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REVIEW ARTICLE

Vibrations of the S–S bond in elemental sulfur and organic polysulfides: a structural guide

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This review summarizes and analyzes in comparative manner the S–S bond vibrations in IR and Raman spectra of elemental sulfur and organosulfur compounds containing disulfide and polysulfide moieties. It is intentionally biased toward application of the experimental S–S bond frequencies for structural elucidation of sulfur compounds. It was shown that the S–S bond frequencies are a useful tool for identification of the elemental sulfur modifications, organic disulfides and polysulfides. Particular attention is paid to the correlation between the S–S bond frequencies and the molecular structure.

Keywords: Raman and infrared spectra; elemental sulfur; disulfides; polysulfides

1. Introduction

The rapid development of sulfur chemistry is due to its importance both in the organic synthesis and industry. Sulfur and its compounds with S–S bonds are widely represented in nature (mineral sulfur, coal, oil, natural gas, oil shale) and play an important role in the metabolism of living beings. Prospects of organosulfur chemistry including organosulfur polymers are bright and actually difficult for exact evaluation. Particular attention is paid to the active involvement of elemental sulfur in fine and industrial organic synthesis owing to the fact that sulfur is available, cheap, non-toxic, easy to handle and store. The S–S bond is a frequent structural motif in diverse biologically active compounds participating in chemical and biological processes (1, 2). Many peptides and peptide mimetics possess S–S bonds (3). Pentasulfides occur in a number of plants and animals (4). Some organic pentasulfides, diallyl pentasulfide (5, 6) and varacin (7) show antitumor, antifungal, cytotoxic and antifouling activities. Disulfides find applications in the preparation of self-assembled monolayers (8–10). Among unsymmetrical aromatic disulfides were found those exhibiting second-order non-linear optical properties (11). These molecules are potent in optical data processing and communication (2). Compounds containing S–S linkage have been used for the preparation of dynamic combinatorial libraries (12), catenanes (13, 14), macrocycles (15), carceplexes (16), dendrimers (17), rotaxanes and micelles (18, 19). In high-performance Li/S

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rechargeable batteries, a number of compounds with disulfide and polysulfide moieties up to octasulfides interplay during the charge–discharge processes (20–24). The identification of these polysulfides is important for further improvement of these cells (24). Polysulfide polymers were developed as cathode materials for modified Li/S batteries (25–30).

In the synthesis of sulfur compounds with S–S bonds or their isolation from natural objects, questions concerning their structure and reaction mechanism have always arisen. To answer these questions, invaluable help for researchers comes from vibrational spectroscopy. Advances and potential of vibrational spectroscopy related to sulfur compounds were highlighted in a number of monographs and manuals (31–51).

This review is an attempt to analyze the S–S stretching frequencies in the vibrational spectra of diverse modifications of elemental sulfur, organic disulfides and polysulfides as well as to consider in detail the existing correlations between the S–S stretching values and structural surroundings or find out new ones. Although the major body of the spectral data refers to the last decades of the past century, owing to their experimental character, they are not devaluated. Indeed, in vibrational spectroscopy, a great many correlations between vibrational frequencies of S–S bond and the structure of the fragments where this bond built in are known. However, only some of them find application in structural analyses, because the S–S stretching absorption is of low intensity and strongly dependent on the structural surroundings. Often, assignment of these vibrations is not easy. But just because of their high sensitivity to the molecular structure, it is sometimes possible to arrive at valuable information about the compounds under study. This is why, unlike the monographs (31–45, 47) and manuals (46, 48, 50), here we analyze with a special scrutiny the correlations of the S–S stretching vibrations with the structure of the moieties where they are. It is this approach that makes the review different from other compilations covering these topics. We intentionally do not aggravate the review with the frequency assignment issues based on quantum-chemical computations, since this field represents a special challenge and stands outside the scope of the paper.

In the review, the tables of the S–S stretching vibrations of frequently occurring modifications of elemental sulfur and important organosulfur compounds with S–S bonds are given and thoroughly analyzed.

2. S–S bond vibrations in elemental sulfur

Among the numerous allotropic modifications of elemental sulfur, the S₈ (cyclic octamer) is the most thermodynamically stable, as well as the best studied both chemically (41, 49–60) and spectrally (61–97). Octatomic sulfur occurs by nature in a free state, and under normal conditions (25 °C), exists as rhombic yellow crystals (41, 49). Figure 1a–f shows cyclic modifications of elemental sulfur, whose vibrational spectra have been reported: S₆ (50, 76–79), S₇ (50, 82–84), S₈ (50, 61–75), S₉ (50, 51), S₁₀ (50, 79), S₁₁ (50), S₁₂ (50, 51, 80, 81), S₁₃ (50), S₁₄ (50), α -S₁₈ (50, 97), S₂₀ (50, 51, 97). It is pertinent to note that the structure of these cyclic molecules (except for cyclodecanesulfane) has been determined using X-ray diffraction analysis method (49).

In addition, vibrational spectra of four allotropes of the S₇ (α , β , γ and δ), obtained by recrystallization of S₇ from different solvents at low temperatures (–50/–100 °C), were thoroughly studied (83).

The vibrational spectra of unstable acyclic modifications of sulfur (S₂, S₃ and S₄) was briefly reported (98–106), recorded under special conditions at low temperatures or in gas phase.

In this section, there is a good reason to consider the vibrational spectra of the aforementioned allotropes of elemental sulfur in the following order. First, we analyzed the spectra of S₈, S₆, S₁₂ (molecules with high-symmetrical rings, D_{4d} and D_{3d}) (63) and S₇ (molecules with low-symmetrical rings, C_s) (63), which were the most extensively studied (both calculated and

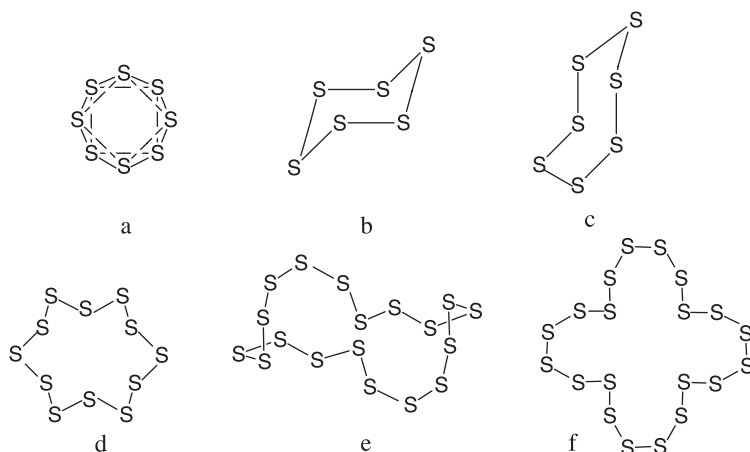


Figure 1. Allotropic modifications of sulfur: a – S₈, b – S₆, c – S₇, d – S₁₂, e – α -S₁₈, f – S₂₀ (49).

observed spectral characteristics were available). In this issue, we focused on vibrational spectra of S₈ because they were well investigated and widely used for the interpretation of spectra of other allotropic modifications of sulfur. Vibrational spectra of instable cyclic allotropes of sulfur, S₁₀, α -S₁₈ and S₂₀, for which Raman spectra were recorded at low temperatures (–80/–90 °C), were analyzed in separate section. For these compounds, only observed vibrational spectra were briefly reported (79, 97).

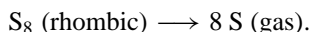
Special part of the work was devoted to the spectra of unstable acyclic modifications of S₂, S₃ and S₄, which turned to be the least known as yet (98–106).

Since the spectra analyzed were recorded at different times and on various devices, there were some contradictions in spectral data that were specially discussed in the review.

2.1. Vibrational spectra of S₈

Vibrational spectra of crystalline (rhombic) sulfur S₈ were investigated in (61–75), where Raman (61, 62, 65–73) and IR (61, 62, 66, 74, 75) absorption spectra were given. Vibrational assignment using theoretical calculations was made in (61–64, 67). It should be mentioned that not all the data obtained in these works were unambiguous and correct.

In one of the first works (61), the assignment of S₈ absorption bands was made based on normal-coordinate calculations. The validity of these spectra interpretations was supported by the fact that the calculated value of enthalpy ($\Delta H^\circ = 24.51 \text{ kcal mol}^{-1}$) fitted the plotted value well ($\Delta H^\circ = 25.29 \pm 0.05 \text{ kcal mol}^{-1}$) for the reaction (65):



At the same time, Table 1 (column 3 and 6) shows the differences between the observed and calculated values of vibrational frequencies for S₈ (up to 34 cm^{–1}), which is presumably due to the inaccuracy of the force field employed in the work.

In the spectra of rhombic S₈ discussed in (61, 62), there were discrepancies. For example, the frequencies at 400, 225, 184 and 150 cm^{–1} (61) were replaced by 411, 243, 248 and 191 cm^{–1}, correspondingly (62) (Table 1, column 3 and 4). In the latter work (62), the assignment of absorption bands was made on the basis of normal-coordinate treatment using the modified Urey–Bradley constant, taking into account the field interactions between stretching, bending and torsion vibrations in the S₈ molecule. In the result, a good agreement between the calculated

Table 1. Observed and calculated vibrational spectra of S₈ (cm⁻¹).

Assignment ^a	Vibration	Observed frequencies			Calculated frequencies			
		(61)	(62)	(66)	(61)	(62)	(63, 67)	(64)
1	2	3	4	5	6	7	8	9
<i>e</i> ₁	<i>ν</i>			532 ^b				532 ^b
<i>e</i> ₃	<i>ν</i>			520 ^b				509 ^b
<i>a</i> ₁	<i>ν</i>	475 ^c	475 ^c	470	456	473	475	470
<i>e</i> ₂	<i>ν</i>	(475) ^c	(475) ^c	434	480	474	475	428
<i>e</i> ₁	<i>ν</i>	471	471	465	461	474	471	465
<i>e</i> ₃	<i>ν</i>	437	437		438	436	437	
<i>b</i> ₁	<i>ν</i>	400	411		398	412	415	
<i>b</i> ₂	<i>δ</i>	225	243	267	226	245	239	267
<i>a</i> ₁	<i>δ</i>	218	218	216	198	216	218	216
<i>e</i> ₂	<i>δ</i>			185				196
<i>e</i> ₃	<i>δ</i>	184	248	243	190	239	248	230
<i>e</i> ₂	<i>δ</i>	152	152	152	122	161	152	149
<i>e</i> ₁	<i>τ</i>	150	191	190	184	192	186	212
<i>e</i> ₂	<i>τ</i>	86	86		82	88	86	

Notes: ^aSymmetry species labeling was given in the papers (31, 33, 36, 38). ^bThe frequencies in the region of 509–532 cm⁻¹ (64, 66) were not typical for vibrational spectra of the S₈ molecule. ^cThe authors (61, 62) supposed that the frequencies of *a*₁ and *e*₂ species were overlapped.

and observed spectral characteristics was achieved (Table 1, column 4 and 7). Analogous results for the calculated vibrational spectra were reported in (63, 67) (Table 1, column 8).

Thus, the data obtained in (61–63, 67) allowed one to determine quite adequately the regions of stretching (*ν*, 400–475 cm⁻¹), bending (*δ*, 152–267 cm⁻¹) and torsion (*τ*, 86 and 150–191 cm⁻¹) vibrations in the spectra of S₈ molecule (Table 1).

One should bear in mind that in (64), the vibrational spectra of S₈ were assigned on the basis of the Wilson matrix method, where the force constants were chosen so that the calculated vibrational frequencies would correspond to the experimental data obtained in the manuscript (66) (Table 1, column 9 and 5), *i.e.* less correct than in the papers (61–63, 67). For example, the calculated value of torsion frequencies at 186–196 cm⁻¹ (62, 63) and belonging to *e*₁, in (64) was mistakenly defined as bending vibration in the S₈ molecule and assigned to *e*₂. Besides, experimental data given in (66), and consequently the calculated frequencies described in (64), demand, in our opinion, a sharp criticism. For instance, in these works (64, 66), the frequencies of the S–S bond stretching vibrations in the region of 510–532 cm⁻¹ non-typical for the S₈ molecules were reported. Furthermore, the authors (64, 66) pointed only to three frequencies of stretching vibrations for the S–S bond at 400–475 cm⁻¹, whereas in the papers (61, 62) four frequencies were shown (Table 1). In the works (64, 66), the frequency of bending vibration was likely to be given in the wrong region (267 cm⁻¹), because according to Scott and McCullough (61, 62) it was shifted to low-frequency field (225–243 cm⁻¹) (Table 1). Here and further, the following abbreviation was used: *ν* stretching, *δ* bending, *τ* torsion mode; *s* strong, *vs* very strong, *m* medium, *w* weak, *vw* very weak, *sh* shoulder.

Let us consider the changes in the vibrational spectra of S₈ molecule depending on its aggregate state: crystals (62, 66, 70–75), melt at 122 °C (69, 72), vapors at 180 °C (68, 69) and solutions in organic solvents (62, 69, 70, 75).

2.1.1. Raman spectra of S₈

Single-crystal Raman polarization data, obtained at 25 °C, were used to assign the spectrum of crystalline rhombic sulfur S₈ (Figure 1a) to *a*₁, *e*₂ and *e*₃ symmetry modes (Table 2) (62, 70–72).

Table 2. Raman spectra of elemental sulfur in various aggregate states (cm^{-1}).

Symmetry	Vibration	Observed frequencies in Raman spectra of sulfur						
		S ₈ (cryst. ^a , 25°C)	Melted sulfur (122°C)	Sulfur vapors (180°C) (68, 69)	S ₈ solution			
1	2	3	4	5	CS ₂	MeNH ₂ (70)	PrNH ₂ (70)	(NH ₂ CH ₂) ₂ (70)
1	2	3	4	5	6	7	8	9
						535 ^b <i>m</i>	535 ^b <i>m</i>	535 ^b <i>m</i> 510 ^b <i>w</i>
<i>a</i> ₁ (<i>e</i> ₂)	<i>v</i>	470 <i>s</i> (62) 474 <i>vs</i> (70) 474 <i>s</i> , 470 <i>sh</i> (72)	474 <i>s</i> (69) 474 <i>s</i> (72)	483 ^c <i>m</i> 451 ^d <i>w</i>	475 <i>s</i> (62) 474 <i>m</i> (69) 475 <i>m</i> (70)	505 ^b <i>s</i>	505 ^b <i>w</i> 465 <i>m</i>	505 ^b <i>w</i> 475 <i>vs</i>
<i>e</i> ₃	<i>v</i>	434 <i>m</i> (62) 438 (70) 441 <i>w</i> (69, 70) 441 <i>w</i> , 434 <i>w</i> (72)	439 <i>w</i> (69) 441 <i>w</i> , 434 <i>w</i> (72)	445 <i>w</i>	437 <i>s</i> (62) 438 <i>m</i> (69) 440 <i>vw</i> (70)	440 <i>s</i>	438 <i>s</i>	438 <i>m</i>
				269 ^d <i>w</i>		400 <i>s</i>	400 <i>s</i>	400 <i>s</i> 345 <i>m</i>
<i>e</i> ₃	δ	243 <i>w</i> (62) 246 <i>w</i> (70) 252 <i>sh</i> 247 <i>w</i> (72)	239 <i>w</i> (69) 243 <i>w</i> (72)	237 ^e <i>s</i>	248 <i>w</i> (62) 242 <i>w</i> (69) 245 <i>vw</i> (69)			
<i>a</i> ₁	δ	218 <i>s</i> (62, 70) 215 <i>w</i> (70) 216 <i>s</i> (68) 218 <i>s</i> , 215 <i>sh</i> (72)	219 <i>s</i> (69) 218 <i>s</i> (72)	218 <i>s</i>	218 <i>s</i> (62) 216 <i>s</i> (69) 218 <i>s</i> (68, 69)			
				201 ^d <i>w</i>				
<i>e</i> ₂	τ	152 <i>s</i> (62, 70) 151 <i>s</i> , 147 <i>sh</i> (72) 114 <i>w</i> (62)	153 <i>s</i> (69) 151 <i>s</i> (72)	151 <i>s</i>	152 <i>s</i> (62, 70) 151 <i>s</i> (69)			
	Lattice vibrations							
<i>e</i> ₂	τ	85 <i>s</i> (62) 84 <i>m</i> (68) 86 <i>m</i> , 82 <i>m</i> (72)	80 <i>s</i> (69) 77 <i>m</i> (72)	76 <i>m</i>	86 <i>s</i> (62)			
	Lattice vibrations	49 <i>c</i> (62)						

Notes: ^aCryst (here and after) – crystalline state. ^bBands at 505–535 and 333–400 cm^{-1} were assigned to bonds vibration in ions of polysulfides sulfur. ^cThe band at 483 cm^{-1} was attributed simultaneously to stretching vibrations in S₈ and S₆. ^dBands at 451, 269 and 201 cm^{-1} were assigned to bonds vibration in S₆. ^eBand at 237 cm^{-1} was attributed simultaneously to stretching vibrations in S₈ and S₇.

The polarization measurements showed (71) that the vibrations in the Raman spectra of rhombic sulfur corresponded to the bands at 474 [*v*, *a*₁ + *e*₂], 438 (*v*, *e*₃), 248 (δ , *e*₃), 216 (δ , *a*₁), 152 (δ , *e*₂) and 84 (τ , *e*₂) cm^{-1} (Table 2). One should note that the authors (72), describing similar Raman spectra, pointed to doublet structure of all the bands, which may be explained in terms of crystal-field effects of rhombic S₈ (Table 2). The peaks of the corresponding doublets were observed at 474 and 470, 441 and 434, 252 and 247, 218 and 215, 151 and 147, 86 and 82 cm^{-1} (72). The peak centered at 188 cm^{-1} was presumably the Raman-forbidden *b*₁ fundamental appearing in violation of selection rules (72).

In Table 2 (69, 72) is shown the Raman spectrum of molten sulfur (122 °C), where (as opposed to Raman spectrum of rhombic sulfur, measured at 25 °C), changes in line width, relative intensity as well as erasing the doublet structure (except for the band of e_3 species with peaks at 441 and 434 cm^{-1}) occur (72).

The Raman spectra of elemental sulfur, measured at 258 °C showed three broad bands at 474 (ν), 218 (δ) and 151 (δ) cm^{-1} , where the intensity of bending vibrations decreased drastically as compared with the spectra obtained at 122 °C (72).

The works (68, 69) dealt with Raman spectra of saturated sulfur vapors obtained at 180 °C (Table 2). In these spectra, in the authors' opinion (68, 69), appeared the bands corresponding to the S–S bond's vibration not only in S_8 , but also in S_7 и S_6 species that were likely to be formed due to rhombic sulfur thermolysis (49). So, the weak bands at 445 and 451 cm^{-1} were associated with S–S stretching vibration in S_8 (e_3) and S_6 species, whereas the strong band at 483 cm^{-1} was assigned to the S–S stretching vibrations ($a_1 + e_2$) in S_8 and S_6 molecules (Table 2). The strongest bands observed at 218 and 237 cm^{-1} were attributed to the bending vibration in S_8 and S_7 species, respectively. In its turn, the band at 269 cm^{-1} was assigned to the ring bending in S_6 molecule (68, 69). The authors pointed out (68, 69) that three bands at 218, 237 and 269 cm^{-1} may be associated with a ring bending of the species S_8 , S_7 and S_6 , respectively, in which the rise to higher frequency was in the order expected for decreasing ring size and increasing ring strain (Figure 1a,b,d).

The Raman spectra of rhombic sulfur dissolved in CS_2 , documented in (62, 69, 70), showed two bands at 437–475 cm^{-1} assigned to S–S bonds stretching vibrations, whereas bending vibrations were presented as three bands in the region of 151–245 cm^{-1} (Table 2). It was reported (62) on strong depolarized band at 86 cm^{-1} assigned to torsion vibration of e_2 -mode. At the same time, the bands observed in Raman spectra of S_8 dissolved in CS_2 (62, 69, 70) showed a slight high-frequency shift (by 2–5 cm^{-1}) as compared with the similar bands appearing in the Raman spectrum of rhombic crystalline S_8 , obtained at 25 °C (62, 70–72).

Interestingly, the Raman spectra of rhombic sulfur solution in CS_2 investigated in (62, 69, 70) were inconsistent with the Raman spectra of S_8 dissolved in amines (methylamine, propylamine, ethylenediamine), where the bands corresponding to bending vibrations at 150–250 cm^{-1} disappeared, while they were observed in the region of 505–535 and 333–400 cm^{-1} (Table 2) (70). It was the authors' opinion (70) that these bands were associated with bond vibrations in ions of polysulfide sulfur, for example, S_3^- , formed due to the reaction of elemental sulfur with amines. The fact that primary amines, possessing high basicity, activated readily sulfur and could react with it to furnish, in particular, polysulfide ions, was also reported (49).

2.1.2. IR absorption spectra of S_8

The IR spectra of crystalline and rhombic sulfur and its solution were investigated in (61, 62, 66, 74, 75). The results obtained are shown in Table 3. According to the papers (61, 62, 66), the stretching vibrations of the S–S bonds in crystalline S_8 were observed at 465 (s , e_1) and 435 (w , e_3) cm^{-1} (Table 3) that correlated well with the above-given Raman spectra (Table 2). At the same time, it should be stressed that the authors (66) presented another two bands of the S–S band stretching vibrations at 520 and 532 cm^{-1} (Table 3), which, as stated above, were not assigned to S_8 (Table 1).

The paper (75) covered only the far region of the IR spectra of crystalline S_8 , where the strong band at 239 cm^{-1} was observed. Besides, the authors described the doublet with peaks at 186 and 197 cm^{-1} assigned to bending vibrations (Table 3). It was also reported (but not discussed) on a weak absorption band at 290 cm^{-1} (Table 3) (75), which was not mentioned in the works (61–63, 67) (Table 1).

Table 3. IR absorption spectra of rhombic sulfur (cm^{-1}).

Assignment	Vibration	Frequencies of S_8		
		Crystalline	Solution S_8	
			CS_2	C_6H_6
1	2	3	3	5
b_1	ν	532 (66) ^a		
e_3	ν	520 (66) ^a		
e_1	ν	465 s (61, 62, 66)	471 m (62)	471 m (62)
e_3	ν	435 w (61, 62, 66)		
		290 w (75)	300 w (75)	
b_2	δ		243 s (62)	243 s (62)
e_1	δ	239 s (75)	239 s (75)	
b_2	δ		186 s (75)	
a_1	τ	214 m (75)		
e_2	δ	197 m, 186 s (75)		
e_1	τ		191 s (62)	191 s (62)

Note: ^aAbsorption bands at 520 and 532 cm^{-1} given in (66) are not related to vibrations in S_8 species.

According to the paper (62), the spectra of these solutions contained a medium-intensity stretching vibration band of the S–S bond at 471 (e_1) cm^{-1} as well as two strong absorption bands of bending and torsion vibrations at 243 (b_2) and 191 (e_1) cm^{-1} , respectively (Table 3). From the data of theoretical analysis of normal vibrations of S_8 molecule followed that these bands were active (62). Besides, it was suggested (62, 75) that the IR spectrum of S_8 dissolved in CS_2 showed the weak bands at 500–1000 cm^{-1} , which corresponded to combination vibrations.

One should bear in mind that the authors (75) describing the IR spectra of S_8 dissolved in CS_2 , listed a weak-absorption band at 300 cm^{-1} (the assignment, however, was not discussed) as well as the strong bands of sulfur bending vibration at 239 (e_1) and 186 (b_2) cm^{-1} (Table 3). Nevertheless, symmetry species for the first band and assignment and symmetry species for the second band were inconsistent with the data given in the paper (62). The latter was reciprocated and cited by many authors (63, 67) as a fundamental work in the interpretation of vibrational spectra of elemental sulfur.

2.2. Vibrational spectra of S_6 and S_{12}

Let us consider the vibrational spectra of two relatively stable molecular forms of sulfur – S_6 and S_{12} , with similar symmetry mode D_{3d} . Cyclic structure of these molecules is given in Figure 1b,d.

To calculate vibrational spectra of S_6 , the valence force fields as well as the modified Urey–Bradley force constants were used. At the same time, the force constants of S_8 taking into account, however, the geometry of S_6 (63, 76–78) were employed as zero approximation. In the result, the force constants for stretching and bending vibrations of S_8 and S_6 turned out to be almost equivalent. The only exception was the constants calculated for torsion mode that were 16% higher for S_6 than for S_8 (77). It was also shown (63, 76, 77) that the transfer of force constants, used for the calculations of basic vibrations of S_8 to S_6 species gave quite reasonable calculated frequency values that got fair agreement with the values observed (Table 4). But the same cannot be said of the results reported in (78): the calculated frequencies of some stretching, bending and torsion vibrations did not accord with the observed data (Table 4).

Table 4. Observed and calculated vibrational spectra of S₆ (cm⁻¹)^a.

Symmetry	Vibration	Observed frequencies				Calculated frequencies	
		Raman		IR		(63)	(78)
		Cryst. S ₆	Cryst. in CS ₂	Cryst. S ₆	Solution in CS ₂		
1	2	3	4	5	6	7	8
<i>a</i> _{1g}	<i>ν</i>	471 <i>vs</i> (76) 471 (78) 471 <i>vs</i> (79)	476 <i>m</i> (76) 478 (78)			477	501
<i>e</i> _u	<i>ν</i>	461 <i>w</i> (79)		463 <i>s</i> (76) 462 (78)	462 <i>s</i> (76)	462	476
<i>e</i> _g	<i>ν</i>	448 <i>s</i> (76) 449 (78) 451 <i>s</i> (79)	451 <i>w</i> (76) 450 (78)			451	425
<i>a</i> _{1u}	<i>ν</i>			390 <i>vw</i> (76)		390	386
<i>a</i> _{2u}	<i>δ</i>			313 <i>s</i> (76) 312 (78)	312 <i>s</i> (76)	312	312
<i>a</i> _{1g}	<i>δ</i>	262 <i>s</i> (76) 264 (78) 266 <i>s</i> (79)	266 <i>w</i> (76) 264 (78)			265	240
<i>e</i> _g	<i>δ</i>	202 <i>s</i> (76) 203 (78) 203 <i>s</i> (79)	204 <i>w</i> (76) 201 (78)			203	204
<i>e</i> _u	<i>δ</i>	106 <i>w</i> (79) 84 <i>s</i> (79) 79 (79)		180 <i>s</i> (76)		180	155

Note: ^aIn the works (76, 78) vibrational spectra of S₆ in crystalline state as well as in CS₂ solution were recorded at 25°C; in the paper (79) the Raman spectrum of crystalline S₆ was recorded at -90°C.

2.2.1. Raman spectra of S₆

In the Raman spectra of S₆ crystalline molecule, measured at room temperature, the strong bands at 471 and ~448 cm⁻¹ (76, 78) were assigned to stretching vibrations of the S–S bonds, while the strong bands at 162–266 and ~202 cm⁻¹ corresponded to bending vibrations (Table 4) (76, 78). In an analogous Raman spectrum, recorded at -90°C, the bands at 471 (*s*, *a*_{1g}), 461 (*w*, *e*_u) and 451 cm⁻¹ (*s*, *e*_g) were assigned to stretching vibrations, and the bands at 266 (*s*, *a*_{1g}) and 203 (*s*, *e*_g) were attributed to bending type motions (Table 4) (63). In both Raman spectra of S₆ molecule, a weak band at 106, a medium band at 84 and a strong band at 79 cm⁻¹ corresponded to the lattice vibration of the crystal (Table 4) (63, 76).

Raman spectra of S₆ molecule dissolved in CS₂ showed that stretching and bending bands were slightly shifted (by ~1–7 cm⁻¹) to the high-frequency region (as compared with those of crystalline sulfur S₆) and appeared at 476–478, ~450, 264–266 and 201–204 cm⁻¹ (Table 4).

2.2.2. IR absorption spectra of S₆

In IR spectra of crystalline sulfur S₆, a strong absorption band at 463 cm⁻¹ (*e*_g) and a very weak band at 390 cm⁻¹ (*a*_{2u}) were assigned to the stretching vibrations of S–S bond (76, 78). Strong

absorption bands at ~ 312 and 180 cm^{-1} were attributed to the bending and torsion vibrations, respectively (76, 78).

The IR spectrum of S_6 molecule dissolved in CS_2 as well as the IR spectrum of solid S_6 , contained strong absorption bands of stretching vibrations of the S–S bond at 462 cm^{-1} and bending vibrations at 312 cm^{-1} (76, 78), whereas a very weak band of stretching vibrations at 390 cm^{-1} and a strong band of torsion vibrations at 180 cm^{-1} were absent (Table 4).

In the papers (63, 80, 81) were given the observed and calculated frequencies of vibrational spectra of S_{12} molecule, as well as symmetry and vibration assignments (Table 5). The studies showed that the stretching vibrations of the S–S bond were observed at $405\text{--}480\text{ cm}^{-1}$, bending vibrations appeared at $115\text{--}290\text{ cm}^{-1}$, and torsion vibrations were presented in the region of $45\text{--}100\text{ cm}^{-1}$.

Theoretical analysis of vibrational spectra of S_{12} was performed using the valence force field as well as a modified Urey–Bradley force field (63, 80, 81). Interestingly, when force constants of S_8 , recalculated taking into account the geometrical data of S_{12} , were applied to the calculations as zero approximation, the calculated and observed frequencies in S_{12} spectrum were in a good agreement (Table 5, columns 3, 4 and 5) (63, 81). In contrast, calculated frequencies of S_{12} with force field, where force constants as well as geometry of S_8 molecule were taken (62), differed (by as much as 35 cm^{-1}) from the observed frequencies (Table 5, columns 3 and 6) (81). As far as torsion frequencies of S_{12} molecule was concerned, the observed frequencies (80, 81) correlated to a great extent with the calculated values published in the manuscript (63) (Table 5, columns 3 and 4).

The potential energy distribution allowing one to evaluate the contribution of a specific coordinate (stretching, bending or torsion) to the corresponding vibration mode (ν , δ and τ) in S_{12} molecule was calculated (81).

Table 5. Observed and calculated frequencies of S_{12} (cm^{-1}).

Assignment	Vibration	Observed frequencies (81)	Calculated frequencies		
			(63)	(81) ^a	(81) ^b
1	2	3	4	5	6
a_{1g}	ν	459	459	454	465
a_{2u}	ν	465	465	464	463
e_g	ν	459	459	469	476
e_u	ν	465	465	464	463
a_{1u}	ν		464	464	446
e_g	ν	447	447	448	444
e_u	ν	425	425	423	419
a_{2g}	ν		410	410	405
a_{1g}	δ	288	288	278	253
a_{2u}	δ	266	266		247
e_u	δ	253	253	256	235
e_g	δ	243	243	245	226
e_g	δ	177	177	189	187
a_{1u}	δ		158	158	166
e_u	δ	165	165	167	161
a_{1g}	δ	128	128	118	120
a_{2g}	τ		85	85	101
a_{2u}	τ	72	72	48	93
e_u	τ	62	62	49	57
e_g	τ	51	51	47	56

Notes: ^aCalculated using force constants of S_8 taking into account geometry data of S_{12} . ^bCalculated using geometry data and force constants of S_8 .

2.2.3. Raman spectra of S_{12}

In the Raman spectra of solid S_{12} , the strong line at 459 and medium intense line at 447 cm^{-1} were assigned to the stretching vibrations of the S–S bond, whereas weak bands at 288, 243, 177 cm^{-1} and a very weak band at 128 cm^{-1} corresponded to bending vibrations; torsion vibrations appeared at 51 cm^{-1} (Table 6) (50, 51, 80, 81). The lines at 67, 43 and 32 cm^{-1} , as postulated in (50, 51, 80, 81) were assigned to lattice vibrations. In Raman spectra, there were some weak lines at 237, 180, 169 and 155 cm^{-1} , which were interpreted as combination vibrations.

2.2.4. IR absorption spectra of S_{12}

In the IR spectrum of crystalline S_{12} were detected the following absorption bands (cm^{-1}): 465 ($m, \nu, a_{2u} + e_u$), 425 ($\nu w, \nu, e_u$), 266 ($\nu w, \delta, a_{2u}$), 253 ($\nu w, \delta, e_u$), 165 ($\nu w, \delta, e_u$), 72 (m, τ, a_{2u}), 62 (m, τ, e_u) (Table 6) (80, 81). The assignments and intensities of vibrational frequencies, observed in the Raman and IR spectra of S_{12} molecule, did not coincide (Table 6), which was the known fact for the molecules showing high symmetry (32).

2.3. Vibrational spectra of S_7

The works (50, 63, 82–84) were dedicated to the analysis of observed and calculated spectra of allotropic modification of sulfur, S_7 . Assuming C_s , molecular point group of symmetry of the latter, the 15 fundamentals of the discrete molecule transformed as $8a'$ and $7a''$ modes (63, 82, 83) (Table 7). In addition, the vibrational spectra of four allotropes of cycloheptasulfur, α -, β -, γ - and δ - S_7 , were reported (83).

Table 6. Observed Raman and IR spectra of crystalline S_{12} (cm^{-1}).

Assignment	Vibration	Raman (80, 81)	IR (80, 81)
1	2	3	4
$a_{2u} + e_u$	ν	463 ^a νw	465 m
$a_{1g} + e_g$	ν	459 s	
e_g	ν	447 m	
e_u	ν		425 νw
a_{1g}	δ	288 w	
a_{2u}	δ		266 νs
e_u	δ		253 νs
e_g	δ	243 w	
		237 w	
		219 ^a νw	
		180 νw	
e_g	δ	177 m	
		169 w	
e_u	δ		165 νs
		155 νw	
a_{1g}	δ	128 νs	
a_{2u}	τ		72 m
Lattice vibrations		67 s	
e_u			62 m
e_g	τ	51 m	
Lattice vibrations		43 νs	
Lattice vibrations		32 νs	

Note: ^aBands were assigned to vibrations in S_8 molecule (80, 81).

Table 7. Observed and calculated vibrational spectra of S_7 (cm^{-1}).

Assignment	Vibration	Observed frequencies		Calculated frequencies				
		(82)	(83)	(83)	(63)	(82) ^a	(82) ^b	(82) ^c
1	2	3	4	5	6	7	8	9
a'	ν	517	518	521	517	603	481	530
a''	ν	510	527	529	510	602	457	516
a'	ν	483	480	477	483	543	468	512
a''	ν	477	460	464	477	552	425	485
a'	ν	402	400	403	402	484	454	471
a''	ν	397	396	393	397	449	422	448
a'	ν	362	360	360	362	405	424	443
a''	δ	288	285	280	288	266	268	288
a'	δ	268	270	273	268	275	276	280
a''	τ	242	239	244	242	225	228	266
a'	δ	236	239	238	236	229	226	264
a''	δ	193	185	190	193	140	141	159
a'	δ	184	195	193	184	135	133	156
a''	τ	155	147	142	153	103	193	152
a'	δ	145	155	153	145	128	114	117

Notes: ^aCalculated using incorrect data of S_7 geometry. ^bForce field, calculated in (61) for S_8 was used incorrectly. ^cForce field, calculated in (62) for S_8 was used incorrectly.

The theoretical analysis of vibrational spectra was carried out using the valence force field as well as an extended Urey–Bradley force field (63, 82, 83).

Vibrational spectra of S_7 , described in (63), were calculated using a force field and taking into consideration the fact that S_7 was a chair-like cycle with the S–S bond distances ranging from 1.71 to 2.17 Å (Figure 1c). The results provided a fair agreement between the calculated (63) and observed frequencies of S_7 (82, 83).

Furthermore, the authors (83) calculated force constants for S_7 molecule, using the force field applied to S_8 molecule (62) as well as geometry data obtained in (85, 98) for γ - and δ - S_7 with the help of X-ray structure analysis. The latter showed that the S–S bond distances in δ - S_7 changed from 1.996 to 2.179 Å, while bending and torsion angles were 102.2–107.1° and 1.1–107.5°, respectively (85, 98). These calculations resulted in a good agreement between calculated and observed frequencies of vibrational spectra of the S_7 molecule (Table 7). From Table 7, it can be seen that the bands at 360–530 cm^{-1} were assigned to stretching vibrations of the S–S bond in S_7 , the bands at 145–290 cm^{-1} corresponded to bending vibrations, and bands at 147–155 and 239–242 cm^{-1} were interpreted as torsion motions (63, 83).

At the same time in (82), there were differences in values of the calculated and observed frequencies in the vibrational spectrum of the S_7 molecule (Table 7). Obviously, the reason was that the authors tried to calculate the force constants using incorrect S–S bond distances in the S_7 molecule assuming that the latter were identical and equal to 2.17 Å (82). Another reason was in incorrect application of the force field calculated for S_8 in (61) and (62).

2.3.1. Raman spectra of S_7

Let us consider Raman spectra of solid sulfur S_7 and its allotropes (α -, β -, γ - and δ - S_7), recorded at room temperature (82) and at -100°C (83). The lines at 355–530 cm^{-1} were assigned to stretching vibrations of the S–S bond in all aforementioned molecules, while the bending vibrations were presented in the region of 145–285 cm^{-1} . The lines at ~ 242 and 145–155 cm^{-1} were attributed to the torsion motions, and the lines at 19–95 cm^{-1} were believed to be the lattice modes (Table 8) (82, 83). In addition, the Raman spectra of four allotropes, α -, β -, γ - и δ - S_7 , showed typical

Table 8. Raman spectra of S₇ (cm⁻¹).

Assignment	Symmetry	Observed frequencies of S ₇					Solution in CS ₂
		Cryst. S ₇ ^a (82)	Allotropes of S ₇ ^b (83)				
			α -S ₇	β -S ₇	γ -S ₇	δ -S ₇	
1	2	3	4	5	6	7	8
<i>a</i> ''	ν		530 <i>w</i>	528 <i>w</i>	523 <i>w</i>	527 <i>w</i>	
<i>a</i> '	ν	519 <i>m</i>	518 <i>s</i>	518 <i>s</i>	510 <i>m</i> ^b	518 <i>m</i>	517 <i>m</i> (82)
			514 <i>sh</i>	511 <i>sh</i>		510 <i>sh</i>	520 <i>m</i> , 515 <i>sh</i> (83)
<i>a</i> ''	ν	516 <i>sh</i>					510 <i>sh</i> (82)
<i>a</i> '	ν	481 <i>vs</i>	481 <i>vs</i>	480 <i>vs</i>	481 <i>s</i>	480 <i>s</i>	483 <i>s</i> (82)
							485 <i>s</i> (83)
<i>a</i> ''	ν	477 <i>sh</i>	459 <i>m</i>	459 <i>m</i>	459 <i>w</i>	460 <i>w</i>	462 <i>w</i> (83)
			420 <i>w</i>	420 <i>w</i>	420 <i>w</i>	419 <i>w</i>	
	ν	403 <i>vs</i>	400 <i>vs</i>	400 <i>vs</i>	400 <i>s</i>	400 <i>vs</i>	402 <i>m</i> (82)
							402 <i>m</i> (83)
<i>a</i> ''	ν	397 <i>sh</i>		395 <i>sh</i>		396 <i>sh</i>	
<i>a</i> '	ν			362 <i>s</i>	364 <i>s</i>	363 <i>m</i>	362 <i>s</i> (82)
							362 <i>s</i> (83)
<i>a</i> '	ν	356 <i>s</i>	355 <i>s</i>	358 <i>s</i>		358 <i>s</i>	
					292 <i>w</i>		
<i>a</i> ''	δ	285 <i>w</i>	285 <i>m</i>	285 <i>m</i>	285 <i>m</i>	285 <i>w</i>	288 <i>w</i> (82)
							289 <i>w</i> (83)
<i>a</i> '	δ	270 <i>w</i>	270 <i>m</i>	270 <i>m</i>	270 <i>m</i>	270 <i>w</i>	268 <i>w</i> (82)
							274 <i>w</i> (83)
<i>a</i> ' + <i>a</i> ''	τ	242 <i>sh</i>	241 <i>sh</i>		242 <i>vs</i>		
<i>a</i> ' + <i>a</i> ''	δ	238 <i>vs</i>	239 <i>s</i>	239 <i>vs</i>	237 <i>sh</i>	239 <i>s</i>	236 <i>vs</i> (82)
							238 <i>vs</i> (83)
<i>a</i> '	δ	184 <i>s</i>			199 <i>w</i>	201 <i>w</i>	
<i>a</i> ''	δ		185 <i>m</i>	185 <i>m</i>		185 <i>m</i>	174 <i>m</i> (83)
<i>a</i> ''	δ		180 <i>m</i>	182 <i>sh</i>	178 <i>m</i>		
					159 <i>m</i>		
<i>a</i> '	δ	145 <i>w</i>	157 <i>m</i>	155 <i>m</i>	151 <i>s</i>	155 <i>m</i>	
			150 <i>m</i>			150 <i>w</i>	
<i>a</i> ''	<i>t</i>	155 <i>s</i>	145 <i>m</i>	146 <i>m</i>	143 <i>sh</i>	147 <i>w</i>	153 <i>s</i> (82)
		90 <i>sh</i>	95 <i>m</i>	93 <i>m</i>	85 <i>s</i>	93 <i>m</i>	
			79 <i>vs</i>	80 <i>vs</i>	79 <i>s</i>	80 <i>vs</i>	
		76 <i>vs</i>		75 <i>sh</i>	71 <i>m</i>	75 <i>m</i>	
				68 <i>m</i>	62 <i>vs</i>	68 <i>m</i>	
		54 <i>vs</i>	57 <i>vs</i>	60 <i>vs</i>	59 <i>vs</i>	60 <i>m</i>	
		50 <i>vs</i>	52 <i>vs</i>	55 <i>s</i>	54 <i>vs</i>	56 <i>m</i>	
				47 <i>m</i>	49 <i>vs</i>	50 <i>m</i>	
			41 <i>m</i>	39 <i>m</i>	39 <i>m</i>	40 <i>m</i>	
			33 <i>m</i>	33 <i>m</i>		33 <i>w</i>	
				19 <i>m</i>		20 <i>m</i>	

Notes: ^aThe spectra of S₇ in crystalline state and in CS₂ solution were recorded at 20°C. ^bThe spectra of allotropes of S₇ were obtained at -100°C.

lines of stretching vibrations of the S-S bond at 530, 528, 523 and 527 cm⁻¹ (83), whereas in the spectrum of crystalline sulfur S₇ these lines were not observed (82).

In the paper (82), there were made the following assignments of vibration modes and symmetry species in the Raman spectra of crystalline sulfur S₇ (cm⁻¹): 519 (*m*, ν , *a*'), 516 (*m*, ν , *a*''), 481 (*vs*, ν , *a*'), 477 (*sh*, ν , *a*''), 403 (*vs*, ν , *a*'), 397 (*sh*, ν , *a*''), 356 (*s*, ν , *a*'), 285 (*w*, δ , *a*''), 270 (*w*, δ , *a*'), 242 (*sh*, τ , *a*' + *a*''), 238 (*vs*, δ , *a*' + *a*''), 184 (*s*, δ , *a*'), 145 (*w*, δ , *a*'), 155 (*s*, τ , *a*''), 90 (*w*, *sh*), 76 (*vs*), 54 (*vs*), 50 (*vs*) (Table 8). As mentioned above (Table 2), the intensive polarized band at 237 cm⁻¹ in the Raman spectra of elemental sulfur vapors, recorded at 180°C, was (68, 69) also attributed to bending vibrations in S₇ molecule.

In α -, β - и δ -S₇ allotropes, the strong line of stretching vibration of the a' -mode was observed at 518 with a shoulder in the region of 510–514 cm⁻¹, whereas for γ -S₇ allotrope it was presented by wide band at 510 cm⁻¹ (Table 8) (83). At 400–480 cm⁻¹, the Raman spectra of α -, β -, γ - and δ -S₇ allotropes were almost identical: they contained four lines of stretching vibrations at \sim 480, 459, 420 and 400 cm⁻¹. Notably, in the spectra of β - and δ -S₇ allotropes the latter line had a shoulder at \sim 395 cm⁻¹. At the same time, in the Raman spectra of crystalline S₇, as shown above, instead of four lines were observed only two very strong bands at 481 and 403 cm⁻¹, having shoulders at 477 and 397 cm⁻¹, respectively (82). It should be remarked that the strong lines of stretching vibrations at 362, 364 and 363 cm⁻¹ were characteristic of only β -, γ - and δ -S₇ allotropes, whereas lines at 355–358 cm⁻¹ were presented in the Raman spectra of both α -, β -, δ -S₇ allotropes and crystalline sulfur S₇ (Table 8).

In the Raman spectra of α -, β -, γ - and δ -S₇ allotropes, the bands at 285 and 270 cm⁻¹ as well as the lines in the region of 151–200 cm⁻¹ (Table 8) were assigned to the bending vibrations (83). Besides, the spectra of α -, β - and δ -S₇ allotropes showed a strong line at 239 cm⁻¹ (Table 8).

The lines at 157, 155, 151 and 155 cm⁻¹ belonged to torsion modes of α -, β -, γ - and δ -S₇ allotropes, respectively (Table 8) (83). In addition, in the spectrum of γ -S₇ allotrope presented an intensive line of torsion mode at 242 cm⁻¹ with a shoulder at 237 cm⁻¹. This shoulder was assigned (83) to the bending vibration of $a' + a''$ -mode. On the other hand, the line of torsion vibration of $a' + a''$ -mode, observed as shoulder at 241 cm⁻¹ on a line of bending vibration (239 cm⁻¹), was presented only in the Raman spectrum of α -S₇ allotrope (Table 8) (83).

A number of weak bands in Raman spectra of α -, β -, γ - and δ -S₇ allotropes at \sim 420, 292, 159, 150 cm⁻¹ corresponded to the combination vibrations (83), and the lines in the region of 20–95 cm⁻¹ were attributed to the lattice vibrations. Significant differences observed in the Raman spectra of α -, β -, γ - and δ -S₇ allotropes as well as crystalline sulfur below 100 cm⁻¹ were likely due to the character of molecules packaging in these structures (82, 83).

In the Raman spectra of S₇ dissolved in CS₂, measured at room temperature, the lines were presented at 153–520 cm⁻¹ (Table 8) (82, 83). Basically, these spectra were in a good agreement with the spectra of crystalline sulfur S₇ (Table 8). For example, in the Raman spectra of S₇ dissolved in CS₂, stretching vibrations of the S–S-bonds were observed at 360–520 cm⁻¹, bending vibrations were presented at 175–290 cm⁻¹ and torsion modes were attributed to a band at 153 cm⁻¹ (Table 8). It must be emphasized that these data given in (82, 83) were in close agreement with each other, except for some lines. So, the authors (82) did not report the lines at 462 and 174 cm⁻¹ (82), whereas in the work (83) the line at 153 cm⁻¹ was not documented (83).

2.3.2. IR absorption spectra of S₇

The IR absorption spectra of crystalline S₇, recorded at room temperature (50) and at 30 °C (83) as well as in CS₂ solution (83) are given in Table 9.

Stretching vibrations of the S–S bond in the IR spectra of solid S₇ were observed at 357–526 cm⁻¹, bending vibrations – in the region of 146–282 cm⁻¹, and torsion mode corresponded to the vibration band at 146 cm⁻¹ (Table 9). These values almost coincided with those found in the Raman spectrum of this molecule (Table 8). It should also be remarked that the values of the IR spectra of crystalline S₇, reported in (82) and (83), were in good conformity with each other, apart from the absorption band at 146 cm⁻¹, which was assigned (50) to bending vibration of a' -mode (Table 9), and later (51) was attributed to torsion vibration of a'' -mode.

In the IR spectra of S₇ dissolved in CS₂, the absorption bands at 518, 482 and 463 cm⁻¹ were assigned to stretching vibrations of the S–S bond, and bands at 195–290 cm⁻¹ corresponded to bending vibrations (Table 9) (83). Absorption bands of stretching (463 cm⁻¹) and bending

Table 9. IR absorption spectra of S₇ (cm⁻¹).

Assignment	Vibration	Observed frequencies	
		Solid S ₇ ^a	Solution S ₇ in CS ₂ (83) ^b
1	2	3	4
<i>a''</i>	ν	526 <i>sh</i> (83)	
<i>a'</i>	ν	518 <i>m</i> (82)	518 <i>vs</i>
		513 <i>vs</i> (83)	
<i>a''</i>	ν	515 <i>m</i> (82)	
<i>a'</i>	ν	482 <i>s</i> (82)	482 <i>m</i>
		480 <i>s</i> (83)	
<i>a''</i>	ν	476 <i>sh</i> (82)	463 <i>s</i>
		461 <i>m</i> (83)	
<i>a'</i>	ν	402 <i>s</i> (82)	
		400 <i>vs</i> (83)	
<i>a''</i>	ν	396 <i>sh</i> (82)	
<i>a'</i>	ν	360 <i>sh</i> (82)	
		357 <i>vw</i> (83)	
<i>a''</i>	δ	282 <i>sh</i> (83)	288 <i>vw</i>
<i>a'</i>	δ	274 <i>vs</i> (82)	270 <i>s</i>
		270 <i>vs</i> (83)	
<i>a'</i>	δ	239 <i>vs</i> (82)	236 <i>s</i>
		235 <i>s</i> (83)	
<i>a''</i>	δ	197 <i>m</i> (82)	195 <i>m</i>
		194 <i>m</i> (83)	
<i>a''</i>	δ	193 <i>m</i> (82)	
		180 <i>m</i> (83)	
<i>a'</i>	δ	146 <i>m</i> (82)	
<i>a''</i>	τ	146 <i>m</i> (83)	

Notes: ^aSpectra of solid S₇ were recorded at 22–30°C. ^bSpectra of S₇ dissolved in CS₂ were recorded at room temperature.

(270 cm⁻¹) vibrations in the IR spectrum were intense (Table 9), whereas in the Raman spectrum the lines at 462 and 288 cm⁻¹ corresponding to these vibration modes were of low intensity (Table 9) (83).

2.4. Vibrational spectra of S₉

The Raman spectra of solid S₉ revealed that this compound crystallized as two allotropes, termed α -S₉ and β -S₉ (50, 51, 87, 88). The crystal and molecular structures of α -S₉ were determined by X-ray diffraction on single crystals (88). The molecular symmetry was C₂ but the site was C₁. In the Raman spectra of these molecules, the lines at 414–485 cm⁻¹ should be assigned to stretching vibrations, lines at 151–300 cm⁻¹ belonged to bending vibrations, while lines observed in the region below 100 cm⁻¹ were attributed to bending, torsion and lattice modes (50, 51, 88) (Table 10). The assignment to specific types of vibrations in the region below 100 cm⁻¹ was not done in the works (50, 51, 88) (Table 10).

2.5. Vibrational spectra of S₁₀

In the monoclinic crystals of *cyclo*-decasulfur, the molecules occupied sites of C₂ symmetry, although the molecular symmetry was close to D₂ (89, 90). Vibrational spectra of cyclic S₁₀ were poorly understood both chemically and spectrally (50, 79, 89). Theoretical calculations of vibrational spectra of the aforementioned sulfur allotrope S₁₀ were also lacking in the literature.

Table 10. Observed Raman spectra of α -S₉ and β -S₉ (cm⁻¹).

Vibration	α -S ₉ (50, 51) ^a	α -S ₉ (50, 51, 88) ^b	β -S ₉ (88) ^b
ν		485 <i>m</i>	483 <i>m</i>
ν	477 <i>m</i>	477 <i>m</i>	476 <i>m</i>
ν		463 <i>sh</i>	460 <i>s</i>
ν	456 <i>s</i>	454 <i>s</i>	454 <i>s</i>
ν		442 <i>sh</i>	440 <i>sh</i>
ν	437 <i>s</i>	436 <i>s</i>	437 <i>s</i>
ν	417 <i>m</i>	416 <i>m</i>	414 <i>m</i>
δ	298.5 <i>m</i>	297 <i>m</i>	300 <i>m</i>
δ	257 <i>m</i>	256 <i>m</i>	251 <i>sh</i>
δ	245 <i>m</i>	245 <i>m</i>	248 <i>m</i>
δ		222 <i>m</i>	224 <i>m</i>
δ	219 <i>m</i>	215 <i>m</i>	218 <i>m</i>
δ	186 <i>s</i>	188 <i>s</i>	181 <i>s</i>
δ		181 <i>sh</i>	
δ	160.5 <i>s</i>	161 <i>s</i>	167 <i>m</i>
δ	157 <i>m</i>	155 <i>m</i>	153 <i>m</i>
δ		151 <i>sh</i>	
		117 <i>m</i>	114 <i>s</i>
		111 <i>sh</i>	
	105.5 <i>s</i>	104 <i>s</i>	104 <i>sh</i>
		100 <i>sh</i>	84 <i>s</i>
	80 <i>s</i>	78 <i>s</i>	71 <i>m</i>
		57 <i>s</i>	61 <i>m</i>
		46 <i>m</i>	59 <i>sh</i>
		43 <i>sh</i>	47 <i>m</i>
		41 <i>sh</i>	44 <i>sh</i>
		27 <i>m</i>	33 <i>s</i>

Notes: ^aSpectra of α -S₉ were recorded at room temperature. ^bSpectra of β -S₉ were recorded at -100°C.

Interestingly, S₁₀ was constituent of another allotrope of composition S₆·S₁₀ in which the layers of S₆ and S₁₀ molecules alternated with each other (89). The vibrational spectra of S₆·S₁₀ crystals were practically a superimposition of the spectra of the two components (50, 79, 89). The full-vibrational spectra and assignment of S₁₀ and S₆·S₁₀ are given in Table 11 (50, 79, 89). In vibrational spectra of adduct S₆·S₁₀, the lines of bending vibrations (a_g and e_g) were cleaved into two lines at 272 and 265 cm⁻¹ and 207 and 201 cm⁻¹, that was indicative of the presence of two rings S₆ and S₁₀ in S₆·S₁₀ (79).

2.5.1. Raman spectra of S₁₀

In the Raman spectra of these molecules (S₁₀ and S₆·S₁₀), lines at 400–495 cm⁻¹ should be assigned to stretching vibrations, lines at 130–272 cm⁻¹ belonged to bending vibrations, while lines observed in the region below 100 cm⁻¹ were attributed to torsion mode (50, 79, 89) (Table 11).

2.5.2. IR absorption spectra of S₁₀

The IR spectrum of the S₁₀ molecule contained the following absorption bands: 482 (w, ν), 456 ($\nu w, \nu$), 244 (sh, δ), 239 ($\nu s, \delta$), 226 (sh, δ), 220 (s, δ), 204 (m, δ) (50, 79, 94) (Table 11). In the IR spectra of S₆·S₁₀, crystals were practically a superimposition of the spectra of the two components S₆ (50, 76) and S₁₀ (50, 79, 89) (Table 11).

Table 11. Vibrational spectra of S₁₀ and S₆·S₁₀ (cm⁻¹).

Vibration	S ₁₀ (50, 79, 89)		S ₆ ·S ₁₀ (50, 79, 89)	
	Raman ^a	IR ^a	Raman ^a	IR ^a
1	2	3	4	5
ν	495 <i>w</i>			
ν	487 <i>m</i>	482 <i>w</i>	489 <i>w</i>	483 <i>w</i>
ν	481 <i>sh</i>		479 <i>s</i>	
ν	469 <i>s</i>		466 <i>s</i>	
	466 <i>sh</i>		461 <i>sh</i>	
ν		456 <i>vw</i>	455 <i>sh</i>	461 <i>vs</i>
ν			451 <i>m</i>	
ν	425 <i>m</i>		428 <i>m</i>	
ν	403 <i>w</i>		408 <i>w</i>	
δ				310 <i>m</i>
δ			272 <i>s</i>	
δ	255 <i>w</i>		265 <i>w</i>	264 <i>vw</i>
δ	246 <i>sh</i>		249 <i>w</i>	264 <i>vw</i>
δ	243 <i>m</i>	244 <i>sh</i>	240 <i>m</i>	242 <i>vs</i>
		239 <i>vs</i>		240 <i>sh</i>
δ	231 <i>w</i>	226 <i>sh</i>	228 <i>w</i>	231 <i>sh</i>
δ		220 <i>s</i>	225 <i>w</i>	221 <i>m</i>
δ			207 <i>m</i>	211 <i>s</i>
δ		204 <i>m</i>	201 <i>m</i>	207 <i>sh</i>
δ	178 <i>m</i>		172 <i>m</i>	
δ	155 <i>w</i>		145 <i>w</i>	
δ	131 <i>m</i>		136 <i>m</i>	
	100 <i>m</i>		103 <i>m</i>	
	85 <i>m</i>			
	73 <i>vw</i>			
	51 <i>w</i>			
	39 <i>m</i>			
	29 <i>m</i>			

Notes: ^aRaman spectra of S₁₀ and S₆·S₁₀ were measured at -90°C; IR spectra of all sulfur modifications were recorded at 25°C.

2.6. Vibrational spectra of S₁₁ and S₁₃

Cyclo-undecasulfur S₁₁ and cyclo-tridecasulfur S₁₃ was first prepared in 1982, and molecular and crystal structures were determined by X-ray diffraction (91, 92). The S₁₁ and S₁₃ molecules were of C₂ symmetry but occupied the sites of C₁ symmetry. In Raman spectra of these molecules, the lines at 386–497 cm⁻¹ should be assigned to S–S stretching vibrations, the lines at 169–286 cm⁻¹ belonged to bending vibrations, while the lines observed in the region below 132 cm⁻¹ were attributed to torsion and lattice modes (50) and bending, torsion and lattice vibrations belong to 281 cm⁻¹ (50, 93, 94) (Table 12).

2.7. Vibrational spectra of S₁₄

Crystals of S₁₄ contained molecules of approximate C_s symmetry but occupied the sites of C₁ symmetry (95, 96). Their Raman spectra recorded at -100 °C and lines at 444–483 cm⁻¹ should be assigned to stretching vibrations, the bending, torsional and lattice modes were observed in the region below 270 cm⁻¹ (50, 95, 96) (Table 13).

Table 12. Observed Raman spectra of S₁₁ and S₁₃ at -100°C (cm^{-1}).

Vibration	S ₁₁ (93)	S ₁₃ (93)
ν		497 <i>m</i>
ν	480 <i>m</i>	480 <i>m</i>
ν	464 <i>s</i>	461 <i>s</i>
ν	442 <i>w</i>	440 <i>m</i>
ν	411 <i>m</i>	413 <i>w</i>
ν		386 <i>m</i>
δ	286 <i>w</i>	281 <i>m</i>
δ	266 <i>w</i>	263 <i>w</i>
δ	248 <i>w</i>	247 <i>m</i>
δ	221 <i>m</i>	222 <i>w</i>
δ	201 <i>w</i>	202 <i>m</i>
δ		191 <i>m</i>
δ	178 <i>s</i>	174 <i>s</i>
δ	169 <i>m</i>	162 <i>m</i>
	132 <i>m</i>	136 <i>m</i>
		122 <i>w</i>
	110 <i>sh</i>	
	102 <i>m</i>	102 <i>m</i>
	85 <i>sh</i>	
	71 <i>s</i>	
	53 <i>s</i>	
	42 <i>m</i>	
	33 <i>m</i>	

Table 13. Observed Raman spectra of S₁₄ at -100°C (cm^{-1}).

Vibration	S ₁₄ (50, 95, 96) 237
ν	483 <i>w</i>
ν	474 <i>w</i>
ν	468 <i>s</i>
ν	462 <i>sh</i>
ν	460 <i>s</i>
ν	453 <i>sh</i>
ν	447 <i>m</i>
ν	444 <i>m</i>
δ	270 <i>w</i>
δ	252 <i>w</i>
δ	243 <i>w</i>
δ	234 <i>m</i>
δ	212 <i>w</i>
δ	198 <i>m</i>
δ	189 <i>w</i>
δ	177 <i>m</i>
δ	163 <i>m</i>
δ	153 <i>m</i>
	128 <i>s</i>
	122 <i>w</i>
	90 <i>s</i>
	79 <i>m</i>
	69 <i>s</i>
	61 <i>s</i>
	57 <i>s</i>
	47 <i>s</i>
	34 <i>s</i>

2.8. Vibrational spectra of α -S₁₈, S₂₀

Vibrational spectra of cyclic α -S₁₈ and S₂₀ were less understood than that of S₈, S₆, S₇ and S₁₂, both chemically and spectrally (50, 51, 97). Theoretical calculations of vibrational spectra of the aforementioned sulfur allotropes were lacking in the literature.

At the same time, on the basis of data on vibrational spectra S₆–S₈ and S₁₂ molecules given above, we felt it worthwhile to interpret the vibrational spectra α -S₁₈, S₂₀ described in (51, 97) and made the corresponding assignments (Table 14).

2.8.1. Raman spectra of α -S₁₈, S₂₀

In Raman spectra of these molecules, the lines at 411–478 cm⁻¹ should be assigned to stretching vibrations, the lines at 131–280 cm⁻¹ belonged to bending vibrations, whereas the lines observed in the region below 100 cm⁻¹ were attributed to torsion mode. In the IR spectra of α -S₁₈, S₂₀

Table 14. Vibrational spectra of α -S₁₈ and S₂₀ allotropes (cm⁻¹).^a

Vibration	α -S ₁₈ (97)		S ₂₀ (51, 97)	
	Raman	IR	Raman	IR
1	2	3	4	5
ν	478 <i>s</i>	465 <i>s</i>	470.5 <i>m</i>	470 <i>m</i>
	469 <i>sh</i>			
ν	462 <i>m</i>		466 <i>vs</i>	
			462 <i>sh</i>	
ν	458 <i>vs</i>	456 <i>m</i>	454 <i>m</i>	
ν	445 <i>s</i>		444 <i>m</i>	
ν	420 <i>w</i>	427 <i>m</i>	428 <i>m</i>	423 <i>vw</i>
ν			416 <i>w</i>	
ν			411 <i>w</i>	
δ	276 <i>m</i>			278 <i>m</i>
δ		271 <i>s</i>	270 <i>s</i>	270 <i>m</i>
δ		263 <i>vs</i>		260 <i>s</i>
δ	257 <i>m</i>			
δ	250 <i>m</i>	253 <i>s</i>	254 <i>sh</i>	252 <i>s</i>
			250 <i>s</i>	
δ	234 <i>w</i>			
δ	228 <i>s</i>			
δ			213 <i>w</i>	
δ			207 <i>w</i>	
δ			188 <i>m</i>	
δ	166 <i>s</i>		167 <i>m</i>	
δ	153 <i>m</i>			
δ	136 <i>m</i>		136 <i>s</i>	
	131 <i>sh</i>			
τ	99 <i>m</i>		93 <i>s</i>	
τ	85 <i>m</i>			
τ	69 <i>vw</i>		66 <i>s</i>	
τ	59 <i>s</i>		54 <i>m</i>	
τ	36 <i>m</i>		48 <i>m</i>	
			40 <i>sh</i>	
τ	30 <i>m</i>		32 <i>m</i>	
			29 <i>sh</i>	
τ	20 <i>m</i>		18 <i>w</i>	

Notes: ^aRaman spectra of α -S₁₈ and S₂₀ were obtained at -80°C. IR spectra of S₁₈ and S₂₀ recorded at 25°C.

allotropes, absorption bands of stretching vibrations of the S–S bonds were presented practically in the same region (423–470 cm^{-1}), whereas bands of bending vibrations appeared within narrower region –252–278 cm^{-1} (97) (Table 14).

Comparative analysis of vibrational spectra of α -S₁₈, S₂₀ molecules suggested that the spectra were similar to each other. For example, in the Raman spectra of α -S₁₈ and S₂₀ allotropes, the lines of stretching vibrations of the S–S bonds appeared at 411–478 cm^{-1} (97).

Alternatively, the region of bending vibrations in Raman spectra of α -S₁₈ and S₂₀ allotropes (131–278 cm^{-1}) (97), *i.e.* in this case lines at 276 (*m*) and 270 (*s*) cm^{-1} were believed to be characteristics of α -S₁₈ and S₂₀ molecules (Table 14). Furthermore, the lines of bending vibrations at 213 (*w*), 207 (*w*) and 188 (*m*) cm^{-1} (97) were observed in the Raman spectra of only S₂₀ molecule, whereas for α -S₁₈ allotrope another typical strong band appeared at 228 cm^{-1} (Table 14) (97).

2.8.2. IR absorption spectra of α -S₁₈, S₂₀

In the IR spectra of α -S₁₈ and S₂₀ allotropes, the bands at 465 (*s*), 456 (*m*) and 427 (*m*) – (α -S₁₈) and 470 (*m*) and 423 (*v w*) (S₂₀) cm^{-1} were assigned to stretching vibrations of the S–S bonds, *i.e.* absorption band at 456 cm^{-1} was a characteristic of α -S₁₈ molecule (Table 14) (97). The strong absorption bands at \sim 270, \sim 260 and \sim 250 cm^{-1} were attributed to bending vibrations in α -S₁₈ and S₂₀ allotropes (Table 14) (97). It should be emphasized that in the IR spectrum of S₂₀, another band of bending vibrations was presented at 278 (*m*) cm^{-1} , which can be considered as typical for this allotrope of elemental sulfur.

2.9. Vibrational spectra of S₂, S₃ and S₄

The simplest allotropes of sulfur, S₂, S₃ and S₄ having acyclic structure were very unstable. Therefore, their synthesis requires tough unusual conditions: thermal (up to 900 °C) excitation of rhombic S₈ (49, 98, 99) as well as radio-wave or microwave irradiation of SO₂ (100, 101). In the literature (98–105), only observed vibrational spectra of the allotropes mentioned were briefly outlined. It is pertinent to note that these works covered the spectra of not individual allotropes S₂, S₃ and S₄, but their mixtures with other compounds (98–104).

The works (98, 99) described Raman spectra of elemental sulfur recorded at high temperatures (300–900 °C) and pressure (up to 16 atm). The spectra contained along with the lines typical for S₆–S₈ and S₁₀ molecules, the lines in the region of 715–718 cm^{-1} , which were assigned to vibrations in S₂ allotrope (Table 15) (98, 99). Moreover, the authors (99) observed in the Raman spectra the lines at 575 and 250 cm^{-1} , attributed to stretching and bending vibrations in S₃, respectively (Table 15).

It was reported on the line at 716 cm^{-1} in the Raman spectrum of elemental sulfur, isolated in argon matrix at low temperatures (Table 15) (100). This line was assigned to the S–S bond vibration in S₂ molecule (100).

In the papers (100, 101) were discussed vibrational spectra (Raman and IR) of radiowave and microwave discharges in atmosphere of SO₂, SO₂ + O₂, SO₂ + Ar, SO₂ + O₂ + Ar, condensed at low temperatures (–253 °C). The spectral data made it possible to identify in the condensate the obtained S₂ (100), S₃ (101) and S₄ (101) allotropes as well as ozone and sulfur oxides: SO₃, S₂O (S₂O₃)_x (100, 101). In the Raman spectrum, S₂ molecule was presented by a strong band at 718 cm^{-1} (*v*) (Table 15). The lines at 650 (*w*) and 585 (*m*) cm^{-1} in the Raman spectra of S₃ molecule were assigned to anti-symmetric and symmetric stretching vibrations of the S–S bonds, whereas the weak lines at 490 and 310 cm^{-1} were attributed to bending vibrations. Raman spectrum of S₄ allotrope was described as follows (cm^{-1}): the strong lines at 668 and 601 were

Table 15. Observed vibrational spectra of S₄, S₃ and S₂ (cm⁻¹).

Vibration	S ₂		S ₃		S ₄	
	Raman		Raman	IR	Raman	IR
1	2		3	4	5	6
ν	715(98) ^a					
ν	716 (99) ^a , (102) ^b					
ν	718 (99) ^a , (100) ^b				674 m (105) ^c	
ν			662 (103) ^b		668 s (101) ^b	668 (106) ^b
ν			650 w (101) ^b		653.5 w (105) ^c	
ν			585 m (101) ^b		601 s (101) ^b	
ν			583 (103) ^b			
ν			575 (98) ^a			
δ			490 w (101) ^b	495 w (101)		483(106) ^b
δ					440 w (101) ^a	
δ			310 w (101) ^b			320 (106) ^b
δ			250 (98) ^a		352 s (105) ^c	270 (106) ^c

Notes: ^aRaman spectra of S₂ and S₃ allotropes were recorded in gas phase at 300–900°C (along with lines assigned to S₂ and S₃ the characteristic lines of S₆–S₈ and S₁₀ molecules are observed). ^bVibrational (IR and Raman) spectra were obtained at low temperatures (–193/253°C). ^cRaman spectra of red ultramarine were measured.

assigned to stretching vibrations of the S–S bond, and a weak line at 440 corresponded to bending vibrations (Table 15) (101).

The Raman spectra of S₂O molecule isolated in argon matrix at low temperatures (–243 to –253 °C) were studied (103). The authors indicated specifically the line at 583 cm⁻¹, which was assigned to stretching vibrations of the S–S bonds in S₃ allotrope (Table 15). The correctness of this line assignment was also supported by the data given in (106), where electron absorption spectrum of elemental sulfur vapors in visible region was investigated (450 °C, pressure 20 Hg mm). It was found that stretching vibrations in S₃ molecule in basic state corresponded also to the band at ~590 cm⁻¹.

In the IR spectrum of S₃ allotrope, the bending vibration was assigned to a weak line at 495 cm⁻¹ (Table 15) (101).

The studies of Raman spectra of red ultramarine (105) enabled to find the lines assigned to vibrations in S₂⁻ and S₃⁻ ions, the medium and weak lines at 674 and 653 cm⁻¹, as well as a strong broad line at 352 cm⁻¹. The former lines were attributed to stretching vibrations of the S–S bond in S₄ molecule, and the latter line was interpreted as bending vibration in this molecule (Table 15) (105).

The investigations of the IR spectra of elemental sulfur, isolated in inert gas matrix at –253 °C showed that absorption lines at 668 (ν), 483 (δ), 320 (δ) and 270 (δ) cm⁻¹ were assigned to vibrations in S₄ molecule (Table 15) (106).

Analysis of the data given in Table 15 allowed us to draw the following conclusions. In Raman spectra of S₂, stretching vibrations of the S–S bonds were observed in higher frequency region (715–718 cm⁻¹) than those of the S₃ and S₄ allotropes. Besides, the region of stretching vibrations in the S₃ molecule (575–662 cm⁻¹) was somewhat broader than that of the S₄ allotrope (601–674 cm⁻¹), and was shifted to low-frequency region of the spectra. The same picture was observed for bending vibrations of these allotropes: a broader region (250–490 cm⁻¹) was typical also for S₃ molecule (Table 15).

2.10. Comparative analysis of vibrational spectra of elemental sulfur allotropes

As is evident from the above, the vibrational spectra of cyclic allotropes S₈, S₆, S₁₂ and S₇ are most extensively studied. Moreover, calculated vibrational spectra were described only for these

molecules (61–64, 78, 81–83). In this connection, we found it reasonable to make a comparative analysis of calculated and observed vibrational spectra of S_8 , S_6 , S_{12} and S_7 allotropes belonging to D_{4d} , D_{3d} , D_{3d} and C_s point symmetry species, respectively.

As is seen from Table 16, in spectra of S_8 , S_6 and S_{12} allotropes, the frequencies of stretching vibrations of the S–S bonds are almost unaltered and located in the region of 410–477 cm^{-1} , whereas for S_7 molecule they appear at 477–517 and 362–402 cm^{-1} . As regards bending vibrations in these molecules, particular emphasis was placed (63) on the dependence between growth of frequencies of the same bending vibrations and the ring size of the molecules studied. For example, for S_{12} , S_8 , S_7 , S_6 molecules, the following calculated frequencies of bending vibrations were reported: 128 (a_{1g}), 218 (a_1), 238 (a'), 265 (a_{1g}) cm^{-1} (63). Similar dependence was valid also for calculated frequencies of torsion vibrations in S_{12} , S_8 , S_6 allotropes observed at 51 (e_g), 86 (e_2), 180 (e_u) cm^{-1} , respectively (63). Interestingly, such torsion vibration (mode e) did not manifest itself in the spectra of S_7 (63).

The observed frequencies in vibrational spectra of S_8 , S_6 , S_{12} and S_7 molecules corresponded basically to theoretical data (63), *i.e.* the spectra of S_8 , S_6 , S_{12} allotropes were most similar (Tables 16 and 17). At the same time, one can assign inherent bands and lines, presented in IR and Raman spectra, to each unique allotrope. This fact is of prime importance for identification purposes.

Table 16. Calculated vibrational frequencies of S_6 , S_7 , S_8 and S_{12} (cm^{-1}) (63).

S_8 (D_{4d})	S_6 (D_{3d})	S_{12} (D_{3d})	S_7 (C_s)
1	2	3	4
			517 (ν , a')
			510 (ν , a'')
			483 (ν , a')
			477 (ν , a'')
475 (ν , a_1)	477 (ν , a_{1g})		
475 (ν , e_2)			
471 (ν , e_1)		465 (ν , a_{2u})	
		465 (ν , e_u)	
		517 (ν , a')	
	462 (ν , e_g)	459 (ν , a_{1g})	
		459 (ν , e_g)	
	451 (ν , e_g)	447 (ν , e_g)	
437 (ν , e_3)			
		425 (ν , e_u)	
415 (ν , b_1)		(410) (ν , a_{2g})	
	390 (ν , a_{1u})		402 (ν , a')
			397 (ν , a'')
	312 (δ , a_{2u})		362 (ν , a')
		288 (δ , a_{1g})	288 (δ , a'')
	265 (δ , a_{1g})	266 (δ , a_{2u})	268 (δ , a')
248 (δ , e_3)		253 (δ , e_u)	
239 (ν , b_2)		243 (δ , e_g)	242 (τ , a'')
218 (δ , a_1)			
	203 (δ , e_g)		193 (δ , a'')
186 (τ , e_1)	180 (τ , e_u)	177 (δ , e_g)	184 (δ , a')
		165 (δ , e_u)	
152 (δ , e_2)		158 (δ , a_{1u})	153 (τ , a'')
			145 (δ , a')
		128 (δ , a_{1g})	
86 (τ , e_2)		85 (τ , a_{2g})	
		72 (τ , a_{2u})	
		62 (τ , e_u)	
		51 (τ , e_g)	

Table 17. Observed vibrational spectra of S₈, S₆, S₁₂ and S₇^a (cm⁻¹).

Vibrations	S ₈ (D _{4d})		S ₆ (D _{3d})		S ₁₂ (D _{3d})		S ₇ (C _s)	
	Raman	IR	Raman	IR	Raman	IR	Raman	IR
1	2	3	4	5	6	7	8	9
ν								526 <i>sh</i>
ν							519 <i>m</i>	526 <i>sh</i>
								518 <i>m</i>
								516 <i>sh</i>
ν								515 <i>m</i>
ν								482 <i>s</i>
ν	470 <i>s</i>		471 <i>vs</i>				481 <i>vs</i>	480 <i>s</i>
ν		465 <i>s</i>		463 <i>vs</i>	463 <i>vw</i>	465 <i>m</i>	477 <i>sh</i>	476 <i>sh</i>
ν					459 <i>m</i>			461 <i>m</i>
ν	434 <i>m</i>	435 <i>w</i>	448 <i>s</i>		447 <i>m</i>			
ν						425 <i>vw</i>		
ν							403 <i>vs</i>	402 <i>s</i>
ν							397 <i>sh</i>	
ν							356 <i>s</i>	
ν				390 <i>vw</i>				400 <i>vs</i>
								396 <i>sh</i>
ν							356 <i>s</i>	360 <i>sh</i>
								357 <i>vw</i>
δ				313 <i>s</i>				
δ		290 <i>w</i>		290 <i>w</i>	288 <i>w</i>		285 <i>w</i>	282 <i>sh</i>
δ			262 <i>vs</i>			266 <i>vs</i>	270 <i>w</i>	274 <i>vs</i>
δ						253 <i>vs</i>		
δ	243 <i>w</i>				243 <i>w</i>		242 <i>sh</i>	
δ		239 <i>s</i>			237 <i>w</i>		238 <i>vs</i>	239 <i>vs</i>
δ	218 <i>s</i>				219 <i>vw</i>			
δ					180 <i>vw</i>			
δ		197 <i>m</i>	202 <i>s</i>		177 <i>w</i>	165 <i>vs</i>		197 <i>m</i>
δ	152 <i>s</i>				169 <i>w</i>			
δ		186 <i>m</i>					184 <i>s</i>	193 <i>m</i>
δ					155 <i>vw</i>			
δ							145 <i>w</i>	146 <i>m</i>
δ					128 <i>vs</i>		155 <i>s</i>	
τ	85 <i>s</i>		106 <i>w</i>	180 <i>s</i>		72 <i>m</i>	76 <i>vs</i>	
τ			84 <i>m</i>		67 <i>s</i>	62 <i>m</i>	54 <i>vs</i>	
τ			79 <i>m</i>		51 <i>m</i>		50 <i>vs</i>	
τ					43 <i>vs</i>			
τ					32 <i>vs</i>			

Note: ^aRaman and IR spectra were recorded in crystalline state.

For instance, S₈ allotrope was identified by strong lines of bending vibrations observed in the Raman spectra at 218 and 152 cm⁻¹, as well as by absorption lines of bending vibrations at 239 (*s*), 197 (*m*) and 186 (*m*) cm⁻¹.

Strong lines of bending vibrations in the Raman spectra at 262 and 202 cm⁻¹ as well as weak band of torsion mode at 106 cm⁻¹ were assigned to S₆ allotrope. The IR spectra of S₆ molecule showed the absorption bands characteristic of this allotrope at 390 (*vs*, ν), 313 (*s*, δ) and 180 (*s*, τ) cm⁻¹.

Medium line of stretching vibrations at 459 cm⁻¹ and a very strong line of bending vibration at 128 cm⁻¹ were observed in the Raman spectra of only S₁₂ allotrope. In the IR spectra of this molecule, the following absorption bands can be used for identification purposes: 425 (*vs*, ν), 253 (*vs*, δ), 165 (*vs*, δ).

It should be mentioned that in the Raman and IR spectra of S_7 molecule were observed significant differences as compared with the spectra of S_6 , S_8 , S_{12} allotropes. Only the spectra of S_7 molecule showed absorption lines of stretching vibrations of the S–S bonds at 480–520 and 350–405 cm^{-1} , as well as a very strong absorption band of bending vibrations at 274 cm^{-1} and medium intensity absorption band at 193 cm^{-1} (IR spectrum).

As said above, vibrational spectra of cyclic molecules S_9 , S_{10} , S_{11} , S_{13} , S_{14} , α - S_{18} and S_{20} were investigated to a lesser extent than those of S_8 , S_6 , S_{12} and S_7 allotropes. The Raman spectra for S_9 , S_{10} , S_{11} , S_{13} , S_{14} , α - S_{18} and S_{20} molecules were recorded only at low temperatures (–80/–100 °C). In the Raman spectra of these molecules, the lines at 386–497 cm^{-1} should be assigned to stretching vibrations, the lines at 351–300 cm^{-1} belonged to bending vibrations, while the lines observed in the region below 100 cm^{-1} were attributed to torsion mode (50, 51, 79, 81–83, 85, 89).

Vibrational spectra of unstable acyclic molecules S_2 – S_4 were studied even worse. These spectra as well as the allotropes themselves were obtained under tough and unusual conditions (in mixture with other products). In the spectra of acyclic molecules of elemental sulfur (S_2 , S_3 and S_4), the stretching vibrations of the S–S bonds were shifted to high-frequency region: 575–718 cm^{-1} .

Thus, the analysis carried out enabled to reveal specific features and characteristic (convenient for identification purposes) frequencies in vibrational spectra of S_2 – S_4 , S_6 – S_{14} , α - S_{18} , S_{20} molecules. Furthermore, the analysis has demonstrated that vibrational spectroscopy is a handy tool used for the identification of diverse allotropes of elemental sulfur.

3. S–S bond vibrations in disulfides

3.1. S–S bond vibrations in dialkyl disulfides

Vibrational spectra of dialkyl disulfides were investigated in earlier publications (107–124). As in vibrational spectra of elemental sulfur (62, 76, 83, 97), the line of stretching vibration of the S–S bond in Raman spectra of dialkyl disulfides was quite intensive, whereas in the IR spectra it was presented as a weak absorption band. Summarized data on these spectra carry valuable information used for identification of dialkyl disulfides and their mixtures.

3.1.1. Calculated data

In the studies of vibrational spectra of dialkyl disulfides, much attention was paid to the interpretation of normal frequencies in approximation of the valence force field, as well as the problems related to probable conformations of these molecules. Stretching vibrations of the S–S bonds of dialkyl disulfides rotational isomers were clearly observed at 505–550 cm^{-1} (107–124).

The work (125) reviewed the vibrational spectra of H_2S_2 molecule, which can be considered as the simplest model of dialkyl disulfides, R_2S_2 (R=H). This molecule was likely to be *gauche*-isomer (126, 127), *i.e.* in H_2S_2 one S–H bond was located approximately at a right angle to the other bond. In H_2S_2 , the observed and calculated frequencies of the stretching vibration of the S–S bond (509 cm^{-1}) coincided (Table 18) (125).

Analysis of vibrational spectra of dialkyl disulfides using theoretical calculations was given in a number of publications (107–110, 112, 123). To calculate vibrational frequencies in these molecules (107), the valence force field with force constants of dialkyl disulfides (128) was applied. In another paper (108), the same calculations were carried out on the basis of modified Urey–Bradley force constants refined by the method of least squares. Interpretation of vibrational spectra of dimethyl disulfide reported in (109) rested on spectral data of its deuterated species

Table 18. Observed and calculated frequencies of the S–S stretching vibrations in H₂S₂ and aliphatic disulfides (cm⁻¹).

RSSR	Conformer	Observed frequencies	Calculated frequencies
H ₂ S ₂	<i>gauche</i>	509 (125)	509 (125)
MeSSMe	<i>gauche</i>	509 (105, 108), 510 _m (110)	505 (108, 109), 511 (107), 516 (110)
MeSSEt	<i>gauche-gauche</i>	507 (107), 509 (108)	507 (108), 511 (107)
	<i>gauche-trans</i>	522 (107), 525 (108)	524 (107), 527 (108)
EtSSEt	<i>gauche-gauche</i>	507 (107), 509 (108)	508 (108), 511 (107)
	<i>gauche-trans</i>	524 (107, 108)	524 (107), 528 (108)
MeSSBu- <i>t</i>	<i>gauche</i>	528 (108)	529 (108)
<i>t</i> -BuSSBu- <i>t</i>	<i>gauche</i>	547 (107)	534 (107)
		543 (108, 112, 123)	546 (108)

CD₃SSCD₃, as well as on calculation of normal vibrations. The investigations resulted in good agreement between calculated and observed frequencies of the stretching vibrations of the S–S bonds in dialkyl disulfides; these frequencies were presented at 505–547 cm⁻¹ (Table 18).

In addition, from vibrational spectra, it was possible to extract a good deal of information on rotational isomers in dialkyl disulfide molecules, which had non-planar conformation (along with H₂S₂) with dihedral angle CSSC varying from 74° to 105° (42, 126, 127).

For example, in the vibrational spectrum of dimethyl disulfide, the stretching mode of the S–S bond was observed at 509 cm⁻¹ (105, 108), whereas the calculated values of this frequency were at 505 (108, 109), 511 (107) and 516 (110) cm⁻¹ (Table 18). It was suggested that these values corresponded to *gauche*-conformation of dimethyl disulfide (107–110).

At the same time, the vibrational spectra of dimethylethyl disulfide showing two bands of stretching vibrations of the S–S bond at 507 and 522 cm⁻¹ (107) or 509 and 525 cm⁻¹ (108) indicated that two conformations must be present in this molecule: *gauche-gauche* and *gauche-trans*, respectively (Table 18). The calculated frequencies for these conformations appeared in the region of 507–511 and 524–527 cm⁻¹ (Table 18) (107, 108).

In the observed vibrational spectrum of diethyl disulfide, there were two bands of the S–S stretching vibrations at 507–509 and 524 cm⁻¹ (107, 108), which were characteristic of *gauche-gauche*- and *gauche-trans*-conformers (Table 18). Frequencies of the S–S stretching vibrations at 508–511 and 524–528 cm⁻¹ were assigned to these conformers (107, 108) (Table 18). It should be borne in mind that *gauche-gauche*-conformation was energy favorable (107).

It seemed likely that *t*-butylmethyl- and di-*t*-butyl disulfides existed as *gauche*-conformer, since in vibrational spectra of these disulfides only one frequency of the S–S stretching vibration was observed at 528 cm⁻¹ for MeSSBu-*t* (108) as well as the corresponding frequency at 543–547 cm⁻¹ for *t*-BuSSBu-*t* (107, 108, 112, 123). As is seen from Table 18, the calculated (108) band of the S–S stretching vibration in *t*-BuSSBu-*t* (*gauche*-conformer, 546 cm⁻¹) correlated well with the observed band 543 cm⁻¹ (108, 112, 123). At the same time, the similar band calculated for this conformer in (107), was shifted to low-frequency region by 13 cm⁻¹ with respect to the observed band and was located at 534 cm⁻¹ (Table 18). This discrepancy between the calculated and observed frequencies of *gauche*-conformer of di-*t*-butyl disulfide may be due to poor set of the force constants used in the work (107).

It was found (108) that the S–S stretching frequency varied little with the CSSC torsion angles in dialkyl disulfides.

Thus, the data obtained on the basis of analysis of vibrational spectra and calculation of normal vibration frequencies of dialkyl disulfides made it possible to determine the structure of these molecules. For example, in vibrational spectra of dimethyl-, methyl(*t*-butyl)- and di(*t*-butyl) disulfides, one frequency of the S–S stretching vibrations was observed at 509–543 cm⁻¹

attributable to *gauche*-conformers, whereas in the spectra of dialkyl disulfides bearing longer alkyl radical (methylethyl- and diethyl disulfides) appeared two frequencies of the S–S stretching vibrations at 507–525 cm⁻¹, assigned to two conformations (*gauche-gauche* and *gauche-trans*) (Table 18).

3.1.2. Raman spectra of dialkyl disulfides

Raman spectra of different dialkyl disulfides of general formula RSSR', where R=R'=Me, Et, Pr, *i*-Pr, Bu, *i*-Bu, *sec*-Bu, *t*-Bu, *t*-Am, C₈H₁₇, C₁₂H₂₅; R=Me, R'=Et; R=Me, R'=*t*-Bu were studied. In the spectra of these molecules, the S–S stretching vibrations were observed at 505–545 cm⁻¹ (Table 18) (107–121, 123).

Raman spectra of dimethyl-, methyl(*t*-butyl)-, di(*t*-butyl)- and di(*t*-amyl) disulfides contained one strong (or very strong) line assigned to *gauche*-conformer (Table 19) (108–110, 112–114, 116, 117, 121, 123). In the Raman spectrum of dimethyl disulfide, this line emerged at 508–512 cm⁻¹ (108–110, 113, 114, 117, 119, 120), while in the similar spectrum of methyl(*t*-butyl) disulfide it was observed at 528 cm⁻¹ (Table 18) (108, 117), *i.e.* the substitution of one methyl moiety by *t*-butyl radical in dimethyl disulfide resulted in the shift of the line to the high-frequency region (~ by 18 cm⁻¹). In its turn, in Raman spectra of di(*t*-butyl)- and di(*t*-amyl) disulfides, this vibration line was even more shifted to a high-frequency region and appeared at 543 cm⁻¹ (108, 112, 117, 123).

The spectra of other dialkyl disulfides studied (RSSR', where R=R'=Et, Pr, *i*-Pr, Bu, *i*-Bu, *sec*-Bu; R=Me, R'=Et) showed two lines of the S–S stretching vibrations at 506–512 cm⁻¹

Table 19. S–S stretching vibrations (ν) of dialkyl disulfides (cm⁻¹).^a

RSSR	Conformer	Observed frequencies	
		Raman	IR
MeSSMe	<i>gauche</i>	512 <i>s</i> (113, 121), 509 <i>s</i> (108, 114), 510 (109, 110, 116, 120), 508 <i>ws</i> (117, 119)	509 <i>s</i> (109, 114, 117)
CF ₃ SSCF ₃	^b	^b	545 (122)
MeSSEt	<i>gauche-gauche</i>	507 <i>s</i> (107), 509 <i>s</i> (108)	507 <i>w</i> (115), 510 <i>w</i> (117)
	<i>gauche-trans</i>	522 <i>m</i> (107), 524 <i>m</i> (108, 117, 119)	522 <i>w</i> (115), 526 <i>w</i> (117)
EtSSEt	<i>gauche-gauche</i>	506–509 (113), 507 <i>s</i> (111), 508 <i>s</i> (114, 117, 119), 509 (108, 121)	509 <i>w</i> (113), 510 (121)
	<i>gauche-trans</i>	520–525 (113), 522 <i>m</i> (111), 523 <i>s</i> (114, 117, 119), 524 (108)	510 <i>m</i> (117) 525 <i>w</i> (117)
MeSSBu- <i>t</i>	<i>gauche</i>	528 <i>vs</i> (108, 117)	529 <i>m</i> (117)
PrSSPr	<i>gauche-gauche</i>	510 <i>vs</i> (117)	500 (113), 511 <i>w</i> (117)
	<i>gauche-trans</i>	523 <i>s</i> (117)	524 <i>w</i> (117)
<i>i</i> -PrSSPr- <i>i</i>	<i>gauche-gauche</i>	512 <i>s</i> (117)	513 <i>w</i> (117)
	<i>gauche-trans</i>	525 <i>m</i> (117)	525 <i>w</i> (117)
BuSSBu	<i>gauche-gauche</i>	511 <i>s</i> (115)	510 <i>m</i> (115)
	<i>gauche-trans</i>	525 <i>m</i> (115)	525 <i>w</i> (115)
<i>i</i> -BuSSBu- <i>i</i>	<i>gauche-gauche</i>	511 <i>s</i> (115)	513 <i>w</i> (117)
	<i>gauche-trans</i>	525 <i>m</i> (115)	527 <i>w</i> (117)
<i>Sec</i> -BuSSBu- <i>sec</i>	<i>gauche-gauche</i>	512 <i>s</i> (117)	512 <i>s</i> (117)
	<i>gauche-trans</i>	525 <i>m</i> (117)	525 <i>m</i> (117)
<i>t</i> -BuSSBu- <i>t</i>	<i>gauche</i>	543 <i>s</i> (108, 112, 117, 123)	545 <i>w</i> (117), 544 <i>w</i> (115), (123)
<i>t</i> -AmSSAm- <i>t</i>	<i>gauche</i>	543 <i>s</i> (117)	543 <i>w</i> (117)
C ₈ H ₁₇ SSC ₈ H ₁₇	^c	^b	512 <i>m</i> , 526 <i>w</i> (115)
C ₁₂ H ₂₅ SSC ₁₂ H ₂₅	^c	516 <i>w</i> (115)	525 <i>w</i> (115)

Notes: ^aSpectra were measured at room temperature. ^bFor (CF₃S)₂ and (C₈H₁₇S)₂ the Raman spectra were not described. ^cAssignment of the spectra was not discussed.

and 522–525 cm^{-1} , assigned to *gauche-gauche*- and *gauche-trans*-conformers, respectively (Table 19) (107–111, 113, 117–119, 121). Furthermore, the structure of radical in these molecules affected neither position nor intensity of these lines (Table 19).

Raman spectra of methylethyl- and diethyl disulfides were measured in the liquid state at different temperatures ($-68/ + 20^\circ\text{C}$). It was shown that *gauche-gauche*-isomer was more stable than *gauche-trans*-isomer by about $0.9 \pm 0.2 \text{ kcal mol}^{-1}$ (for MeSSEt) and $0.6 \pm 0.2 \text{ kcal mol}^{-1}$ (for EtSSEt) (117).

It should be mentioned that in the work (119) *gauche-gauche*-conformers in methylethyl- and diethyl disulfides were mistakenly considered as *trans-trans*-isomers. Such a mistake was due to the incorrect application of spectral characteristics obtained for dithioglycolic acid (HOOCCH_2S)₂. In the Raman spectra of the latter, the S–S stretching vibration was observed at 508 cm^{-1} and the molecule existed predominantly as *trans*-conformer (X-ray analysis data) (119).

The Raman spectra of didodecyl disulfide were briefly reported (115) (no discussion and assignments were given). In the paper, only one line at 516 cm^{-1} (weak!) attributable to the S–S stretching vibrations was given (Table 19) (115).

3.1.3. IR absorption spectra of dialkyl disulfides

In the IR spectra of dialkyl disulfides, the weak absorption bands at 500–545 cm^{-1} were assigned to the S–S stretching vibrations (Table 18) (109, 111, 113–115, 117, 121–124).

The IR spectra of dimethyl-, bis(trifluoromethyl)-, methyl(*tert*-butyl)-, di(*tert*-butyl)- and di(*tert*-amyl) disulfides showed also the band of S–S stretching vibrations assigned to *gauche*-isomer, which appeared in the IR spectrum of dimethyl disulfide at 509 cm^{-1} , whereas in bis(trifluoromethyl)-, methyl(*tert*-butyl)-, di(*tert*-butyl)- and di(*tert*-amyl) disulfides this band was shifted to a high-frequency region (by 36 cm^{-1}) and was observed at 545 (122), 529 (117), ~545 (115, 117, 123) and 543 cm^{-1} , respectively (117) (Table 19).

In the IR spectra of other studied dialkyl disulfides (RSSR' , where $\text{R}=\text{R}'=\text{Et, Pr, } i\text{-Pr, Bu, } i\text{-Bu, } sec\text{-Bu, C}_8\text{H}_{25}$; $\text{R}=\text{Me, R}'=\text{Et}$), two bands of stretching vibrations of the S–S bond were presented in the region of 507–513 cm^{-1} and 522–526 cm^{-1} , which were attributed to *gauche-gauche*- and *gauche-trans*-conformers, respectively (Table 19) (115, 117). However, contrary to the expectations, structure of the radicals mentioned did not effect on the position of the absorption band of stretching vibrations of the S–S bonds. At the same time, it was reported (115), that in the IR spectra of di-*n*-dodecyl sulfide only one weak band of the S–S stretching vibrations was observed at 525 cm^{-1} (without assignment to any conformer) (Table 19).

On the example of the IR spectra of methylethyl- and diethyl disulfides measured at -196°C , it was shown (117) that in the solid state these compounds existed as the most stable *gauche-gauche*-conformer that was supported by the presence of the S–S stretching vibrations at 510 cm^{-1} (117).

3.2. S–S bond vibrations in allyl- and benzyl disulfides

This section deals with the vibrational spectra of allyl- and benzyl disulfides. We consider it possible to combine these disulfides in one section because, first of all, their chemical properties and inductive effects are similar to those of their radicals.

Interpretation of vibrational spectra of allyl methyl- and diallyl disulfides allowed one to find the frequencies of the S–S (478–510 cm^{-1}) and C–S (620–730 cm^{-1}) stretching vibrations (129–131).

It was found (129, 130) that the allyl moieties in allyl methyl- and diallyl disulfides were in the same *gauche*-configuration, in which a CCCS dihedral angle (between the sulfur atoms and the terminal vinyl carbons) was equal to 105–120°.

In the Raman spectra of allyl methyl disulfide, the strong band of S–S stretching vibration was located at 510 cm^{-1} and was assigned to *gauche*-conformer with a CSSC dihedral angle of approximately 70° (Table 20) (129). At the same time, in the Raman spectra of diallyl disulfide in liquid state (130, 131), two bands appeared in the region of $510\text{--}512\text{ cm}^{-1}$ (strong) and $490\text{--}492\text{ cm}^{-1}$ (middle). These bands were attributed to *gauche*-conformer (CSSC dihedral angle is 70°) and *cis*-conformer with a CSSC dihedral angle of 25° (Table 20) (130). Since in the Raman spectra (recorded at -120°C) of solid diallyl disulfide presented only one band at 510 cm^{-1} corresponding to *gauche*-conformer (130), the latter was more stable than *cis*-conformer (by $0.24 \pm 0.02\text{ kkal mol}^{-1}$) according to (130).

It is pertinent to note that in the IR spectra of bis(3-phenylallyl) disulfide, $(\text{PhCH}=\text{CHCH}_2\text{S})_2$, only one weak band of S–S stretching vibration is observed (but not discussed in detail) at 508 cm^{-1} (Table 20) (115). However, the intensity mentioned is not typical for the Raman spectra of diorganyl disulfides (107, 114, 117, 119).

As expected, in the Raman spectra (130, 131) of diallyl disulfide, two weak absorption bands were registered at $512\text{--}515\text{ cm}^{-1}$ and $\sim 478\text{ cm}^{-1}$, assigned to *gauche*- and *cis*-conformers (Table 20) (130, 131), while earlier it was reported (115) only one weak absorption band at 510 cm^{-1} (type of conformer was not discussed). In the same work (115), the authors described the IR spectra of $(\text{PhCH}=\text{CHCH}_2\text{S})_2$ molecule and indicated to only one band of S–S stretching vibration at 506 cm^{-1} . The band turned to be unexpectedly strong that was not correlated with the known and commonly adopted data (34, 130, 131) (Table 20).

Vibrational spectra of dibenzyl disulfide were briefly (without detailed analysis) documented (115, 132). The Raman spectra of this compound in the solid state contained one band (middle in intensity) of S–S stretching vibration at 517 cm^{-1} (115). In the IR spectra of dibenzyl disulfide, the absorption band at 507 cm^{-1} was attributed to the same vibrational mode (115). When the IR spectra were recorded in CS_2 solution or Vaseline oil, this band was shifted to a low-frequency region up to 503 and 497 cm^{-1} , respectively (Table 20) (132).

3.3. S–S bond vibrations in diaryl disulfides

The vibrational spectra of diphenyl disulfide and its derivatives containing in the aromatic ring such substituents as Me, NH_2 , OH, CN, COOH, COOMe and CONH_2 were described (115, 124, 133, 134) (Table 21).

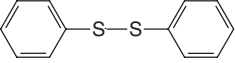
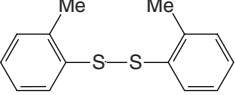
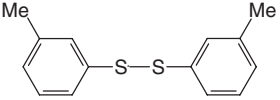
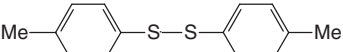
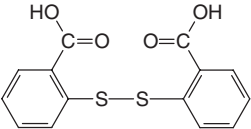
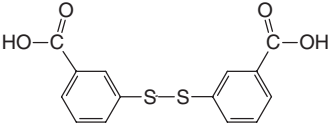
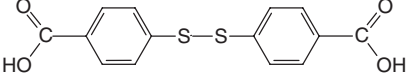
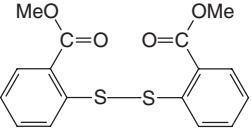
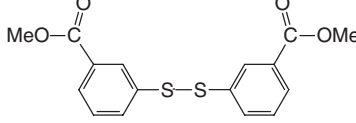
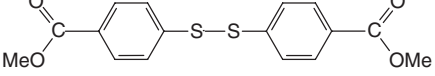
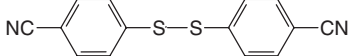
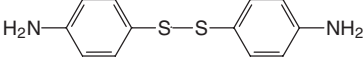
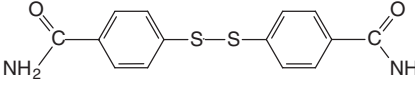
The strong line of S–S stretching vibration was observed in the Raman spectra of diphenyl disulfide at 523 cm^{-1} (Table 21) (115). Introduction of the methyl moiety to the aromatic ring of diphenyl disulfide at the position 2 and 4 did not practically affect the frequency of this vibration,

Table 20. S–S stretching vibration (ν) of allyl- and benzyl disulfides (cm^{-1}).

RSSR	Conformer	Observed frequencies	
		Raman	IR
$\text{CH}_2=\text{CHCH}_2\text{SSMe}$	<i>gauche</i>	510 s (129)	^a
$(\text{CH}_2=\text{CHCH}_2\text{S})_2$	<i>gauche</i>	510 s (130), 512 (131)	515 vw (130), 512 (131)
	<i>cis</i>	492 m (130), 490 sh (131)	478 w (130), 479 (131)
$(\text{PhCH}=\text{CHCH}_2\text{S})_2$	^b	508 w^c (115)	506 s^c (115)
$(\text{PhCH}_2\text{S})_2$	^b	517 m (115)	507 m (115)
			503^d (132)
			497^e (132)

Notes: ^aIR spectra were not recorded. ^bTypes of conformers were not discussed. ^cThe data on intensity of the bands indicated were not in agreement with commonly accepted (34). ^dThe spectra of $(\text{PhCH}_2\text{S})_2$ were measured in CS_2 solution. ^eThe spectra of $(\text{PhCH}_2\text{S})_2$ were measured in Vaseline oil.

Table 21. S–S stretching vibrations (ν) in diaryl disulfides (cm^{-1}).

RSSR	Observed frequencies	
	Raman	IR
	523 <i>s</i> (115)	473 <i>w</i> (133)
	521 <i>m</i> (115)	521 <i>w</i> (115), 430–490 (133) ^a
	538 <i>w</i> (115)	542 <i>w</i> (115), 430–490 (133) ^a
	519 <i>m</i> (115)	523 <i>vw</i> (115), 430–490 (133) ^a
	^b	468–510 <i>s</i> (124) ^a
	^b	468–10 <i>s</i> (124) ^a
	^b	468–510 <i>s</i> (124) ^a
	^b	468–510 <i>s</i> (124) ^a
	^b	468–510 <i>s</i> (124) ^a
	^b	468–510 <i>s</i> (124) ^a
	^b	430–490 (133) ^a
	^b	430–490 (133) ^a
	^b	430–490 (133) ^a

Notes: ^aGeneral internal of frequencies was given. ^bRaman spectra were not measured.

which appeared in the Raman spectra of bis(2-methylphenyl)- and bis(4-methylphenyl) disulfides at 521 (*m*) and 519 (*m*) cm^{-1} , respectively (Table 21) (115). At the same time, in the Raman spectra of bis(3-methylphenyl) disulfide, the band of S–S bond (in this case – unexpectedly weak) was shifted to a high-frequency region and was demonstrated itself at 538 cm^{-1} (Table 21) (115).

From Table 20 follows that the data of the IR spectra of diphenyl disulfide and its substituents are contradictory. For example, in (133) the S–S bond stretching vibrations in diphenyl disulfide were assigned to a weak band at 473 cm^{-1} (Table 21), whereas the authors of other paper (115) considered this assignment incorrect and attributed this band to bending vibrations of the phenyl ring. As far as ditolyl disulfides is concerned, we supposed that the results given in (115) were more correct because they were well correlated with the data of the Raman spectra (Table 21) (115). So, the IR spectra of bis(2-methylphenyl)- and bis(4-methylphenyl) disulfides showed weak absorption bands of the S–S stretching vibrations at 521 and 519 cm^{-1} , respectively, whereas in the spectra of bis(3-methylphenyl) disulfide this band was observed in a high-frequency region at 542 cm^{-1} (Table 21) (115). However, a broad and lower-frequency region (430–490 cm^{-1}) was observed (133) for the S–S stretching vibrations in ditolyl disulfides (Table 21).

The IR spectra of diphenyl disulfide substituents bearing HO(O)C- and MeO(O)C-moieties in the aromatic ring (at positions 2, 3 and 4) were studied (124). The authors pointed to the fact that S–S stretching vibrations in all these compounds appeared in the same broad region (468–510 cm^{-1}) and were presented as strong absorption bands that were not typical for the IR spectra (Table 21) (124).

Also, a broad region of S–S stretching vibrations (430–490 cm^{-1}) was reported (133) and the IR spectra of bis(4-aminophenyl)-, bis(4-cyanophenyl)- and bis(4-aminocarbonylphenyl) disulfides were discussed.

3.4. S–S bond vibrations in cystine and its derivatives

This section is dedicated to vibrational spectra of cystine [$\text{HOOCH}(\text{NH}_2)\text{CHCH}_2\text{S}$]₂, its analogs, substituents and derivatives (Table 22) (118, 135). These α -amino acids, containing disulfide fragment, can also be considered as functional derivatives of dialkyl disulfides, namely the derivatives of diethyl- (Table 22, no. 1–10), dipropyl- (Table 22, no. 11, 12) and di(*tert*-butyl) disulfides (Table 22, no. 13), whose molecules contain such groups as NH_2 , NHMe , NMe_2 , COOH , COOMe , COOEt , $^-\text{OOC}(\text{Me}_3\text{N}^+)$, etc. Vibrational spectra of cystine halogenides and its derivatives were analyzed (Table 22, no. 7–10, 12). As is evident from Table 22, the presence of the functional groups aforementioned in dialkyl disulfides does not significantly affect both the location and intensity of the S–S bond stretching vibrations.

For example, in the Raman spectra of aqueous solutions of *gauche*-conformers of these compounds, a strong band of S–S stretching vibrations was observed at 506–511 cm^{-1} (Table 22) (116, 118). Similar bands, as shown in Table 18, appeared also in the Raman spectra of *gauche*–*gauche*-conformers of diethyl- and dipropyl disulfides.

In the Raman spectra of *trans*-conformer of ($[\text{HO}(\text{O})\text{CCH}(\text{NH}_2)\text{C}(\text{Me})_2]_2\text{S}_2$) disulfide, a strong line of S–S stretching vibrations was presented at 546 cm^{-1} (Table 22, no. 13), *i.e.* it was shifted toward high-frequency region that was also characteristics of the Raman spectra of di(*tert*-butyl) disulfide (108, 112, 117, 123).

The Raman spectra of cystine derivatives in solid state showed a more complicated picture. For instance, the spectra of cystine hydrohalogenides and its methyl ether demonstrated two bands of S–S stretching vibrations: a strong band in the region of 518–522 cm^{-1} and a middle one (or shoulder) at 506–510 cm^{-1} (Table 22) (118). At the same time, the authors of the paper (135) assigned only one band 522 cm^{-1} to this type of vibration. In the Raman spectra of solid *trans*-conformer of disulfide $[\text{HO}(\text{O})\text{CCH}(\text{NH}_2)\text{C}(\text{Me})_2]_2\text{S}_2$ (as well as in the spectra measured in

Table 22. Stretching vibrations of S–S bond (ν) in disulfides (R_2S_2) related to cystine (cm^{-1}).

No.	Compound	Conformer (Dihedral angle, CSSC, grad.)	Observed frequencies		
			Raman		IR
			Solution ^a	Cryst.	Cryst.
1	[HOOC(NH ₂)CHCH ₂] ₂ S ₂ (L)	<i>gauche</i> (106° (135))	508 <i>s</i> (118), 510 (116)	498 <i>s</i> (118), 500 (135) ^b	
2	[HOOC(NH ₂)CHCH ₂] ₂ S ₂ (<i>meso</i>)	<i>gauche</i>	506 <i>s</i> (118)	506 <i>s</i> (118)	528 <i>m</i> (118)
3	[HOOC(MeNH)CHCH ₂] ₂ S ₂ (L)	<i>gauche</i>	510 <i>s</i> (118)	508 <i>w</i> (118)	504 <i>m</i> (118)
4	[HOOC(Me ₂ N)CHCH ₂] ₂ S ₂ (L)	<i>gauche</i>	^b	518 <i>s</i> (118)	^b
5	[⁻ OOC(Me ₃ N ⁺)CHCH ₂] ₂ S ₂ (L)	<i>gauche</i>	510 <i>s</i> (118)	^b	^b
6	[HOOCCH(NH ₂)CH ₂ CH ₂ CONHCH (CONHCH ₂ COOH)CH ₂] ₂ S ₂	<i>gauche</i>	510 <i>s</i> ^c (118)	509 <i>s</i> (118)	^b
7	2HCl · [HOOC(NH ₂)CHCH ₂] ₂ S ₂ (L)	<i>gauche</i> (72.2° (135))	508 <i>s</i> (118)	510 <i>sh</i> (118), 518 <i>s</i> (118), 522 (135)	507 <i>s</i> (118)
8	2HBr · [HOOC(NH ₂)CHCH ₂] ₂ S ₂ (L)	<i>gauche</i> (90° (135))	508 <i>s</i> (118)	499 <i>m</i> (118), 518 <i>s</i> (118), 522 (135)	503 <i>m</i> (118)
9	2HCl · [MeOOC(NH ₂)CHCH ₂] ₂ S ₂ (L)	<i>gauche</i>	509 <i>s</i> (118)	508 <i>sh</i> (118), 522 <i>s</i> (118)	510 <i>w</i> (118)
10	2HCl · [NH ₂ OC(NH ₂)CHCH ₂] ₂ S ₂ (L)	<i>gauche</i>	508 <i>s</i> (118)	^b	500 <i>w</i> (118)
11	[HOOC(NH ₂)CHCH ₂ CH ₂] ₂ S ₂ (L)	<i>gauche</i>	511 <i>s</i> (118)	510 <i>s</i> (118)	^b
12	2HCl · [EtOOC(NH ₂)CHCH ₂ CH ₂] ₂ S ₂ (L)	<i>gauche</i>	509 <i>s</i> (118)	504 <i>s</i> (118)	512 <i>w</i> (118)
13	[HOOCCH(NH ₂)C(Me) ₂] ₂ S ₂ (D)	<i>trans</i>	546 <i>s</i> (118)	556 <i>s</i> (118)	552 <i>s</i> (118)

Notes: ^aThe spectra were measured in solution of 1-2 M HCl. ^bRaman and IR spectra were not given. ^cSpectrum in aqueous solution.

liquid state), the S–S stretching vibrations were shifted to a high-frequency region and appeared as a strong band at 556 cm^{-1} .

The IR spectra of cystine derivatives (Table 22, no. 2, 3, 7–10, 12) like those of diethyl- and dipropyl disulfides (Table 19) contained absorption bands of S–S stretching vibrations (middle or weak) in the region of 500–528 cm^{-1} (118, 135). In addition, as it should be anticipated from the IR spectra of di(*tert*-butyl) disulfide (Table 19), S–S-stretching vibrations of *trans*-conformer [HO(O)CCH(NH₂)C(Me)₂]₂S₂ (Table 22, no. 13) were observed in a high-frequency region at 552 cm^{-1} (118).



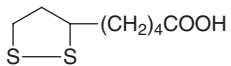
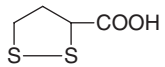
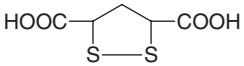
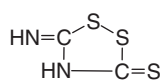
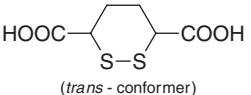
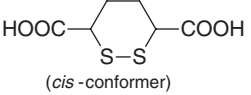
It should be noted that the method of X-ray diffraction analysis was used (135) to determine the dihedral CSSC angles in cystine molecule [HO(O)CH(NH₂)CHCH₂S]₂ (L) and its hydrohalogenides (Table 22, no. 1, 7, 8), which were 106, 72.2 and 90°, respectively (135), that proved *gauche*-structure of these conformers.

3.5. S–S bond vibrations in cyclic disulfides

According to data (118, 135), S–S stretching vibrations in the Raman spectra of 1,2-dithiolane derivatives (4,4-diethyl-1,2-dithioalane, 2,3-dithiaspiro[4,5]decane and 1,2-dithiolane-3-carbonic acid) appeared as strong bands at 509, 509 and 512 cm^{-1} , respectively (Table 23), that was in good agreement with analogous spectra of dimethyl disulfide (Table 19).

In the IR spectra (like the Raman spectra) of 4,4-diethyl-1,2-dithiolane, the absorption band of S–S stretching vibrations was observed at 508 cm^{-1} . However, the expected intensity of the band was substantially lower (Table 23) (118). At the same time, these bands in the IR spectra of 1,2-dithiolane derivatives bearing carboxyl moieties (1,2-dithiolane-3-carbonic and

Table 23. S–S bond stretching vibrations (ν) in cyclic disulfides (cm^{-1}).

Compound	Observed frequencies	
	Raman ^a	IR ^a
	509 <i>s</i> (118)	508 <i>s</i> (118)
	509 <i>s</i> (118)	b
	512 <i>s</i> (135)	b
	b	544 (124)
	b	539 (124)
	b	418 (136)
	b	483 (124)
	b	514 (124)

Notes: ^aRaman and IR spectra were measured in solid state. ^bRaman and IR spectra were not given.

1,2-dithiolane-3,5-dicarboxylic acids) were shifted to a high-frequency region and were registered at 544 and 539 cm^{-1} (Table 23) (124).

In the IR spectra of 5-imino-1,2,4-dithiazolane-3-thione (Table 23), the absorption band of S–S stretching vibrations was significantly shifted to a low-frequency region (418 cm^{-1}) in comparison with the spectra of 1,2-dithiolane derivatives (136).

In the IR spectra of the most energetically favorable *trans*-conformer of (+)-1,2-dithiane-3,6-dicarboxylic acid, the absorption band of S–S stretching vibration appeared at 483 cm^{-1} , whereas a higher frequency band at 514 cm^{-1} corresponded to *cis*-conformer of this compound (Table 23) (124).

4. S–S bond vibrations in polysulfides

4.1. S–S bond vibrations in polysulfanes

Analysis of vibrational spectra of H_2S_n ($n = 3, 4$) molecules, the simplest models of organic polysulfides, showed that in the Raman spectra an intensive band in the region of 484–488 cm^{-1} as well as a weak band at 454–470 cm^{-1} were attributable to S–S stretching vibrations (Table 24)

Table 24. Observed and calculated frequencies of S–S bond stretching vibrations in H_2S_n (cm^{-1}).

HS_nH'	Observed frequencies		Calculated frequencies
	Raman	IR	
H_2S_3	488 s, 470 sh ^a (137)	471 s ^a (137) 487 sh, 477 s ^b (137)	485, 477 (137)
H_2S_4	488 (114) 484 c, 454 w ^a (137)	484 s, 447 m ^a (137) 487 s, 450 m ^b (137)	483, 451 (137)
H_2S_5	484, 454 (114) 488, 460, 440 w (114)		

Notes: ^aThe spectra were measured in CS_2 . ^bThe spectra were recorded in CCl_4 .

(114, 137). In H_2S_5 molecule, three bands 488, 460 and 440 cm^{-1} corresponded to these vibration (Table 24) (114).

In the IR spectra of H_2S_3 measured in CS_2 , S–S stretching vibrations were presented as a strong band at 471 cm^{-1} , whereas in the IR spectra recorded in CCl_4 a strong absorption band at 477 with a shoulder at 487 cm^{-1} was assigned to this type of vibration (Table 24) (137).

At the same time, the IR spectra of H_2S_4 measured in CS_2 and CCl_4 were similar to each other and contained a strong high-frequency band in the region of $484\text{--}487\text{ cm}^{-1}$ and low-intensive band at $447\text{--}450\text{ cm}^{-1}$ (Table 24) (137).

The calculated frequencies of S–S stretching vibrations in H_2S_n ($n = 3, 4$) were well correlated with the experimental data (Table 24) (137).

The comparison of the observed frequencies of S–S-bond stretching vibrations in the vibrational spectra of H_2S_n molecules ($n = 3\text{--}5$) (Table 24) with analogous spectra of H_2S_2 (Table 18) showed that in the latter case the vibrations mentioned were distinctly shifted to a high-frequency region (509 cm^{-1}) (114, 125, 137). These spectral data seem to be valuable information for the identification of di- and polysulfane structure.

4.2. S–S bond vibrations in diorganyl polysulfides

This section deals with the Raman and IR absorption spectra of organic polysulfides bearing alkyl, allyl, arylalkyl and phenyl radicals.

The presence of intensive band of S–S stretching vibrations in the region of $486\text{--}489\text{ cm}^{-1}$ is a characteristic feature of the Raman spectra of dialkyl-, allylmethyl- and diallyl trisulfides (Table 25) (114).

At the same time, in the Raman spectra of dimethyl- and diethyl tetrasulfides, these stretching vibrations were shown as two distinct bands at ~ 486 and $438\text{--}441\text{ cm}^{-1}$ (Table 25) (114). In the Raman spectra of diphenyl tetrasulfide these vibrations were presented by an additional two bands at 472 and 437 cm^{-1} (weak intensity) (Table 25) (114). One might expect that further extension of the sulfide chain should lead to the increase of bands of S–S stretching vibrations. Indeed, in the Raman spectra of diethyl pentasulfide, three bands were observed at 488 (s), 456 and 435 cm^{-1} (m) (Table 25) (114).

One should also underline that the strong band (typical for the spectra of diorganyl polysulfides) in the region of $486\text{--}489\text{ cm}^{-1}$ (Table 25) was shifted to a low-frequency region (\sim by 24 cm^{-1}) as compared with that observed in the Raman spectra of diorganyl disulfides (Table 19), *i.e.* these two bands can be successfully used for identification of diorganyl disulfides and – polysulfides structure.

The Raman spectra of allylmethyl- and diallyl trisulfides were studied (129) on the basis of experimentally measured depolarization degrees of the Raman bands and changes in the spectra

Table 25. S–S-bond stretching vibrations in the Raman spectra of diorganyl polysulfides RS_nR' (cm^{-1}).

RS_nR'	ν S–S
Me_2S_3	486 <i>s</i> (114)
Et_2S_3	486 <i>m</i> , 499 <i>w</i> (114)
$\text{MeS}_3\text{CH}_2\text{CH}=\text{CH}_2$	487 <i>s</i> (129)
	487 <i>s</i> ^a (129)
$(\text{CH}_2=\text{CHCH}_2)_2\text{S}_3$	488 <i>s</i> (129)
	489 <i>s</i> ^a (129)
Me_2S_4	487 <i>s</i> , 441 <i>s</i> (114)
Et_2S_4	486 <i>m</i> , 438 <i>m</i> (114)
Ph_2S_4	472 <i>c\pi</i> , 437 <i>w</i> (114)
Et_2S_5	488 <i>s</i> , 456 <i>m</i> , 435 <i>m</i> (114)

Note: ^aThe spectra were measured at $-110/-118^\circ\text{C}$.

were recorded in various states (liquid and solid) (129). Conformationally, sensitive bands in the region of S–S stretching vibrations were found. In these molecules, like in allylmethyl- and diallyl disulfides, the allyl moieties had *gauche*-configuration relative to the S–S bond with a dihedral angle CCCS of $105-120^\circ$ (129).

In the IR spectra of diarylalkyl polysulfides diethyl tetrasulfide, measured in the solid state, mineral oil and CS_2 solution, the absorption band of S–S stretching vibrations appeared in the region of $470-489\text{ cm}^{-1}$ (Table 26) (132, 138). One should stress that the growth of the sulfide chain in diaryl polysulfides studied (Table 26) resulted in a shift of the bands corresponding to the S–S bond to a high-frequency region in the IR spectra recorded both in mineral oil (by $11/14\text{ cm}^{-1}$) and CS_2 solution (by $18/26\text{ cm}^{-1}$) (132, 138). In addition, this absorption band in the IR spectra of diorganylalkyl polysulfides at $470-491\text{ cm}^{-1}$ (Table 23) as well as in the Raman spectra of the corresponding diorganylalkyl polysulfides was shifted toward a low-frequency region in comparison with the band ($497-507\text{ cm}^{-1}$) observed in the IR spectra of $(\text{PhCH}_2)_2\text{S}_2$ (Table 20) (115, 132).

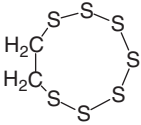
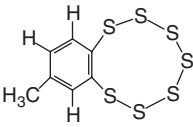
In the IR spectra of $(\text{PhCH}_2)_2\text{S}_n$, where $n = 4/8$, the extinction coefficients in maxima of absorption bands of S–S stretching vibrations and their integral intensities were determined (132).

Table 26. S–S bond stretching vibrations in the IR absorption spectra of diorganyl polysulfides RS_nR' (cm^{-1}).

RS_nR'	ν S–S		
	Solution in CS_2 (132)	Mineral oil (132)	Potassium bromide prism (138)
$(\text{PhCH}_2)_2\text{S}_3$	470	474 (nujol)	
$[(\text{Ph})_2\text{CH}]_2\text{S}_3$			486
Et_2S_4		W	484 ^a
$(\text{PhCH}_2)_2\text{S}_4$	488	474 (nujol)	
$[(\text{Ph})_2\text{CH}]_2\text{S}_4$ (I) ^b			488
$[(\text{Ph})_2\text{CH}]_2\text{S}_4$ (II) ^b			491
$(\text{PhCH}_2)_2\text{S}_5$	487	483 (nujol)	
$[(\text{Ph})_2\text{CH}]_2\text{S}_5$			489
$(\text{PhCH}_2)_2\text{S}_6$	486	483 (oil)	
$(\text{PhCH}_2)_2\text{S}_7$	486	486 (oil)	
$(\text{PhCH}_2)_2\text{S}_8$	486	486 (oil)	

Notes: ^aConditions of recording the spectra were not reported in (124). ^bFor $[(\text{Ph})_2\text{CH}]_2\text{S}_4$ the polymorphic forms were published in (138).

Table 27. S–S bond stretching vibrations in Raman spectra of cyclic heptasulfides (cm^{-1}).

Compound	ν (S–S)
	419, 437, 447, 468, 490, 509 (139)
	463, 491 (139)

It was found that both values increased with the growth of the number of sulfur atoms in the sulfide chain, but the extinction coefficient remained approximately constant ($\sim 21.3 \text{ l mol}^{-1} \text{ cm}^{-1}$) (132).

The authors of the work (138) found two polymorphic forms for the compound $[(\text{Ph})_2\text{CH}]_2\text{S}_4$: (I) – white crystals (needles) with m.p. = 73°C , (II) – and yellow crystals (prisms) with m.p. = 83°C . In the IR spectra (solid state), the S–S stretching vibrations were presented by weak absorption bands at 488 and 491 cm^{-1} , respectively (Table 26). However, for other analogous polysulfides did not show polymorphism.

4.3. S–S bond vibrations in cyclic heptasulfides

It was reported (139, without discussion) on the S–S bond stretching vibrations in Raman spectra of cyclic heptasulfides observed in the region of $419\text{--}510 \text{ cm}^{-1}$ (Table 27) (139). For example, in 1,2,3,4,5,6,7-heptathione these vibrations were presented as bands at 419, 437, 447, 468, 490 and 509 cm^{-1} (139). In the Raman spectra of 9-methyl-1,2,3,4,5,6,7-benzoheptathione, S–S bond stretching vibrations appeared at $419\text{--}500 \text{ cm}^{-1}$, the bands at 463 and 491 cm^{-1} being the strong ones (Table 27) (139).

Interestingly, stretching vibrations (ν S–S) of cyclic heptasulfides (Table 27) were observed practically in the same regions than those characteristics of cyclic molecules S_n ($n = 6\text{--}14, 18, 20$) (Tables 1–14).

5. Conclusion

A thorough analysis of S–S stretching vibrational spectra of various elemental sulfur modifications, organic disulfides and polysulfides has been performed. A number of practically useful correlations between the S–S bond frequencies and molecular structure have been revealed. The influence of structural surroundings on the S–S stretching vibrations has been discussed. The review shows that the vibrational spectroscopy of the S–S bond can serve as a helpful guide, so far underestimated, in analysis and identification of diverse elemental sulfur species, organic disulfides and polysulfides as well as an expedient to monitoring of their transformations.

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