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## Obtaining sulfur from sulfur hexafluoride and studying the sulfur isotopes properties by using vibrational spectroscopy

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### Abstract

Scheme of isotopically enriched SF<sub>6</sub> to elemental sulfur with orthorhombic modification conversion is offered. This scheme includes SF<sub>6</sub> reduction to Li<sub>2</sub>S by using lithium. The yield of isotopically enriched sulfur is not less than 97 % with chemical purity not less than 99.9 %. The results which show the dependence of the experimental frequencies in the vibrational spectra on the molecular weight of the sulfur isotope have been obtained.

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### 1. Introduction

Natural sulfur consists of a mixture of stable isotopes with mass numbers 32, 33, 34 and 36, the relative content of which is 95.04%, 0.75%, 4.20% and 0.015%, respectively<sup>1</sup>. Isotopes of sulfur are applied in biology<sup>2</sup>, geology<sup>3</sup>, geochemistry<sup>4,5</sup>, ecology<sup>6-8</sup>, agrochemistry<sup>9</sup>, archeology<sup>10</sup> and medicine<sup>11</sup>.

Sulfur hexafluoride is used as a working substance in the technology of centrifugal separation of the sulfur isotopes. Parameters of technology of centrifugal separation and properties of SF<sub>6</sub> are known<sup>12</sup>. After obtaining SF<sub>6</sub> we should convert this compound into elemental sulfur which is suitable for storing and selling. This process should be done with the next requirements: to minimize the losses, to eliminate the isotope dilution and to provide necessary chemical purity.

It is known that sulfur has a lot of allotropic modifications and crystal forms, formation of which depends on the

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methods of obtaining and conditions of storage<sup>13</sup>. For this reason, it is desirable to obtain the sulfur modification, as a commercial form which is stable at a room temperature, well packed and lossless and also capable of being the primary form to produce other allotropic forms of sulfur and commercial products. An orthorhombic modification of sulfur ( $\alpha$ -S) fully meets all these requirements.

The purpose of this research was to develop the method of obtaining isotopically enriched elemental sulfur from its hexafluoride in form  $\alpha$ -S.

For conversion  $\text{SF}_6$  to S it is possible to use microwave or plasma-chemical methods and also reduction reactions of  $\text{SF}_6$  by metals or their oxides and hydrides<sup>14-18</sup>. The main disadvantage of microwave and plasma-chemical methods is the complexity of the hardware design and low productivity. While using, for the oxides ( $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{REE}_2\text{O}_3$  and others) or calcium hydride ( $\text{CaH}_2$ ) reduction, the gaseous sulfur-containing products ( $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{SF}_4$  and other compounds of sulfur) are the result of the reaction. This will require additional steps of collecting the product gas recovery, separation of isotopically enriched sulfur from the absorbing solution and its subsequent purification. The increasing number of stages complicates the work of processing and does not allow to exclude losses of the isotopically enriched sulfur which is very expensive.

In paper [20] applying a differential thermal analysis method (DTA) it was found that the vast majority of metals reacts with  $\text{SF}_6$  at a high speed in the range of 500 - 600°C with the formation of only solid phase products - sulfides and fluorides of metals used in the reduction reaction

We used lithium as a reducing agent for processing of the hexafluoride. This reaction is well known<sup>21</sup>. Also while choosing its relatively low vapor pressure at the temperature of the reduction reaction and thus a smaller metal removal from the reaction zone to the cold zone of the reactor was taken into account.

In addition, in this paper we present the IR spectra and the Raman spectra of the polycrystalline of  $\alpha$ -<sup>32</sup>S,  $\alpha$ -<sup>33</sup>S,  $\alpha$ -<sup>34</sup>S, which were obtained at a room temperature.

## 2. Experimental

In this work the commercial  $\text{SF}_6$  (with content of hexafluoride not less 99.9 %), metallic Li (spectra pure), carbon tetrachloride  $\text{CCl}_4$  (analytical grade), KJ (analytical grade),  $\text{I}_2$  (analytical grade),  $\text{HCl}$  (analytical grade), toluene (analytical grade) were used. The experimental work used isotopes of sulfur with an isotopic purity: <sup>32</sup>S = 99.9 %; <sup>33</sup>S = 99.4 %; <sup>34</sup>S = 99.9 %.

The diffractograms were obtained by using diffractometer D8 DISCOVER ( $\text{CuK}\alpha$ - radiation,  $\lambda = 1,54056 \text{ \AA}$ ). The content of the impurities in elemental sulfur was analyzed by using atomic emission spectrometry with inductively coupled plasma iCAP6300 Duo.

IR spectra of the samples of polycrystalline  $\alpha$ -S in KBr tablets were obtained by using FTIR 5700 spectrometer Nicolet at a room temperature with the resolution of  $2 \text{ cm}^{-1}$ . Raman spectra were recorded by using spectrometer Nicolet 5700 with the Raman module at a room temperature with the resolution of  $1 \text{ cm}^{-1}$ . In both situations the laser Nd:YAG ( $\lambda=1064 \text{ nm}$ , 514 mW) was used.

The laboratory unit for  $\text{SF}_6$  reduction by lithium is shown in Fig. 1. The unit consists of the reactor with the cooling cover, the volume of the unit is 2.2 l. The unit also has the molybdenum liner with the thickness around 0.1-0.2 mm for preventing the reactor from corrosion.

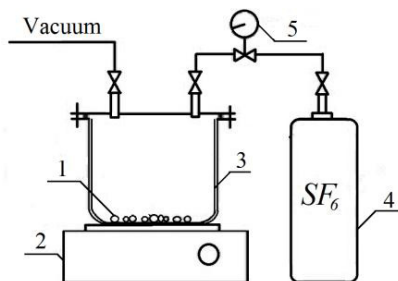


Fig. 1. The laboratory unit for  $\text{SF}_6$  reduction by lithium: 1 – lithium; 2 – rangette; 3 – molybdenum liner; 4 – capacity with  $\text{SF}_6$ ; 5 – vacuum gauge

The amount of lithium was calculated with an excess of 30-40 %, lithium was placed in a molybdenum liner, then the reactor was sealed and evacuated to  $10^{-3}$  mm Hg. After checking the impermeability of the system 40-50 mm Hg  $\text{SF}_6$  was placed into the reactor. This prevented the lithium sublimation during heating and also allowed to define the beginning of the reaction. After that the reactor was heated by using the rangette.

The exothermic reduction reaction of  $\text{SF}_6$  started under heating of the reactor bottom to red heat and proceeded with the formation of solid-phase sulfide and lithium fluoride:



After starting the reaction the heating was turned off and put into the reactor  $\text{SF}_6$  at such a rate that the reaction would not stop and the reactor would not heat to 1000 °C. The reactor was cooled after the reaction. Then the Lugol's solution in 2 N HCl, with a 100% excess of the stoichiometric was put into the reactor using the residual vacuum.

The mixture obtained was left for 12 hours in the reactor at a room temperature. The oxidation reaction of sulphide sulfur proceeded with an elemental sulfur formation.



The suspension was filtered. The precipitate was dried and milled in the mortar. After that the elemental sulfur was extracted by using  $\text{CCl}_4$  and the apparatus of Soxhlet. For obtaining chemically pure product, the elemental sulfur was cleaned by vacuum sublimation.

The sulfur after sublimation was recrystallized from toluene for obtaining the crystals of isotopically pure elemental sulfur with the orthorhombic modification. 250 mg of sulfur were taken for each 10 ml of toluene and then were dissolved by heating. The  $\alpha$ -S was crystallized under cooling to 20 °C from the solution. The yield of crystals  $\alpha$ -S was not less than 99%

The roentgenogram of  $\alpha$ - $^{34}\text{S}$  which was obtained by using this method is shown in Fig. 2. The roentgenogram includes the reflections of crystallographic planes of orthorhombic sulfur. The results of elemental analysis of  $\alpha$ - $\text{S}^{34}$  are shown in table 1.

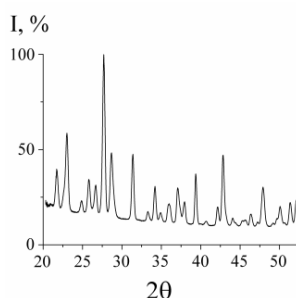


Fig. 2. The XRD pattern of isotopes  $\alpha$ - $^{34}\text{S}$

Table 1. Results of the quantitative chemical analysis of impurities in  $\alpha$ - $\text{S}^{34}$

Element	Content, ppm	Element	Content, ppm
Al	< 10	Li	< 10
B	< 5	Fe	< 5
C	< 5	Mg	< 8
Ca	< 9	Na	< 7
Cr	< 5	Cu	< 2

Sulfur isotopes obtained in this way have a chemical purity of more than 99.9%. The yield of elemental sulfur is not less than 97 %.

Fig. 3 shows the IR spectra, obtained for the polycrystalline samples of the  $\alpha$ - $^{32}\text{S}$ ,  $\alpha$ - $^{33}\text{S}$ ,  $\alpha$ - $^{34}\text{S}$  and  $\alpha$ - $^{\text{nat}}\text{S}$  isotopes. According to the previous study<sup>22</sup>, the observed IR spectra absorption corresponds to the valence vibration (stretching vibration) -  $\nu_5$ . Fig. 3 shows that the position of the lines of oscillation ( $\nu_5$ ) for the  $\alpha$ - $^{33}\text{S}$  and the  $\alpha$ - $^{34}\text{S}$  isotopes are shifted to the low-energy side, and the line corresponding to the  $\alpha$ - $^{32}\text{S}$  isotope has a high-energy shift with respect to the spectrum of  $\alpha$ - $^{\text{nat}}\text{S}$ .

This behavior can be explained by the fact that the positions of the oscillation frequencies in the spectra directly affect the mass of the atoms oscillating around the equilibrium positions in the crystal lattice. This dependence has the form:  $\nu = \propto m^{-1/2}$ .

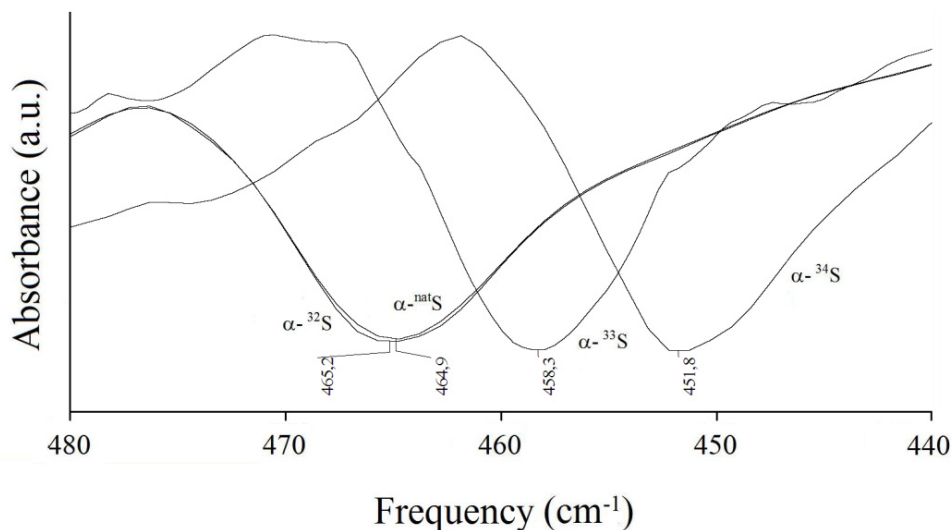


Fig. 3. IR spectra of isotopes  $\alpha$ - $^{32}\text{S}$ ,  $\alpha$ - $^{33}\text{S}$ ,  $\alpha$ - $^{34}\text{S}$  and  $\alpha$ - $^{\text{nat}}\text{S}$

Isotopic dependence of the oscillation frequencies of  $\alpha$ -S in the IR spectra are shown in Fig. 4. The line shows the calculated dependence of the absorption frequency on the atomic mass of the  $\alpha$ -S isotope ( $\nu = 2632.9 m^{-1/2}$ ), which correlates with experimental values.

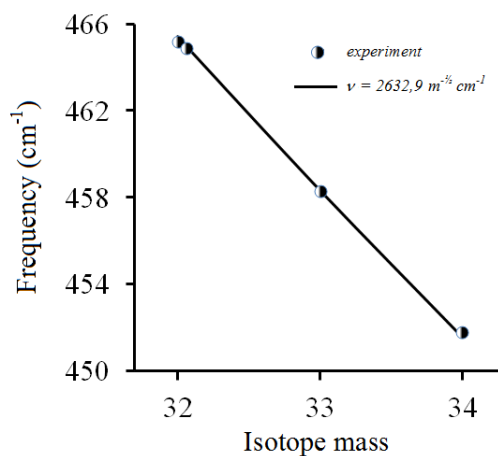


Fig. 4. Isotopic dependence of the oscillation frequencies of  $\alpha$ -S in the IR spectra

Fig. 5 shows the Raman spectra obtained for polycrystalline samples of the isotopes of  $\alpha$ -S. In the spectra of the isotopes all of the absorption bands that are characteristic of  $\alpha$ -S were observed, which, according to the isotope shift, is indicated by:  $\nu = \propto m^{-1/2}$ .

Fig. 6 shows the experimental vibrational frequencies in the Raman spectra of the atomic mass of the  $\alpha$ -S isotope. As shown in the figure, dependencies of the position of crest of bands in the Raman spectra of sulfur isotopes are a linear function of the atomic masses of the isotopes.

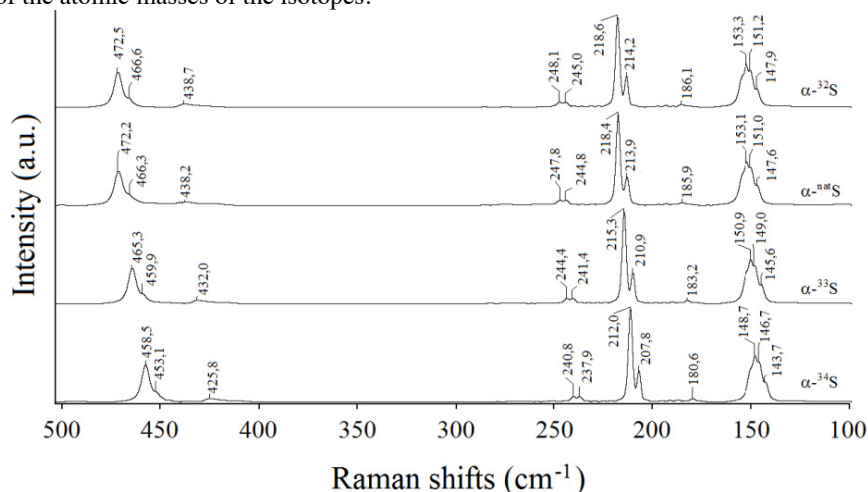


Fig. 5. Raman spectra of the isotopes  $\alpha$ - $^{32}\text{S}$ ,  $\alpha$ - $^{33}\text{S}$ ,  $\alpha$ - $^{34}\text{S}$  and  $\alpha$ -natS

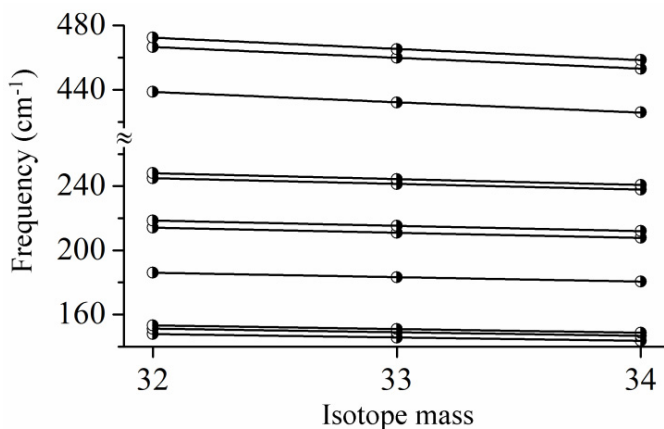


Fig. 6. Isotopic dependence of the oscillation frequencies of  $\alpha$ -S in the Raman spectra

These linear relationships make it possible to know the frequency of isotopes  $\alpha$ - $^{32}\text{S}$ ,  $\alpha$ - $^{33}\text{S}$  and  $\alpha$ - $^{34}\text{S}$  to determine the oscillation frequency in the IR and Raman spectra of the sulfur isotope  $\alpha$ - $^{36}\text{S}$ , for which it is difficult to obtain vibrational spectra due to its high cost connected with its low content in the natural sulfur.

### 3. Conclusion

1. IR spectra and Raman spectra of the polycrystalline isotopes  $\alpha$ - $^{32}\text{S}$ ,  $\alpha$ - $^{33}\text{S}$  and  $\alpha$ - $^{34}\text{S}$  have been obtained.
2. It has been found that experimental frequencies of the vibrational spectra of the isotopes of sulfur decrease in a linear manner with an increasing mass of the isotope. From the experimental correlations, the oscillation frequencies for the isotope  $\alpha$ - $^{36}\text{S}$  have been determined.

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