these have been extensively studied in this group (9) and elsewhere (6). It has been shown that careful reaction of the halosulfane S_xX_2 with excess liquid H_2S at -80°C leads to more than 90 per cent of the sulfane $S_{x+2}H_2$.

The stability of the sulfanes is satisfactory. At -64°C, in excess liquid H_2S, they are stable for many weeks. At room temperature, in CS_2 they equilibrate with each other, within a few days; without solvent, they equilibrate within hours according to

$$S_yH_2 + H_2S_z \longrightarrow S_{y-n}H_2 + H_2S_{z+n}$$

In the present experiment, the spectra were recorded within one hour of the formation of the sulfanes and hence it is reasonable to believe that equilibration was not appreciable.

From the results of the experiment we tentatively conclude that fluorosulfanes are formed by the reaction between AgF and excess elemental sulfur at 120°. The formation of S_4F_2, S_3F_2 and S_2F_2 is indicated by the indirect evidence from proton NMR . spectrum. The formation of SF_2 is not certain because the H_2S_3 peak was weak; equilibration reactions may also account for the peak. More work is needed to establish the best condition for preparation of fluorosulfanes and a detailed study will be needed if individual fluorosulfanes are to be prepared in pure form. The best method for producing pure fluorosulfane could be the reaction of S_2F_2 and SF_2 and condensation in cold dilute freon solution according to the scheme

$$S_2F_2 + H_2S + S_2F_2 \longrightarrow S_5F_2 + 2\ HF$$

$$SF_2 + H_2S + SF_2 \longrightarrow S_3F_2 + 2\ HF$$

B. ^{19}F-NMR Study

Experimental

The AgF/S reaction described in the previous section was repeated with a few modifications:

1. Smaller ampoules (20 ml capacity); only one break seal (in the upper one, containing the AgF)
2. Sulfur was degassed after the ampoules containing the reactants were joined together; the side arm of the lower ampoule was thereby avoided and this enabled the use of the oil bath in heating the upper parts of the ampoule containing the reactants.

3. Two NMR tubes were serially joined to the side tube common to the two ampoules; no traps were used.

By these changes the efficiency of the apparatus was increased. The products were collected in the first NMR tube (nearer to the ampoules) for about two hours and thereafter, in the second NMR tube, both at -196°C. The products collecting in the tubes were colorless both in the liquid and the solid phases. Some $CFCl_3$ was distilled into each tube to serve as an internal standard and the tubes were finally sealed and separated from the apparatus. The ^{19}F-NMR spectrum was recorded at -100°C on an A-100 model NMR spectrometer. Spectra were recorded also 10 minutes after warming the contents to room temperature.

Results and Discussion

Figure 4 shows the NMR spectrum of the first sample. Table I summarizes the observed chemical shifts of the peaks and possible assignments. The latter was done by comparison with the known chemical shifts of SF_4, SSF_2 and FSSF (10). Data obtained by Seel and coworkers (4) are shown for comparison. In contrast with the 11 peaks reported by Seel, the present spectrum contained only 4 peaks. The proportions of SSF_2 and FSSF were approximately equal and the proportion of SF_4 was about one-fourth of that of either SSF_2 or FSSF.

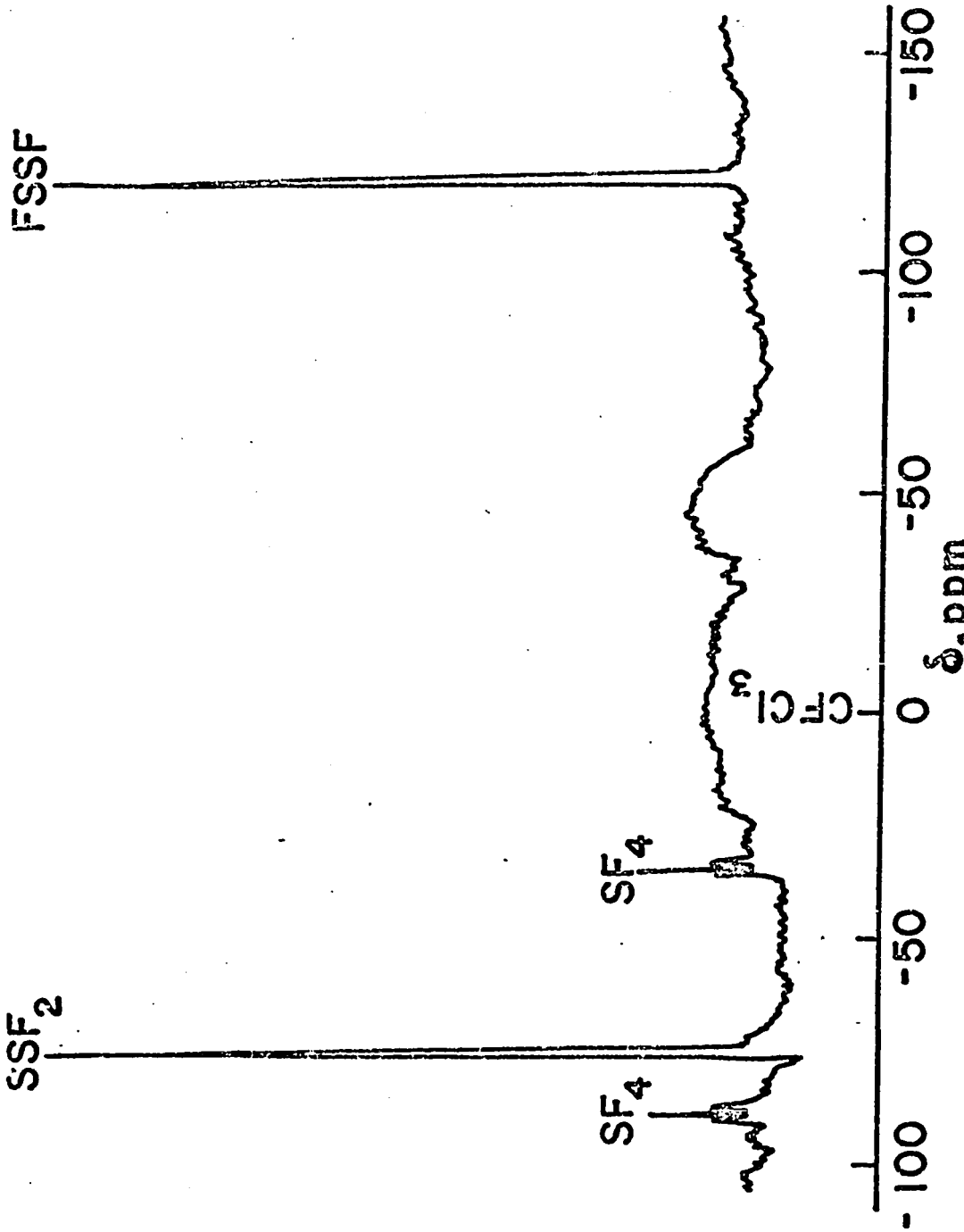


Figure 4. ^{19}F-NMR Spectrum of products of AgF/S reaction

TABLE I

^{19}F-NMR SPECTRUM OF PRODUCT OF AgF/S REACTION AT -100°C

Reference: $CFCl_3$

Chemical Shifts in ppm.

Present Work	Seel's Data	Assignment
- 91.5 (triplet)	-90 (triplet)	SF_4
- 78.3	-79.5	SSF_2
	-71	SF_2 ?
	-52 (octet)	
- 35.3 (triplet)	-34 (triplet)	SF_4
	- 5 (octet)	
	+26.5 (octet)	
+ 122.7	+120	FSSF
	+202	
	+203	
	+215 (octet)	

The spectrum of the second specimen was similar to that of the first but the relative intensities of the peaks were different. SSF_2 was less than half of FSSF in abundance, and SF_4 was approximately equal to the total S_2F_2.

The room temperature spectrum of the products showed a higher proportion of SSF_2 over that of FSSF by about a 10 to one ratio. This confirms that the isomerization of FSSF to SSF_2 is fairly rapid at room temperature. The two SF_4 triplets collapsed and a single broad peak as observed by previous workers (11) was formed.

From this study it appears that neither SF_2 nor the higher members of the fluorosulfane series other than FSSF were formed in our reaction, accepting Seel's proposal about the additional peaks he had observed. It is also possible that these compounds were present but only in negligible quantities. A third possibility is that the chemical shifts of these new compounds coincided with that of FSSF.

If we examine the proton NMR spectrum of the sulfane mixture obtained in the first experiment (Figure 3), we observe some trends in the chemical shifts with increasing sulfur chain length. The chemical shifts are further down field with increase in chain length. The peaks due to H_2S_6, H_2S_5, H_2S_4 and H_2S_3 are very close; the peak of H_2S is considerably displaced to upfield and that of H_2S_2 is in between. If we

apply this trend to fluorosulfanes, F_xS_2, we should expect the peak due to SF_2 to be at a considerable distance from those of S_3F_2, S_4F_2, S_5F_2 etc. and that of FSSF to be in between. This analogy appears to be valid if we consider the peaks at -71, +120, +202, +203 and +215 ppm, reported by Seel. The last three peaks may then be assigned to S_3F_2, S_4F_2 and S_5F_2 . The other peaks reported by Seel do not fit into this scheme; they may be other compounds.

Conclusion

Although Seel's results could not completely be verified from the present brief study, and direct evidence is lacking for the existence of fluorosulfanes other than FSSF, the possibility of formation of these new compounds is indicated both from proton NMR and ^{19}F-NMR studies.

PART III

DIATOMIC SPECIES CONTAINING SULFUR

A LITERATURE STUDY

CHAPTER IX

DIATOMIC SPECIES CONTAINING SULFUR*

A LITERATURE STUDY

Introduction

Diatomics are not normally stable at room temperature. The diatomic species exist only at high temperature and at low pressure, or in inert low temperature solution. Therefore, this chapter deals essentially with high temperature chemistry and cryochemistry.

Some 54 compounds, for example CaS, FeS, CoS, NiS, HgS, seem to contradict the above statement, because they are stable and can be described by diatomic formulas. Their properties are, however, not representative of their diatomic relatives; they are not molecular solids. They are merely binary compounds with a 1:1 molar ratio. This is evidenced by the fact that they have large lattice energies and high melting points and that their vapor consists of many different species.

A detailed review of the properties and preparation of

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*The content of this chapter is under publication: B. Meyer, D. Jensen and T. Oommen, "Diatomic Species Containing Sulfur," Chapter 13, "Sulfur Chemistry, Inorganic and Organic: An Integrated View," A. Senning, editor, M. Dekker, Inc.

gaseous diatomics would exceed the scope of this work. Therefore, this review is general in nature. The literature references do not aspire to be complete; no justice is given to priorities of work. Most references to work summarized in Gmelin (1) and Pascal (2) are omitted. Details on individual species are available in referenced original work and review articles. Instead of presenting sequences of individual description, much of the data is summarized in tables and figures. In many of these compilations predicted properties of diatomics which have not yet been prepared or observed are included.

For discussion of preparation and properties, diatomics are grouped according to the position of the sulfur partner in the periodic chart. The first diatomic is HS. Since diatomic alkali sulfides do not exist, alkaline earth sulfides are next. Then come third to seventh row compounds, followed by those of row Ib and IIb. Transition metal sulfides are listed according to increasing atomic number. Lanthanide elements come next, and actinide sulfides are at the end. In tables of numerical data, the order is different; all diatomics are listed in alphabetical order of chemical symbol.

TABLE I

ORGANIZATION OF SULFIDES

A)	HS	G)	VII
B)	II	H)	Ib
C)	III	I)	IIb
D)	IV	J)	Transition Metals
E)	V	K)	Lanthanides
F)	VI	L)	Actinides

Preparation

General

As mentioned, diatomic sulfides are only stable at elevated temperature. At room temperature, diatomic sulfides react, or they form ionic or metallic and sometimes semiconductor solids. In these the sulfur often dimerizes under formation of S_2^{-2}. A typical example is provided by FeS, in which the sulfur occurs as S_2^{-2} ion and as S^{-2} which is bound to the iron. The sulfur-iron "bond" is so delocalized, that the ratio of iron to sulfur is not fixed; iron sulfides are non-stoichiometric and form stable solids of the composition FeS_x, where $0.81<x<1.00$. Vaporization of such solids does not yield pure diatomic sulfide, but the vapor can be adequately described in terms of elemental species, S_2, and other sulfur molecules, and the metal sulfides MS and MS_2. The relative

yield of diatomic sulfide depends on the sulfur partner, but it can be influenced by the composition of the solid. The presence of elemental silicon, for example, will enhance the diatomic vapor pressure if SiS_2 is sublimed.

Vapors of stable sulfides can be made in quartz furnaces, Figure 1a. Above 1200°C, a King furnace is used, Figure 1b. This type of furnace consists of a graphite tube in which the parent compound is placed. The tube serves as an electrical resistor which is heated by the flow of 200-600 A at 6 volts. Properties of the vapor can be observed through the end of the tubes. The entire tube is inside a vacuum system, and filled with argon at a pressure of about ten torr to delay diffusion from the hot tube to the cold observation window. If sulfides are to be condensed or studied in a molecular beam, the vapor is produced by effusion from crucibles or Knudsen cells. SnS, for example, can be vaporized in, or from, a quartz double furnace, Figure 1c. BeS is vaporized from a carbon cell, Figure 1d. At higher temperature molybdenum or silicon carbide cells, heated by induction or electron bombardment, can be used.

Many sulfides cannot be made under equilibrium conditions. CS, for example, is under no condition the prevalent vapor species. In such cases, molecules must be made as transient species in low pressure vapor, by flash photolysis,

Figure 1

Experimental Apparatus. All Equipment is Described in Reference 3

a) Quartz absorption cell for optical studies; H = heater; Q = quartz cell with side arm; M = metal sulfide mixture.

b) King carbon resistance furnace; V = vacuum port for outgassing and introducing inert argon atmosphere; W = observation window; C = carbon tube heater; MS = metal sulfide.

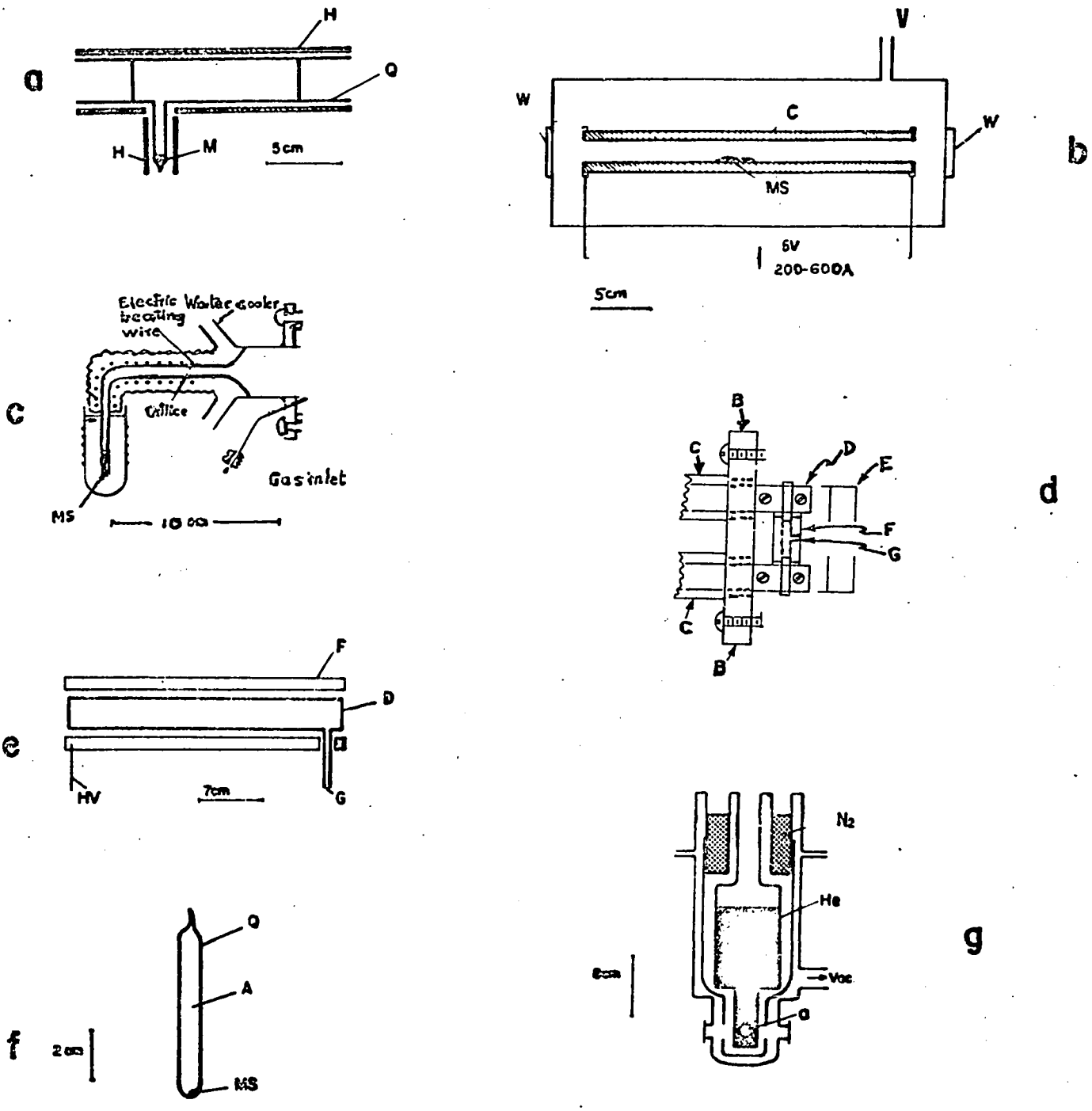
c) Quartz Knudsen double furnace; the orifice diameter is 1/2 mm. The botton furnace temperature is adjusted to control the vapor pressure. The front furnace allows overheating of the vapor. MS = metal sulfide.

d) Carbon Knudsen cell. The sulfide container is a 6 mm diam. carbon tube with a 0.5 mm diam. effusion hole. B: flange; C: water cooled electrodes; E: molybdenum heat shield and collineator; F: Knudsen Cell; G: effusion hole.

e) Flashphotolysis cell. D = cell for reagents; F = xenon flash lamp; G = gas inlet; HV = high voltage leads.

f) Microwave discharge cell. A = 0.1 torr argon as starter gas; G = baked quartz tube; MS = metal sulfide.

g) Matrix isolation Dewar. a = cold sapphire sample carrier; N_2 = liquid nitrogen reservoir with copper shield; He = liquid helium; Vac = vacuum connection.



XBL 702-356

Figure 1

Figure 1e, or discharge techniques. In the flash photolysis experiment, the tube must be refilled with new reactant after each flash. In contrast, a discharge tube can be continuously operated. The lifetime of a discharge tube, as shown in Figure 1f, can be several hours. It contains the parent compounds and about 1 torr of argon as a starter gas. For NS, a flow system is a convenient source. Other molecules can best be made in solid low temperature solution by in situ synthesis, Figure 1g, as discussed for the case of S_2. The same apparatus can be combined with a furnace or flash source to trap metastable diatomic sulfides. References to all these techniques can be found in reference 3. Figure 2 shows all observed solid and gaseous sulfides.

A) HS

HS has been observed in radiofrequency (rf) discharges of H_2S at low pressure (4), in microwave discharges and through photolysis. It can also be made by reaction of $CHCl_3$ + $SOCl_2$ + K at 485°C at 10 torr (5). HS is, normally, unstable in the gas phase. Metastable HS has been prepared by photolysis of H_2S in rare gas matrices at 15°K (6). In such matrices radicals can be stored indefinitely (3,7).

B) Second row sulfides

BeS has been prepared by the reaction of Be with

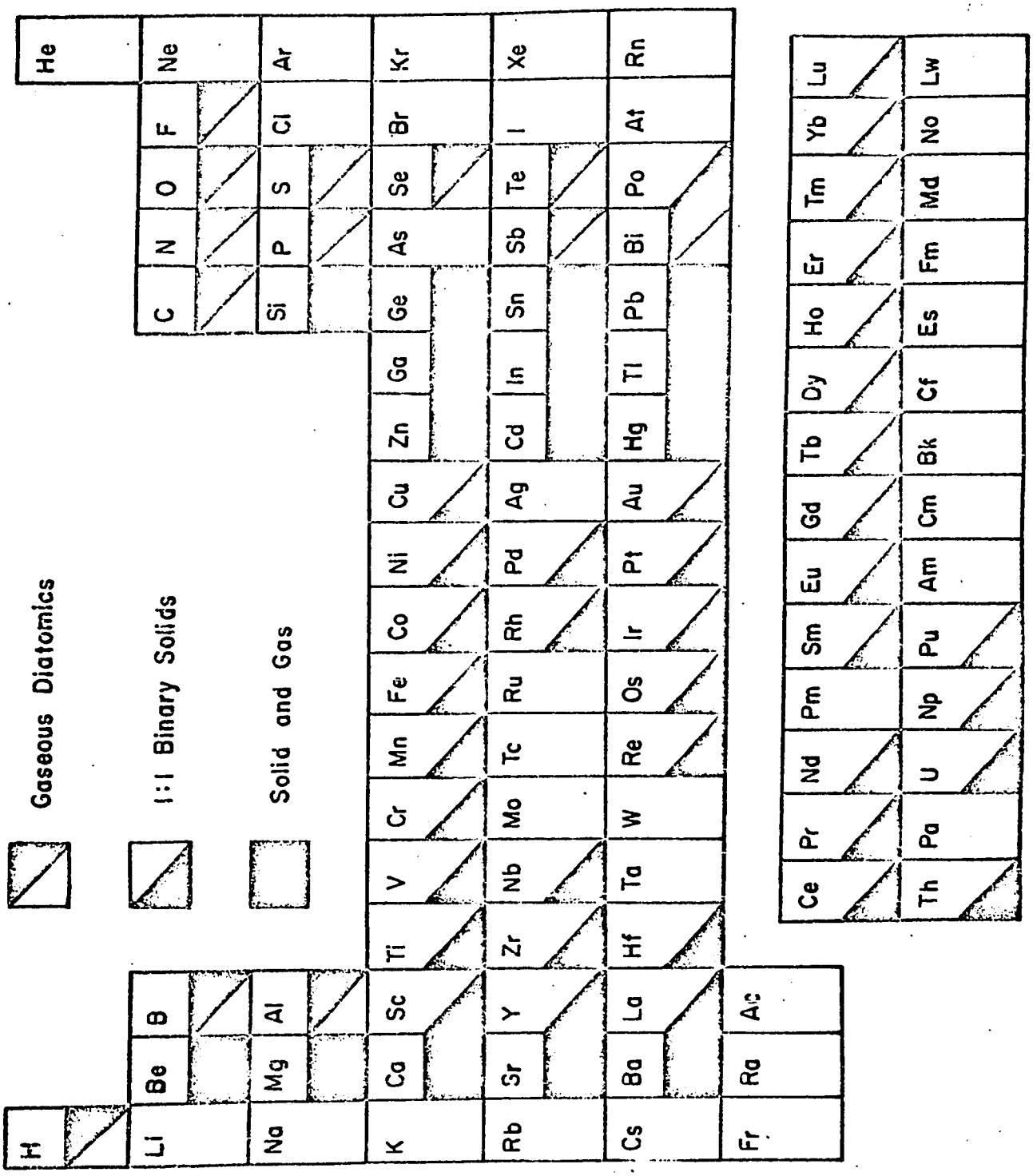


Figure 2. Presently known Diatomic Sulfur Species

sulfur vapor and hydrogen at 1150°C (8), by the reduction of $BeSO_4$ with dry CO, CaC_2 or sulfur (9), or by the reaction of vapors of $BeCl_2$ and H_2S (10). The vaporization of BeS is not a convenient preparation method, because solid alkaline earth sulfides are ionic. Solid BeS melts at 2275°K. The vapor contains Be, S_2, S, and BeS. MgS can be prepared by the reduction of $MgSO_4$ with CS_2 at 750°C (11), and the reaction of Mg with H_2S (12). CaS can be prepared by the reaction of $CaCO_3$ with H_2S at 1000°C (13). SrS and BaS are prepared in the same way. The reduction is accelerated by the presence of hydrogen.

C) Third row sulfides

BS is formed in a discharge of B_2S_3 in helium or argon (14). AlS could probably be formed in analogous discharges and by reaction of $AlCl_3$ and H_2S vapors. GaS is the stable vapor of solid GaS which can be made by direct reaction of the elements at 900°C (15-17). It sublimes at 950°C. InS and TlS are obtained in the same way (18). In all three cases, other sulfides are also stable. Solid sulfides have the composition $(GaS)_4$; InS, In_2S, and TlS, Tl_2S and Tl_2S_3.

D) Fourth row sulfides

CS is formed in discharges through CS_2, but S_2 is also formed (19,20). CS also occurs in carbon arcs through sulfur

vapor, and, at room temperature, in low pressure reactions of CS_2 with excited atoms and molecules (21). SiS is formed by heating SiS_2 and Si, Si and sulfur vapor, or a mixture of Si_2S_3, SiO_2 and Si (22, 23). At low temperature SiS disproportionates into SiS_2 and Si (24). GeS is a stable vapor above solid GeS. It can be made by reacting GeO_2 with H_2S and hydrogen at 500°C, or from $GeCl_2$ and H_2S (25). GeS sublimes at 430°C; it melts at about 530°C. Diatomic GeS can be trapped in rare gas matrices. SnS is the vapor above SnS which is formed by heating the elements (18) or a mixture of SnO_2 and KNCS. It also forms from aqueous Sn^{+2} solutions with H_2S. SnS can be trapped in solid rare gases. PbS is formed in the same way.

E) Fifth row sulfides

NS is formed by reaction of active nitrogen on SCl_2 (26), sulfur vapor mixed with SF_6 and S_2Cl_2 (27), and a discharge through nitrogen and sulfur vapor (26). PS is observed in discharges containing phosphorous and sulfur (27,28). SbS and BiS have been observed in vapor phase by the decomposition of the stable sulfides (29).

F) Sixth row sulfides

SO results by reaction of COS and oxygen atoms (30), a discharge through SO_2 (31,32) and photolysis of S_2O (33). It

is observed in sulfur containing flames, beside SO_2. S_2 occurs in almost all sulfur-rich flames, discharges through CS_2, S_2Cl_2, and sulfur (34). It is a stable component of sulfur vapor, in equilibrium with other sulfur species of the composition S_x, where $1<x<12$ (35). S_2 has been trapped in inert matrices at 20°K (36,37). It can be synthesized in inert low temperature solution through photolysis of H_2S, S_2Br_2, S_2C_2 and COS (38). SeS has been observed with a masspectrometer in the vapor phase (39). TeS has been observed spectroscopically (40). PoS is radioactive. It can be prepared by treating aequeous $PoCl_2$ with H_2S. Above 275°C it decomposes into the elements (41).

G) Seventh row sulfides

SF has been observed in a microwave discharge by the reaction of F atoms, made from CF_4, with COS (42). Other diatomic sulfur halides have not yet been synthesized, but their properties can be predicted by analogy with the oxygen halides. Since the Cl-S and Br-S bonds are weaker than S-S, photolysis of S_2Cl_2 and SCl_2 in the gas phase or in matrices does not yield SCl, but S_2 and Cl atoms, which, on recombination, form larger molecules (43).

H) Row Ib sulfides

CuS forms a stable solid. It is formed by reaction of

Cu^{+2} and H_2S, or reaction of Cu and CS_2 (44). The solid contains S_2^{-2} and S^{-2} ions. Gaseous CuS has not yet been reported. AgS has not yet been made. Although gold is the only element which does not react directly with sulfur, solid AuS can be made by the reaction of $AuCl_3$ and H_2S below 40°C, or $AuCl_3$ with $Na_3Au(S_2O_3)_2$. (45). AuS decomposes above 140°C.

I) Row IIb sulfides

ZnS, made by reaction of Zn^{+2} with H_2S, melts at 1650°C and can be vacuum distilled. It is a colorless semiconductor. At room temperature, it occurs in two different crystal forms (Zincblende and Sphalerite). Above 1000°C it transforms into Wurtzite. CdS also forms two solid stable allotropes. Above 20 kbars ZnS and CdS transform into a rock-salt type form (46). It sublimes at 980°C and melts at about 1750°C. β-HgS is black; on standing or heating it converts into red trigonal α-HgS. α-HgS contains helical -S-Hg-S-Hg- chains (47). It sublimes at 580°C in diatomic form.

J) Transition metal sulfides

Solid ScS is prepared by heating stoichiometric quantities of the elements to 1150°C (48). TiS is reddish and has metallic properties. The structure is Ni-As type (49). VS is prepared by heating V_2S_3 to 1000°C, or by reducting V_2O_5 with H_2S. It melts at about 1900°C (50). CrS is obtained by

heating stoichiometric quantities of the elements to 100°C (18). Above 600°C it disproportionates into metal and higher sulfides. MnS exists in three modifications. α-MnS is formed by $MnCl_2$ and H_2S under a nitrogen atmosphere in the presence of NH_4Cl. FeS can be made directly by heating the elements. As other transition metals, FeS occurs in many non-stoichiometric forms with compositions of $F_{0.85}S$ to FeS_2. CoS has two forms. Other cobalt sulfides with $Co_{1-x}S_x$ up to Co_9S_8 (β-CoS) are formed. The sulfide is formed at 650°C from the elements. α-CoS melts at 1100°C (24). NiS can be made from the elements, or by precipitation of Ni^{+2} with H_2S. In aequeous solution Fe^{+2}, Co^{+2} and Ni^{+2} form mixed sulfides-hydroxides with compositions depending on the pH.

YS exists in stoichiometric and non-stoichiometric compositions. It can be made from elements. ZrS is made in the same way, and also has many different compositions. NbS in two forms is obtained from the elements at 850°C. PdS is formed by the elements at 500°C. HfS is made in the same way, with subsequent annealing at 1450°C. Pt and sulfur react under formation of PtS. The sulfide is also formed from $PtCl_2 + H_2S$; PtS is tetragonal and a semiconductor (51).

K) Lanthanium sulfides

All lanthanide elements, except Pm, form binary sulfides

with the composition 1:1 (24,52). La, Pr and Nd react with elemental sulfur at 1000°C. CeS is formed when Ce_2S_3 is heated to 2200°C in the presence of CaH_2 in molybdenum container.

L) Actinide sulfides

ThS, US, PuS and NpS are made by reaction of the metals with H_2S at 500°C (53). PuS can be made by reduction of PuF_3 with Ba metal in a BaS crucible.

Summary

Twenty-seven elements form stable diatomic sulfides at high temperature; seventeen sulfides can be formed by vaporization of the solid sulfide. However, the diatomic species exist only in a narrow pressure and temperature range, and even then the vapor is normally not pure, but contains measurable, if not appreciable, quantities of atoms, S_2 and polyatomic sulfides. Another thirty-nine sulfides form binary solids with a 1:1 composition, but decompose upon heating. The vapor composition over hot sulfides has been extensively studied by Goldfinger and Drowart (83,84,86). For the preparation of other diatomics, gas phase non-equilibrium synthesis or matrix isolation methods must be used. Gas phase non-equilibrium synthesis has been used for the preparation of NS, HS and CS. NS can be prepared in a flow system by the

reaction of active nitrogen with sulfur vapor. It obtains mainly in the excited B $^2\pi$ state, which relaxes to the ground state under emission of blue light. NS can also be obtained by other techniques, for example in a microwave discharge through a nitrogen and S_2Cl_2 mixture. HS and CS are best obtained by flash photolysis of the stable parent molecules. In all of the above cases, the diatomic sulfides are only short lived and recombine with other vapor components within milliseconds, or a short fraction of a second.

Unstable molecules can be stored and preserved if they are trapped in matrices. Matrices are formed by condensing a mixture of the sulfide and a rare gas at 4° and 20°K (Figure 1g). If enough inert gas is present, diatomic species will be surrounded by weakly interacting rare gas atoms and will not chemically react with other sulfide molecules. Thus, solids are formed, in which the sulfide is metastable. Another advantage of rare gas matrices is that molecules can be synthesized in situ. S_2, for example, can be formed by photolysis of S_2Cl_2 or S_2Br_2. CS can be made by photolysis of CS_2, and BeS and BaS could be made by the reaction of the alkaline earth atom with sulfur atoms prepared by in situ photolysis of CO. For this purpose a molecular beam of Ba and argon, in a molar ratio of 1:500 is condensed on a window at 20°K, simultaneously with a beam of COS in argon (in the

ratio 1:100). COS is photolyzed with 253.65 nm mercury light, yielding S atoms and inert CO. S and Ba atoms are brought to reaction by a temperature increase to 33°K, where diffusion sets in (3). Similar synthetic reactions could be used to make other sulfides. Such matrix syntheses are not far fetched projects for the future. Similar, and much more complicated reactions have already been employed for many years to prepare other new free radicals (5).

Spectral Properties

Spectral properties of 16 diatomic sulfides are summarized in Table II in alphabetical order of the chemical symbol of the sulfur partner. Much of the data on sulfides results from the work of Barrow and his students. Table II lists only references to the latest available publication on each species. Detailed discussions of the spectra exceeds the scope of this chapter. Earlier literature is summarized in books by Rosen (55), Herzberg (54) and Gaydon (34), in an article by Barrow (63), in a newsletter (76), and in a summary by Mulliken (77).

The purpose of Figure 3 is to give a comparison of the presently known states. The figure does not list the character of states and transitions, because this can be obtained from Table II. Table II is probably not complete because

TABLE II

ELECTRONIC STATES OF DIATOMIC SULFIDES*

Electronic State	$T_e(\mu m^{-1})$	$\omega_e(cm^{-1})$	$B_e(cm^{-1})$	$r_e(\AA)$	References
AlS					
$A\ ^2\Sigma^+$	2.3434	510.91	0.2461		McKinney (57)
$X\ ^2\Sigma^+$	0	617.12	0.2799		
BS					
$^2\Pi_{3/2}$	3.8899	884.7	0.702		Zeeman (14)
$^2\Pi_{1/2}$	3.8785	884.7	0.702		
$C\ ^2\Pi_{1/2}$	1.5997	749.4	0.621		
$A\ ^2\Pi_{3/2}$	1.5663	749.4	0.621		
$X\ ^2\Sigma$	0	1173.6	0.775		
BaS					
A (?)	2.5934	253.0			Barrow (58)
X (?)	0	377.1			
BeS					
$B\ ^1\Sigma^+$	2.5868	850.4	0.726	1.818	Gissane (59)
$X\ ^1\Sigma^+$	0	997.4	0.787	1.745	
BiS					
$A\ ^2\Pi_{1/2}$	1.3292	303.7			Barrow (60)
$X\ ^2\Pi_{1/2}$	0	408.7			

TABLE II (CONTINUED)

CS					
A $^1\Pi$	3.8913	1072.3	0.781		Lagerqvist (19)
X $^1\Sigma^+$	0	1285.1	0.821		Barrow (20)
GeS					
B	3.8890	310.4			Drummond (61)
A	3.2890	375.0			Meyer (62)
a $^3\Pi$	2.0000				
X $^1\Sigma^+$	0	575.8			
HS and (DS)					
A $^2\Sigma$	2.1036	1971.0 (1415.0)			Ramsay (4)
X $^2\Pi$	0	2711.6 (1947.0)	9.660 (4.950)	1.34 (1.34)	Pathak (5)
MgS					
B	2.3056	495.3			Barrow (63)
A	0	525.2			
NS					
F $^2\Sigma$	5.6000				Smith (26)
E $^2\Pi$	5.2000				Peyron (27)
(d) $^2\Sigma$	4.4280				
C $^2\Sigma$	4.3385	1401.0	0.827	1.447	
B $^2\Pi$	3.0190 3.0105	800.0	0.612	1.680	
A $^2\Delta$	3.9918 3.9882	942.0 960.0	0.676	1.577	
X $^2\Pi$	0	1219.0	0.774	1.496	

TABLE II (CONTINUED)

OS					
B $^3\Sigma^-$	4.1629	630.4	0.502	1.775	Colin (82)
A $^3\Pi_2$	3.8617	412.7	0.616		Abadie (64)
A $^3\Pi_1$	3.8455	413.3	0.611	1.609	Norrish (32)
A $^3\Pi_0$	3.8293	415.2	0.607		
b $^1\Sigma^+$	1.0510	1067.7	0.703	1.500	
a $^1\Delta$	0.6350		0.709	1.493	
X $^3\Sigma^-$		1148.2	0.721	1.481	
PS					
C	3.4687	535.5	0.260	2.030	Dressler (27, 28)
B	2.2270 2.2170	510.0			
X $^2\Pi$	0	739.5	0.290	1.920	
PbS					
F	4.7770	370.0			Vago (65)
E	2.9651	299.3			
D	2.5024	284.0			
C	2.3213	303.9			
B	2.1848	282.2			
A $^1\Sigma^+$	1.8851	261.1	0.086	2.666	
X $^1\Sigma^+$	0	428.1	0.106	2.394	

TABLE II (CONTINUED)

S_2					
c' $^1\Sigma_u^+$	6.4000	785.0	0.290	1.900	Lakshmina-rayana(66)
$^1\Delta_u$	5.9900				Barrow (67)
c $^1\Sigma_u^-$	5.9900	814.0	0.290	1.900	Barrow (68)
D $^3\Pi_g$	5.8700	786.0	0.306	1.890	Ricks (69)
e $^3\Sigma_u^-$	5.6984		0.290	1.890	
g $^1\Delta_u$	5.6700	811.0	0.322	1.811	
C $^3\Sigma_u^-$	5.5581	822.5	0.321	1.810	
f $^1\Delta_u$	4.1000	432.8	0.227	2.166	
e $^1\Pi_g$	3.7000	533.7	0.240	2.080	
B' $^3\Pi_{g,i}$	3.6000	-	0.244	2.080	
B $^3\Sigma_u^-$	3.1689	428.5	0.224	2.172	
$^1\Pi$	3.2000				
B'' $^3\Pi_u$	3.1700		0.200	2.280	
A $^3\Sigma_u^+$	2.2500	477.0			
c $^1\Sigma_u^-$	2.3000		0.230	2.150	
A' $^3\Delta_{u,i}$	2.1900	483.0	0.228	2.150	
b $^1\Sigma_g^+$	0.9000	693.0			

TABLE II (CONTINUED)

S_2 (cont'd)					
a $^1\Delta_g$	0.5000	695.9	0.293	1.900	
X $^3\Sigma_g^-$	0	719.4	0.295	1.892	
SiS					
E	4.1924	403.5	0.266	2.095	Nilheden (70)
D $^1\Pi$	3.5029	512.0	0.304	1.928	Robinson (71)
X $^1\Sigma^+$	0	749.5			
SnS					
E	3.2940	295.1			Meyer (72, 73)
D $^1\Pi$	2.8360	331.9	0.120	2.357	
C ($^3\Sigma$)	2.3613	324.0			
B ($^3\Sigma$)	2.2756	325.0			
a ($^3\Pi$)	1.8300				
X $^1\Sigma$	0	487.7	0.137	2.209	

*Electronic States of Diatomic Sulfides. T_e = transition energy in reciprocal micrometers; ω_e = vibrational quantum; B_e rotational constant, and r_e = internuclear distance at equilibrium distance. In cases where data is incomplete, T_o and ω_o are listed. For S_2, $\Delta G_{1/2}$ (= $\omega_e - 2\omega_e x_e$) is listed instead of ω_e. The literature always refers to the latest available reference. Earlier work is summarized in references 34, 54, 55, 63, 76 and 77.

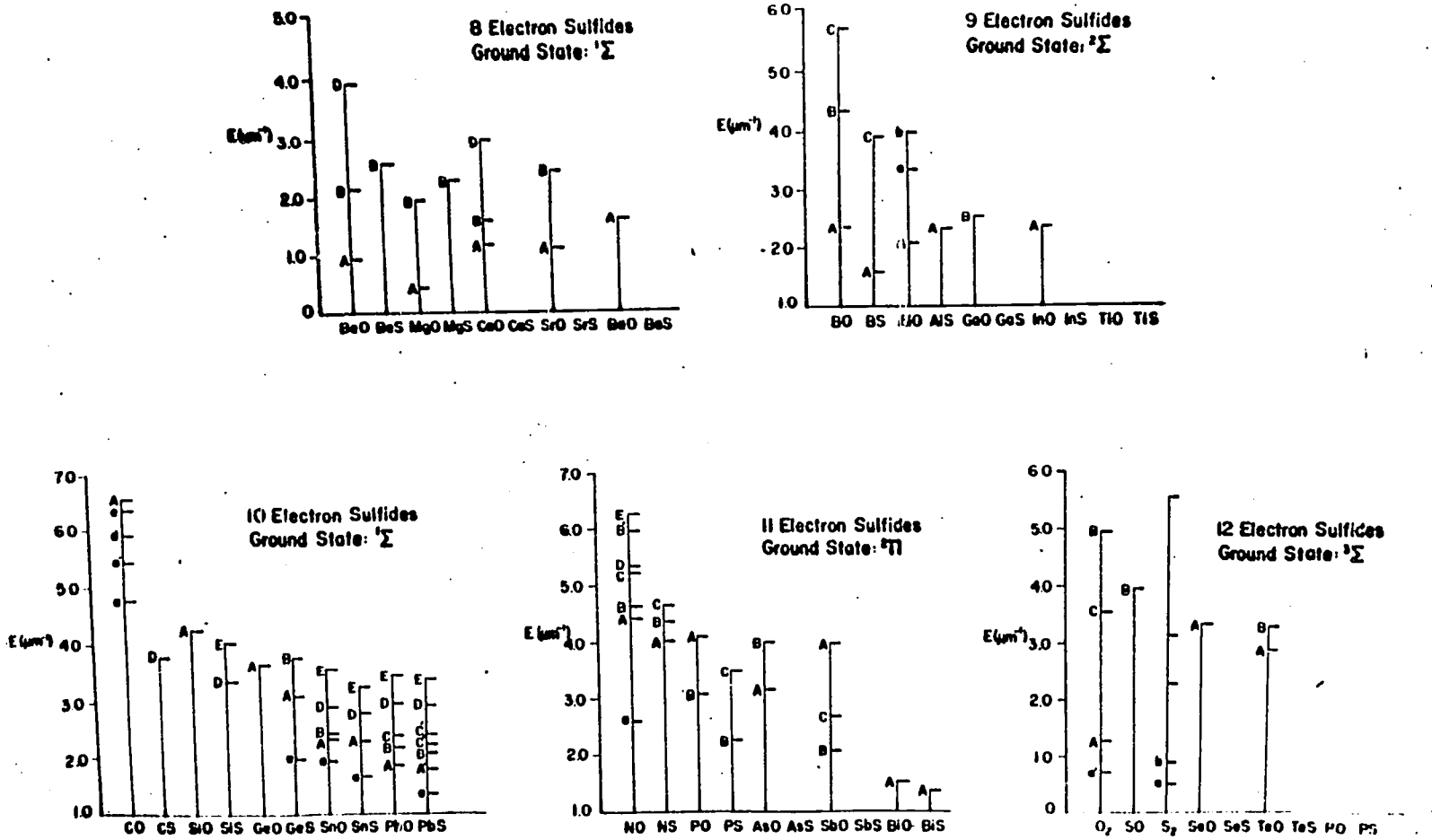


Figure 3. Low-lying Electronic Levels of Diatomic Sulfides. Levels are only Identified by Letter Names. The Full Spectroscopic Characteristics of Each State is Listed in Table II

spectra of new molecules and new data for presently known molecules are continuously reported. So far, only visible spectra of sulfides are known and most correspond to allowed transitions between lower lying states. If only emission is known, it can be assumed that the molecule is not stable enough for absorption studies. In the future, matrix work surely will yield more absorption data on new, unstable molecules, and emission from the lowest excited state which is normally spin forbidden (56). The knowledge of lower lying states is important for computing thermodynamic data, and for understanding the reaction of excited molecules. Data for the electronic transitions of group II, III, IV, V and VI sulfides are represented in Figure 3. The figures also show the data for the corresponding oxides. The abscissa lists molecules in order of increasing atomic weight. It is generally established that for a given electron configuration with increasing atomic weight, the electronic energy levels move towards lower values; as a result, the absorption edge moves toward the red. In Figure 3-c for CO, for example, the first allowed transition is in the vacuum uv. The molecule is colorless. In CS, the transition lies in the far uv. SnS vapor is blue and PbS, with an allowed transition in the visible, is brown. A similar trend is observed for all states of these molecules, for example the lowest excited state,

a $^3\Pi$. Emission of $^3\Pi \rightarrow {}^1\Sigma$ in CS is predicted to be light blue, SiS dark blue, and GeS is observed to be yellow, SnS green and PbS is red. This trend holds only qualitatively, and it is invalid for Rydberg states. However, if for a given molecule the assignment of an observed state or the basis of the spectral analysis is doubtful, it is well worth comparing states of similar molecules. This procedure was used to predict the location of the a $^3\Pi$ states in GeS and SnS, which were all previously unknown, but have now been observed in matrices (62,72).

Group II sulfides have a ground state $^1\Sigma^+$, but they also have a low lying $^3\Pi$ state. Since $^3\Pi \text{-} {}^1\Sigma$ transitions are forbidden and therefore weak, the relative position of the two states is not directly observed. The spectra consist, therefore, of two disconnected systems, one involving singlet states, and the other involving triplet states. Although the corresponding oxides are extensively studied (74), the order of excited states is not yet conclusively established. This is complicated by the occurrence of hydroxide impurities, which further complicate analysis.

Group III sulfides are not well known, because the molecules are not stable. Most data comes from emission studies, where small amounts of the desired molecule emit in the presence of large impurity concentrations. Under such

conditions, the identity of the emitter must be established by thorough rotational analysis, and by analysis of isotope shifts. The recent availability of pure ^{34}S should simplify identification and knowledge of unstable molecules of this group.

Group IV sulfides are relatively well known. In Figure 3c, all molecules have ten valence electrons, like N_2 or CO. The ground state is $^1\Sigma$; the first excited orbital is $\sigma^2\Pi^3\Pi$ which yields one state each with $^3\Pi, ^3\Sigma, ^1\Pi$ and $^1\Sigma$. The lowest lying fully allowed transition is $B\ ^1\Pi \leftrightarrow X\ ^1\Sigma^+$ in N_2, and $^1\Pi \leftrightarrow X\ ^1\Sigma^+$ in CO. The lowest excited state of ten electron molecules is $^3\Pi$, which is close in energy to $^3\Sigma$ of the same electron configuration. The transition $a\ ^3\Pi \rightarrow X\ ^1\Sigma$ is spin forbidden, but appears in matrices as strong phosphorescence because of matrix induced intersystem crossing from the first excited singlet state $^1\Sigma \rightarrow ^3\Pi$ (56).

Group V sulfides are isoelectronic with NO. The ground state is $^2\Pi$, the lowest excited state $^4\Pi$. Only allowed transitions of NS and PS are known. Detailed rotational analysis of sulfur isotopes have been used for identifying the states of NS.

Group VI sulfides are isoelectronic with O_2, and have a ground state $^3\Sigma^-$. The lowest lying allowed transition corresponds to the Schumann-Runge bands, which are responsible

for the atmosphere absorption of ultraviolet light by O_2. In the last five years, several transitions involving singlet states have been observed and analyzed. However, so far, the singlet and triplet states have not been conclusively correlated. For S_2, knowledge of about eighteen states is now available. Due to the work of Barrow and his coworkers (67, 68), data is so thoroughly established and carefully collected that S_2 is probably the best known diatomic molecule.

Thermodynamic Data

A. Dissociation energies

Table III gives the dissociation energies for some diatomic sulfides. The data is subject to some uncertainty, because of conflicting values in the literature. A detailed analysis of the data exceeds the scope of this chapter. Sulfides, in general, have lower dissociation energies than oxides, but, fortunately, the pattern for oxides and sulfides are strikingly similar. This is shown in Figure 4 for Group II and IV elements. The oxides are much better known and are reviewed in a very recent, excellent article (74).

If we compare the dissociation energies as a function of the valence electrons, a trend analogous to that for homonuclear diatomics is obtained (79). Bond energies increase with the number of electrons in bonding orbitals minus the

TABLE III

DISSOCIATION ENERGIES OF GASEOUS DIATOMIC SULFIDES AND OXIDES

Sulfide[a]	D°_{298} kcal/mole	Oxide[b]	D°_{298} kcal/mole
AlS	(95)*	AlO	115 ± 5*
BS	123 ± 18	BO	192 ± 5
BaS	95 ± 5*	BaO	131 ± 5*
CaS	72 ± 5	CaO	84 ± 7
CS	183 ± 5	CO	257 ± 1
CoS	136 ± 2*	CoO	190 ± 2*
GeS	133 ± 4	GeO	158 ± 3
HS	81 ± 0.5*	HO	101 ± 0.3*
HgS	(64.4)	HgO	(65)
InS	68 ± 4*	InO	(76)*
LaS	137 ± 2*	LaO	137 ± 2*
MgS	(68.6)	MgO	79 ± 7
MnS	65 ± 5*	MnO	87 ± 5*
NS	116.6 ± 25	NO	150.8 ± 0.2
PS	124.5 ± 15	PO	119.6 ± 3
PbS	76 ± 5	PbO	89.4 ± 2
S_2	101 ± 0.5*	SO	124 ± 0.5*
ScS	113 ± 2	ScO	161 ± 2
SeS	(90)*	SeO	(100)*

TABLE III (CONTINUED

SiS	158.6 ± 25	SiO	192 ± 2
SnS	111.7 ± 3	SnO	127 ± 2
SrS	80 ± 4*	SrO	92 ± 6*
TeS	(80)*	TeO	(90)*
TiS	108 ± 7*	TiO	160 ± 5*
US	118.6 ± 11	UO	182 ± 3
YS	126 ± 2*	YO	169 ± 2*

* D_o^o values

(a) Main Sources:

JANAF Tables
Spectroscopic Data
Heats of Formation and Heats of Atomization Data
References (80) and (81)

(b) Date from:

Brewer and Rosenblatt, reference (74)
Paul Coppens, reference (80)
Bert Scholliers, reference (81)

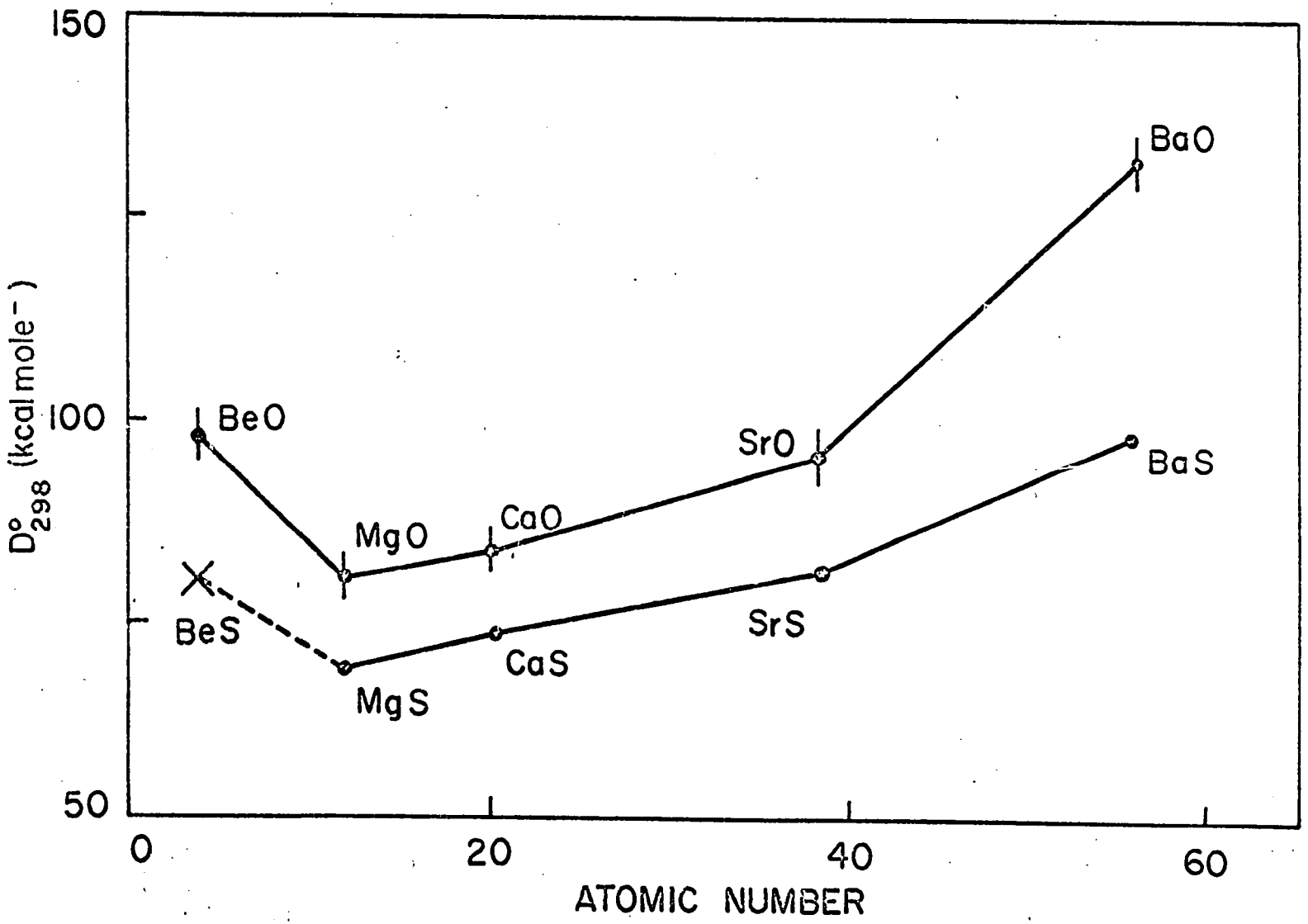


Figure 4. Dissociation Energy of Selected Oxides and Sulfides

a. Row II Compounds

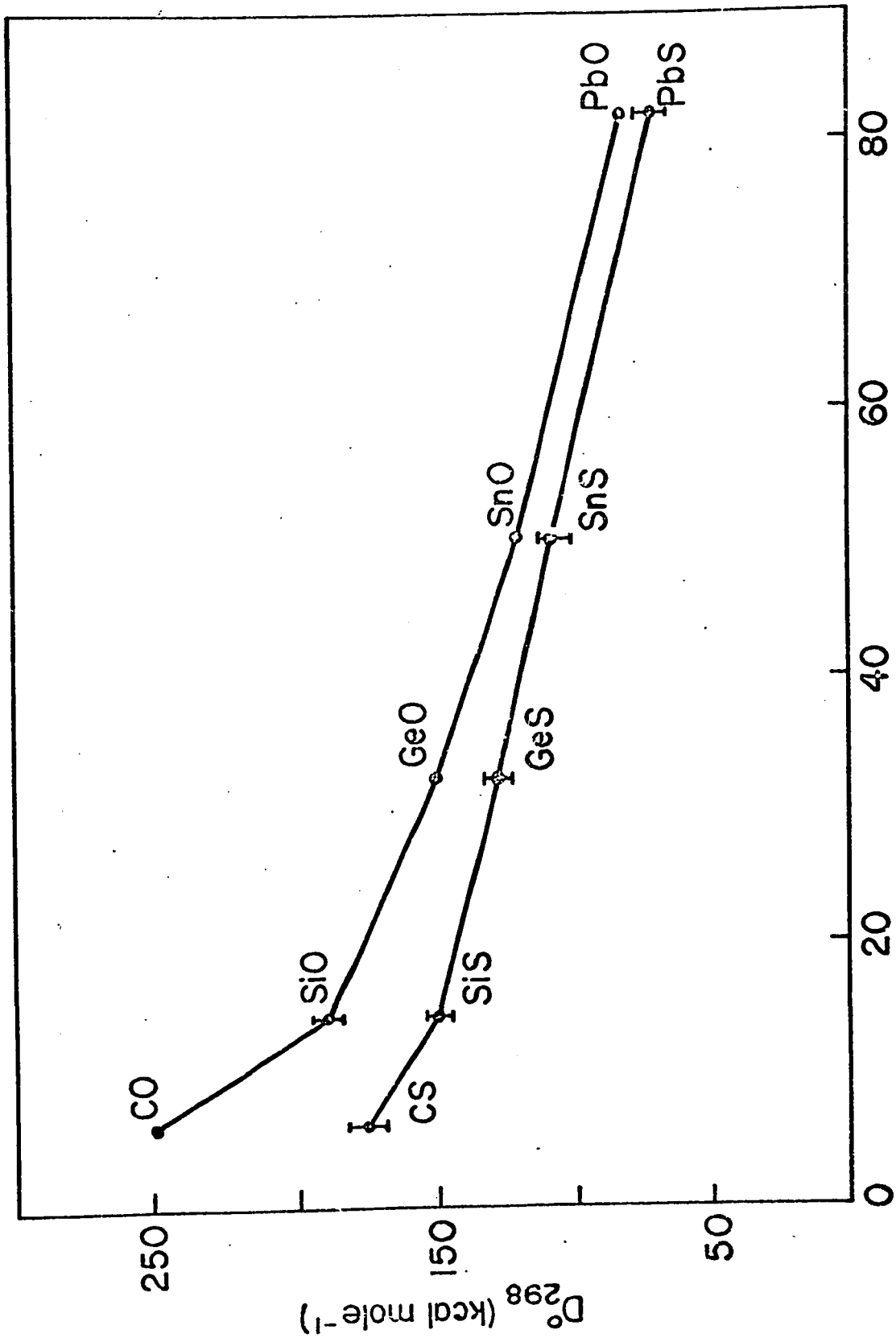


Figure 4. Dissociation Energy of Selected Oxides and Sulfides
b. Row IV Compounds.

number of electrons in the anti-bonding orbitals. The high stability of CS and other Group IV sulfides is thus understood through comparison with N_2.

Comparison with oxides explains why many diatomic sulfides are not observed. The alkali metal and halogen oxides, for example, have very low bond energies. Thus, the sulfides are too unstable to exist, except for SF for which only little is known (42). The most stable of the not yet observed diatomic alkali sulfides should be LiS. The dissociation energy of LiS should be about 60 kcal/mole, which is the value of NaO.

B. Heats of formation

The data in Table IV indicates that diatomic sulfides exist only at high temperatures. Transition element sulfides decompose on heating and cannot be made from solid sulfides. Except for SnS and GeS, diatomic sulfides cannot be prepared in pure form under equilibrium conditions.

The solid sulfides are formed spontaneously from the elements, but preliminary heating is required to overcome the activation energy barrier. The general pattern of sulfide formation reflects the change in the electronegative character of the elements. Lattice forces also play a significant role. The heats of formation of solids decrease across the

TABLE IV

STANDARD HEAT OF FORMATION, $\Delta H^\circ_{f(298)}$ OF DIATOMIC SULFIDES (kcal/mole)*

Molecule	$\Delta H^\circ_{f(298)}$	Molecule	$\Delta H^\circ_{f(298)}$
AlS (g)	+48 ± 20	MgS (s)	-83
BS (g)	+80.5 ± 18	MnS (s)	-49.4 ± 0.4
BaS	+54	NS (g)	+63 ± 25
BaS (s)	-108.1 ± 8.0	NiS (s)	-22.2 ± 1.4
BeS (s)	-55.9 ± 2.0	PS (g)	+22.5 ± 5.0
CS (g)	+55.0 ± 5.0	PbS (g)	+37.2 ± 5.0
CaS (g)	+37	PbS (s)	-23.0 ± 0.5
CaS (s)	-114.5 ± 2.0	PtS (s)	-19.7 ± 2.0
CdS (s)	-37.6 ± 1.0	S_2 (g)	+30.84 ± 0.15
CeS (s)	-109.1 ± 1.0	SO (g)	+1.64 ± 0.3
CoS (s)	-21.1 ± 3.0	SiS (g)	+16.93
CuS (s)	-12.5 ± 0.8	SnS (g)	+27.1 ± 3.0
FeS (s)	-23.7 ± 0.7	SnS (s)	-25.3 ± 10
GaS (s)	-46.4 ± 3.0	SrS (g)	+51.0
GeS (g)	+22.9 ± 4.0	SrS (s)	-108.1 ± 8.0
GeS (s)	-17.0 ± 3.0	TiS (s)	-63.4 ± 6.0
HS (g)	+34.6 ± 4	ThS (s)	-105 ± 10
HgS (s)	-12.7 ± 1.5	US (g)	+74 ± 8
InS (s)	-33.6 ± 3.0	US (s)	-83 ± 8
MgS (g)	+33.2	ZnS (s)	-49.2 ± 0.5

*From R.D. Freeman, "Thermodynamic Properties of Binary Sulfides," Oklahoma State University Research Foundation (1962). Reference (75). JANAF Tables.

transition series, and rise in the group B metals. If the heats of formation from metal atoms rather than from the solid elements are compared, one obtains a pattern almost similar to the metal binding energies, Figure 5. This sequence contains curiously high values for TiS and VS. This may be due to back π-bonding from the S anion into the empty d-orbitals of Ti and V cations. The diatomic sulfides of the first transitional series should be more stable than those of the second and third series, for which a higher oxidation state is preferred, although the heats of formation decrease generally in the order of oxides < sulfides < selenides < tellurides. There is a steadily increasing preference for the more polarizable sulfur, through the transition series, in the order:

Mn(II) > Fe(II) > Co(II) > Ni(II) > Cu(II) >Zn(II).

On reaching the B subgroup this preference decreases again.

Summary

Only 27 sulfide species are truly diatomic. They are all gaseous and exist under equilibrium conditions only at high temperature and at low pressure; even then, the diatomic species is usually not pure, but contaminated with atoms and S_2. According to this behavior, the bond energies of sulfides are low. Their bond strength is always lower, but analogous

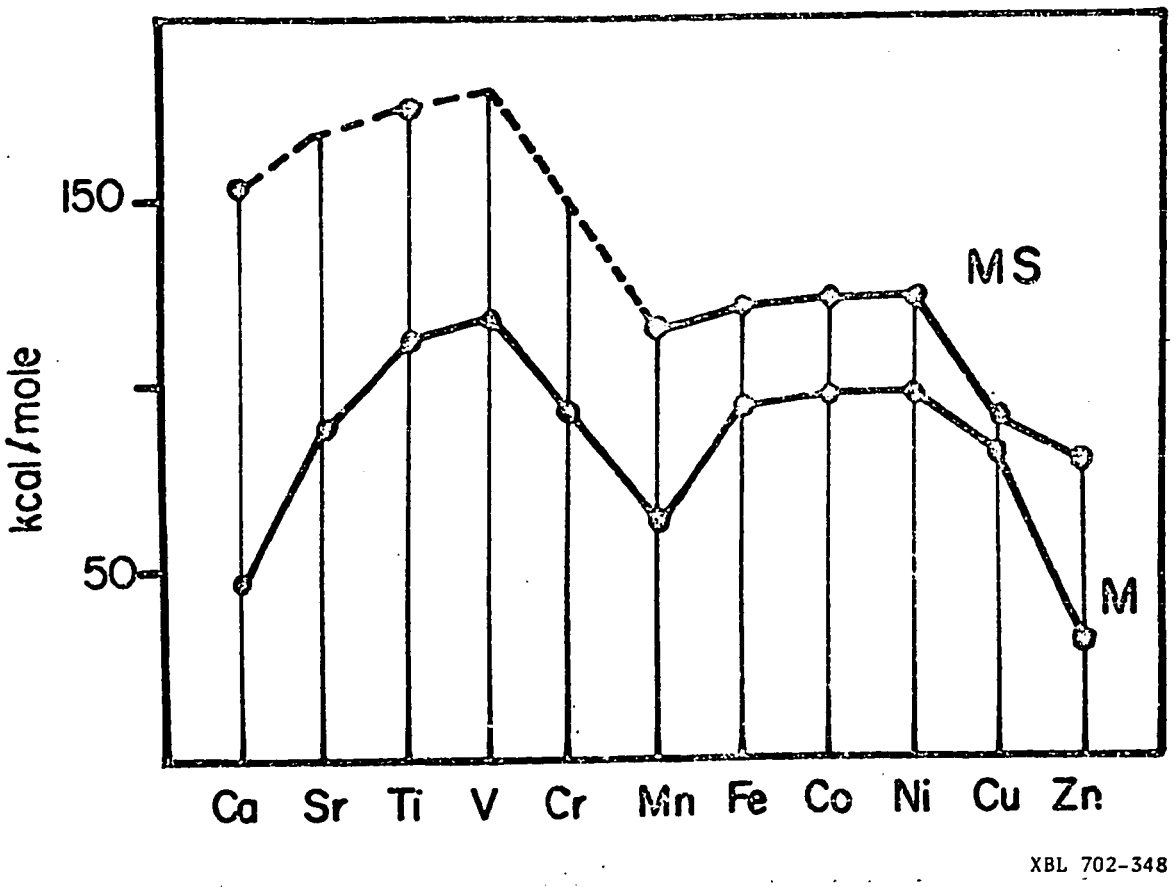


Figure 5. Bond Energies of Metals (M) and Heats of Formation of Sulfides (MS) from Atomic Metal Atoms. For the Upper Curve the Ordinate is ΔH_f - ΔH atomization (metal); for the Lower, it is the Bond Energy of the Pure Metal

to that of the corresponding oxides. The electronic states and properties show the same analogy. The stability of the yet unknown diatomic sulfides is so low that they are not expected to occur as predominant vapor species above their elemental solids and compounds. However, low temperature matrix synthesis is a promising tool for the study of new species, such as SCl, SBr and SI, and for the study of reactions and spectra of all diatomic sulfides.

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