

Study of Sulfur Isotopes by Vibrational Spectroscopy and Quantum Chemistry

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Abstract

Background/Objectives: The article is devoted to the dependence of the experimental and calculated frequencies in the IR- and Raman-spectra from the molecular mass of the sulfur isotope. **Methods/Statistical Analysis:** The calculations of the S₈ molecules containing the different sulfur isotopes were carried out using the GAUSSIAN'03 program package. The geometries were first optimized at the gradient-corrected DFT level using the three-parameter fit of the exchange-correlation potential suggested by Becke in conjunction with the LYP exchange potential (B3LYP). All electron 6-31G(d), and extended cc-PVTZ basis sets were used. The absence of imaginary vibration frequencies confirmed the stationary character of the structures. **Findings:** IR spectra and Raman spectra of the polycrystalline isotopes α -³²S, α -³³S and α -³⁴S were obtained. It was 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 α -³⁶S were determined. The results obtained demonstrate that the quantum-chemical calculations are sensitive to the isotopic shifts in the vibrational spectra of sulfur isotopes and are able to assess changes in their thermodynamic properties. **Applications/Improvements:** The effect of a sulfur isotope shift on the change of thermodynamic parameters.

Keywords: 5-6 Words, Drawn from Title, Word Representing the Work

1. Introduction

Natural sulfur consists of a mixture of stable isotopes with mass numbers 32, 33, 34 and 36, the relative contents of which are 95.04%, 0.75%, 4.20% and 0.015%, respectively¹. Isotopes of sulfur are applied in biology², geology³, geochemistry^{4,5}, ecology⁶⁻⁸, agrochemistry⁹, archeology¹⁰ and medicine¹¹. It is obvious that information regarding the spectral and thermodynamic properties of stable sulfur isotopes is important for both applied and scientific problems. Other groups¹²⁻¹⁵ have studied the vibration spectra of sulfur α -natS и α -³²S at low temperatures in detail, and have studied the effect of temperature on the infrared spectra of natural and isotopically-pure sulfur ³²S₈. These experiments were performed using a single crystal of sulfur. However, in applied research, research-

ers often use the polycrystalline powders of sulfur rather than single crystals of sulfur. Therefore, in this paper, the infrared spectra and Raman spectra of and isotopically-pure polycrystalline α -³²S, α -³³S and α -³⁴S are presented. The experimental data are compared with theoretical calculations of the infrared and Raman spectra, obtained via the theory of functional density. In addition, this paper shows the relationship between the change in Gibbs free energy and the mass of an isotope of sulfur.

2. Experimental Details

The experimental work used isotopes of sulfur with an isotopic purity: ³²S – 99.9%; ³³S – 99.4%; ³⁴S – 99.9%. To obtain a chemically pure orthorhombic sulfur modification (α -S) the isotopes were subjected to triple distillation

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under vacuum with subsequent crystallization from carbon tetrachloride. Isotopes of sulfur obtained in this way have a chemical purity of more than 99.9%.

The IR spectra of polycrystalline samples of α -S in KBr tablets in the range 400–500 cm^{-1} were obtained using the FT-IR spectrometer Nicolet 5700 at room temperature, with a resolution of 2 cm^{-1} . Raman spectra were recorded on a spectrometer Nicolet 5700 with a Raman module in the range 100–500 cm^{-1} at room temperature, with a resolution of 1 cm^{-1} . In both cases a laser was used with Nd:YAG (1=1064nm, 514mW).

3. Computational Details

The calculations of the S_8 molecules containing the different sulfur isotopes were carried out using the GAUSSIAN'03 program package¹⁶. The geometries were first optimized at the gradient-corrected DFT level using the three-parameter fit of the exchange-correlation potential suggested by¹⁷ in conjunction with the¹⁸ exchange potential (B3LYP). This method is now generally accepted to best describe the thermodynamic properties and vibrational spectra, and gives results similar to the MP2 and GMP2 methods. All electron 6-31G(d), and extended cc-PVTZ basis sets were used. The absence of imaginary vibration frequencies confirmed the stationary character of the structures.

Energy calculations were corrected for zero-point vibrational energy and reduced to normal conditions (298.15K, 1 atm) using thermal corrections to enthalpy and free energy.

The optimized geometries of these molecules were also used for the calculations by the ADF'2004 (Amsterdam Density Functional) program. The OPTX exchange functional¹⁹ was used in combination with the PBE correlation functional²⁰ using an all electron triple- ζ + polarization basis set of uncontracted Slater orbitals. Scalar relativistic effects were considered using the zero order regular approximation (ZORA)²¹.

4. Results and Discussion

Figure 1 shows the IR spectra, obtained for the polycrystalline samples of the α - ^{32}S , α - ^{33}S , α - ^{34}S and α - $^{\text{nat}}\text{S}$ isotopes. According to a previous study²², the observed IR spectra absorption corresponds to the valence vibration (stretching vibration) - ν_s . Figure 1 shows that the position of the lines of oscillation (ν_s) for the α - ^{33}S and the α - ^{34}S isotopes

are shifted to the low-energy side, and a line corresponding to the α - ^{32}S isotope has a high-energy shift with respect to the spectrum of α - $^{\text{nat}}\text{S}$.

This behavior can be explained by the fact that the provisions 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: $n = \mu m^{-1/2}$.

Isotopic dependence of the oscillation frequencies of α -S in the IR spectra are shown in Figure 2. The line shows the calculated dependence of the absorption frequency of the atomic mass of the α -S isotope ($n = 2632.9 m^{-1/2}$), which correlates with experimental values. Figure 3 shows the Raman spectra obtained for polycrystalline samples of the isotopes of α -S. In the spectra of the isotopes all of the absorption bands that are characteristic of α -S were observed, which, according to the isotope shift, is indicated by: $n = \mu m^{-1/2}$.

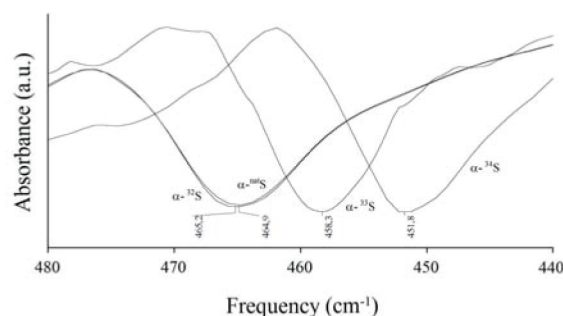


Figure 1. Raman spectra of the ^{32}S , ^{33}S and ^{34}S isotopes, and sulfur with the natural isotopic composition $^{\text{nat}}\text{S}$.

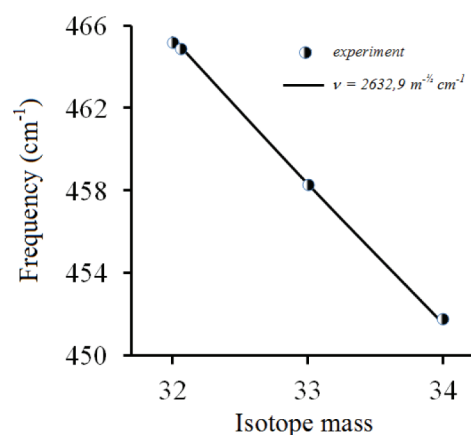


Figure 2. Isotopic dependence of the oscillation frequencies of α -S in the IR spectra.

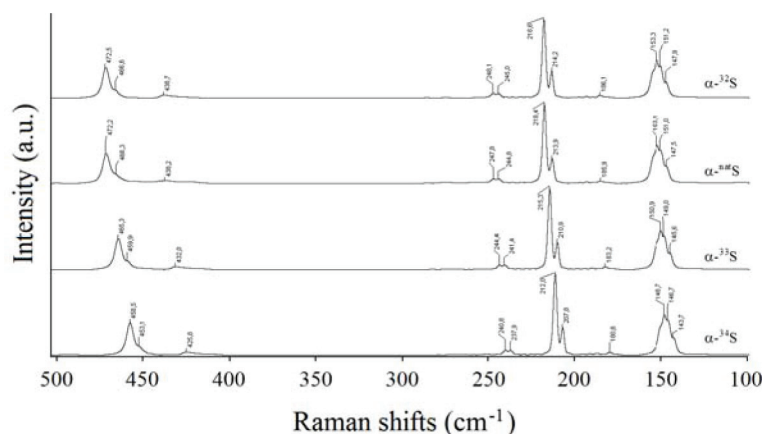


Figure 3. Raman spectra of the isotopes α - ^{32}S , α - ^{33}S , α - ^{34}S and α -natS.

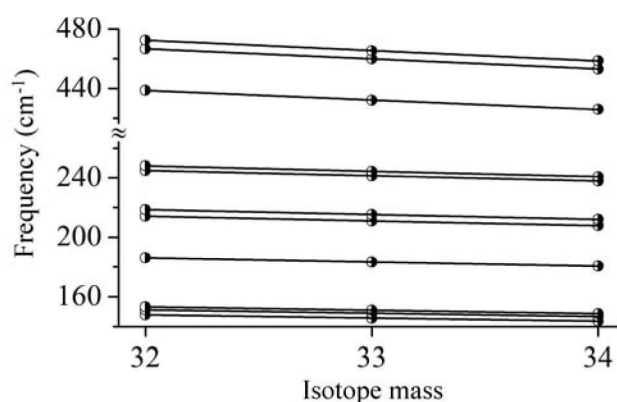


Figure 4. Isotopic dependence of the oscillation frequencies of α -S in the Raman spectra.

Figure 4 shows the experimental vibrational frequencies in the Raman spectra of the atomic mass of the α -S isotope. As can be seen from the Figure, depending on the maximal provisions of the bands in the Raman spectra of sulfur, isotopes are a linear function of the atomic masses of the isotopes.

The obtained linear dependence on the known frequencies of the α - ^{32}S , α - ^{33}S and α - ^{34}S isotopes allows the determination of the oscillation frequency in the IR and Raman spectra of the sulfur isotope α - ^{36}S , for which it is difficult to obtain the vibration spectra due to its high cost, which is associated with its low content in natural sulfur. The calculated vibration frequencies in the α - ^{36}S isotope are shown in Table 1.

It is well known that cyclo-octa-sulfur can form three crystalline allotropic modifications, the first of which, orthorhombic α -S, is stable at room temperature¹⁵. The

structure of this modified version was studied by X-ray analysis, and contains S₈ as main structural elements, which are formed with each other as columns¹⁶. Figure 3 shows the model structure of α -S used in quantum chemical calculations.

As the Figure 5 shows, the resulting structure is not truly orthorhombic, because it is a solid S₈ ring coordinated by adjacent rings. However, the resulting structure has allowed the calculations of the Raman spectra to be performed for the isotopes of sulfur for the unit cell. A full optimization of geometrical parameters was also done.

The calculated length of the S-S bonds (2.09 Å) in the S₈ cluster was close to the experimental value obtained (2.06 Å¹⁵). Table 1 shows the experimental (^{32}S , ^{33}S , ^{34}S) and calculated (^{32}S , ^{33}S , ^{34}S , ^{36}S) values of the basis states in the 6-31G* and cc-PVTZ frequency in the Raman spectra.

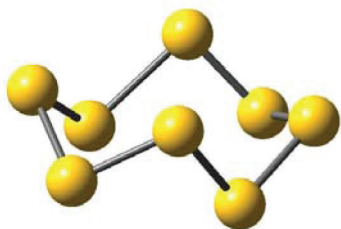
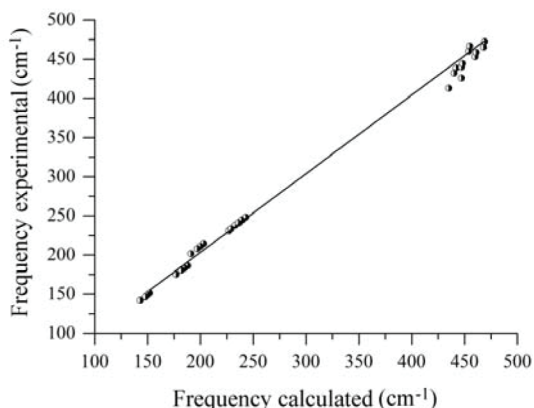
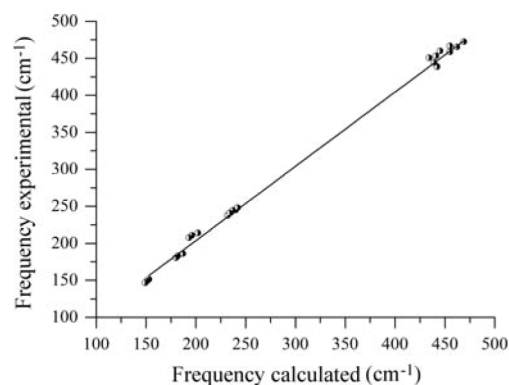
Data from Table 1 also show that, despite the small differences between the masses of the isotopes, the theoretical frequencies are in satisfactory agreement with the experimental data and almost completely describe the vibration spectra of sulfur isotopes. The data also indicates that the used calculation methods are sensitive to changes in the frequency spectra (a few cm⁻¹), depending on the mass of the isotope.

From the correlation ratios (in Figures 4 and 5) it is shown that a significant expansion of the basis for using the cc-PVTZ does not improve the agreement between the calculated and experimental frequencies. The smaller basis 6-31G(d) gives even better results:

$$\omega_{\text{experimental}} = 2.33 + 1.005 \omega_{\text{calculated}} \quad r = 0.999; \text{sd} = 5.6; \quad n = 32 \text{ for basis } 6-31\text{G(d)} \quad (1)$$

Table 1. The experimental and calculated frequencies in the Raman spectra of sulfur isotopes to molecules a-S, cm^{-1}

$\alpha\text{-}^{32}\text{S}$ exp.	6- 31G*	cc- PVITZ	TZ2P	$\alpha\text{-}^{32}\text{S}$ exp.	6- 31G*	cc- PVITZ	TZ2P+	$\alpha\text{-}^{34}\text{S}$ exp.	6- 31G*	cc- PVTZ	TZ2P+	$\alpha\text{-}^{36}\text{S}$ exp.	6- 31G*	$\alpha\text{-}^{\text{nat}}\text{S}$ exp.	Mode and species [23]
147.9				145.6				143.7				139.4		147.5	$\nu_8(\text{E}_2)$
151.2	152	153	143	149.0	150	151	140	146.7	148	149	138	142.2	143	151.0	
153.3				150.9				148.7				144.1		153.1	
186.1	188	187	186	183.2	185	182	183	180.6	182	180	181	175.1	177	185.9	$\nu_6(\text{E}_1)$
214.2	203	202	195	210.9	200	196	192	207.8	197	193	189	201.4	191	213.9	$\nu_2(\text{A}_1)$
218.6				215.3				212.0				205.4		218.4	
245.0	240	240	232	241.4	237	235	228	237.9	233	232	226	230.8	227	244.8	$\nu_4(\text{B}_2)$
248.1	243	242	234	244.4	239	237	230	240.8	236	234	227	233.5	229	247.8	$\nu_{11}(\text{E}_3)$
	426	433	420						433	428	408				
438.7	434	442	444	432.0	440	434	414	425.8	447	439	430	412.8	421	438.2	$\nu_{10}(\text{E}_3)$
466.6	461	455	450	459.9	454	445	444	453.1			437	439.6	435	466.3	$\nu_5(\text{E}_1)$
472.5	476	469	471	465.3	468	462	464	458.5	461	455	457	444.4	448	472.2	$\nu_7(\text{E}_2) + \nu_1(\text{A}_1)$

**Figure 5.** The model structure of a-S used for quantum-chemical calculations.**Figure 6.** The relationship between the experimental and calculated by B3LYP/6-31G method (d) frequencies of oscillation Raman spectra of the sulfur isotopes $\alpha\text{-}^{32}\text{S}$, $\alpha\text{-}^{33}\text{S}$ and $\alpha\text{-}^{34}\text{S}$.**Figure 7.** The relation between the experimental and calculated cc-PVTZ vibration frequencies of the Raman spectra of the sulfur isotopes $\alpha\text{-}^{32}\text{S}$, $\alpha\text{-}^{33}\text{S}$ and $\alpha\text{-}^{34}\text{S}$.

$$\omega_{\text{experimental}} = 2.89 + 1.003 \omega_{\text{calculated}} \quad r=0.999; \text{sd}=5.8; n=24$$

for basis cc-PVTZ (2)

Here and below, r denotes the correlation coefficient, sd signifies the standard deviation, and n indicates the number of connections (Figures 6 and 7).

Similar correlations were obtained using the ratio of the program based on the ADF optimized by the B3LYP/6-31G(d) of the molecular structures (Figure 8):

$$\omega_{\text{experimental}} = 14.7 + 0.979 \omega_{\text{calculated}} \quad r=0.998; \text{sd}=7.9; n=24$$

for basis TZ2P+ (3)

Although the calculations using the software packages GAUSSIAN and ADF use different functionals and basis states, in principle the quantitative relationships are close enough to each other and the experimental frequencies (relative error of the estimate of frequencies in the Raman spectra is about 3-4%).

The resistance of sulfur clusters is determined by their thermodynamic parameters. It should be noted that the experimental formation enthalpy of the transition from S_2 to S_8 was virtually unchanged, while the entropy of formation varies considerably¹⁸. Table 2 shows the experimental and calculated values of the entropy of sulfur cluster formation.

From Table 2 the correlation ratio between the experimental and calculated values of the entropy of the formation of sulfur clusters were obtained:

$$S_{\text{experimental}} = 31.3 + 0.86 S_{\text{calculated}} \quad r=0.996; \text{sd}=17.6; n=8 \quad (\text{in GAUSSIAN}) \quad (4)$$

$$S_{\text{experimental}} = 15.0 + 0.905 S_{\text{calculated}} \quad r=0.985; \text{sd}=21.2; n=8 \quad (\text{in ADF}) \quad (5)$$

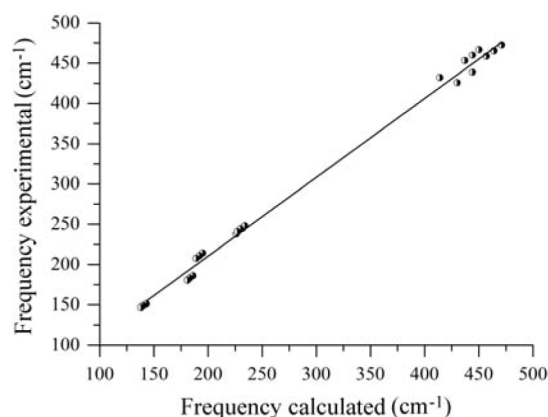


Figure 8. The relation between the experimental and calculated BP86/TZ2P+ oscillation frequencies of the Raman spectra for the sulfur isotopes $\alpha\text{-}^{32}\text{S}$, $\alpha\text{-}^{33}\text{S}$ and $\alpha\text{-}^{34}\text{S}$.

The resulting correlation ratio indicates that the calculated thermodynamic parameters of the different methods of sulfur cluster formation are sufficiently close to the experimental values and that the calculation error is less than 6%^{23,24}.

The resulting thermodynamic characteristics obtained using the B3LYP/6-31G(d) calculation method cannot be directly compared with the enthalpy of formation and the Gibbs free energy. However, the effect of isotope shift in the change of thermodynamic parameters can be estimated. From the data presented in Table 3 a relationship between the change in Gibbs free energy and the mass of a sulfur (S_8) isotope was obtained:

$$M_s = -1402 - 2552 \Delta G \quad r = 0.991; \text{sd} = 0.3; n = 4 \quad (1.0 \% \text{ error}) \quad (6)$$

A similar dependence is obtained using the change of formation enthalpy. In addition, the use of the values of Zero-Point Energy (ZPE) (Table 3.) for calculations in both programs, results in a very close dependence:

Table 2. The experimental and calculated entropy of formation of sulfur clusters (J/mol.K) using B3LYP/6-31G(d) and BP86/TZ2P + methods

Cluster	Experiment [24]	GAUSSIAN B3LYP/6-31G(d)	ADF BP86/TZ2P+
S	168	152	175
S_2	228	219	234
S_3	270	291	276
S_4	311	313	304
S_5	309	349	356
S_6	354	374	380
S_7	408	417	418
S_8	430	456	460

Table 3. The thermodynamic characteristics of sulfur isotopes in the S_8

Isotope	The free Gibbs energy change in relative to 3185 a.u.	The value change of ZPE (B 3LYP/6-31G(d)), eV	The value change of ZPE (BP86/TZ2P+), eV
$\alpha\text{-}^{32}\text{S}$	-0.562094	0.3125824	0.301504
$\alpha\text{-}^{33}\text{S}$	-0.562314	0.3077952	0.296899
$\alpha\text{-}^{34}\text{S}$	-0.562694	0.3032528	0.292512
$\alpha\text{-}^{36}\text{S}$	-0.563598	0.2947120	0.284266

$M_s = 102 - 224 \text{ ZPE } r=0,999; sd=0.06; n=4 \text{ (0.2 \% error)}$
(in GAUSSIAN) (7)

$M_s = 102 - 233 \text{ ZPE } r=0,999; sd=0.06; n=4 \text{ (0.2 \% error)}$
(in ADF) (8)

It can be said that, along with the frequencies of the Raman spectrum, the thermodynamic parameters, in spite of small changes (no more than 0.3%), are quite sensitive to sulfur isotopic shift.

5. Conclusions

- IR spectra and Raman spectra of the polycrystalline isotopes $\alpha\text{-}^{32}\text{S}$, $\alpha\text{-}^{33}\text{S}$ and $\alpha\text{-}^{34}\text{S}$ were obtained.
- It was 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 $\alpha\text{-}^{36}\text{S}$ were determined.
- The results obtained demonstrate that the quantum-chemical calculations are sensitive to the isotopic shifts in the vibrational spectra of sulfur isotopes and are able to assess changes in their thermodynamic properties.

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