

Terahertz spectroscopy of hydrogen sulfide

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Abstract

Pure rotational transitions of hydrogen sulfide (H_2S) in its ground and first excited vibrational states have been recorded at room temperature. The spectrum comprises an average of 1020 scans at 0.005 cm^{-1} resolution recorded in the region $45\text{ to }360\text{ cm}^{-1}$ ($1.4\text{ to }10.5\text{ THz}$) with a global continuum source using a Fourier transform spectrometer located at the AILES beamline of the SOLEIL synchrotron. Over 2000 rotational lines have been detected belonging to ground vibrational state transitions of the four isotopologues H_2^{32}S , H_2^{33}S , H_2^{34}S , and H_2^{36}S observed in natural abundance. 65% of these lines are recorded and assigned for the first time, sampling levels as high as $J = 26$ and $K_a = 17$ for H_2^{32}S . 320 pure rotational transitions of H_2^{32}S in its first excited bending vibrational state are recorded and analysed for the first time and 86 transitions for H_2^{34}S , where some of these transitions belong to new experimental energy levels. Rotational constants have been fitted for all of the isotopologues in both vibrational states using a standard effective Hamiltonian approach. Comprehensive comparisons are made with previously available data as well as the data available in HITRAN, CDMS, and JPL databases. The 91 transitions assigned to H_2^{36}S give the first proper characterization of its rotational spectrum.

Keywords: Hydrogen sulfide, line assignments, atmospheric physics, planetary atmospheres

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1. Introduction

Hydrogen sulfide (H_2S) is produced naturally in volcanoes [1] and is a byproduct of human activity such as water treatment processes [2]; it is therefore a trace species in the Earth's atmosphere. It is known to be more abundant in the atmospheres of solar system gas giants [3] and it thought to be important for the sulfur chemistry of extra-solar planets [4]. Indeed it is also found in the atmospheres of cool stars and is the dominant sulfur-bearing gas-phase species in substellar objects such as brown dwarfs [3]. H_2S has long been known to be present in interstellar clouds in our galaxy [5] and has been also observed in starburst galaxies [6]. Its role in shocks and star formation regions is thought to be of particular importance [7]. Modern astronomical telescopes such as Herschel, SOFIA and ALMA have allowed astronomers to observe species such as H_2S at THz frequencies for the first time [8], thus opening a window on higher-lying rotational levels for this species.

H_2S is a light nonrigid molecule with C_{2v} symmetry. This molecule has three vibrational modes: two overlapped stretching; symmetric (ν_1) and asymmetric (ν_3) respectively at 2615 and 2626 cm^{-1} , and one bending (ν_2) at 1183 cm^{-1} . H_2S is a near oblate asymmetric top rotor with $\kappa = 0.52$. Four sulfur isotopes are stable: ^{32}S , ^{33}S , ^{34}S , and ^{36}S with natural abundances of 95.02%, 0.75%, 4.21% and 0.02% respectively.

Since the work of Burrus et al. [9], numerous studies have been performed of H_2S rotational transitions in the ground vibrational state in the region up to about 9.3 THz (310 cm^{-1}). In the microwave region, 82 lines have been detected for the main isotopologue (H_2^{32}S) [9–15], 40 transitions for H_2^{34}S [9, 10, 12, 16], 155 transitions for H_2^{33}S with hyperfine splitting due to ^{33}S nucleus [9, 16], and 3 experimental transitions for H_2^{36}S as well [16]. In the far infrared (FIR), 443 observed transitions have been reported for H_2^{32}S [15, 17–19], 71 transitions for H_2^{33}S [18], and 173 transitions for H_2^{34}S [18].

Particularly important for this work are the measurements by Flaud et al. [18], who probed the region below 9.3 THz, and of Yamada and Klee [19], who made measurements in the same region. Frequencies from these two works in addition to the available experimental microwave

data, and effective Hamiltonian fits to them, provide the rotational spectra used in recent editions of HITRAN [20, 21] and JPL [22] databases, respectively. However rotational frequencies beyond 10 THz are estimated by extrapolating these formula. In CDMS database [23, 24], the pure rotational transitions have been calculated using all the available measured transitions in the microwave and (FIR) region. We note that the higher rotational states of H₂S are also of interest theoretically [25].

Many other studies have been performed in order to detect the absorption transitions of H₂S molecule and its isotopologues (H₂³³S and H₂³⁴S) in its fundamental, hot, and combination vibrational bands covering the spectrum range up to 16500 cm⁻¹. The most important for this work are the transitions in the fundamental bending mode (ν_2) [26–29]. Among these studies, Ulenikov et al. [29] reported the most accurate experimental upper state energy levels in ν_2 band for H₂³²S, H₂³³S, and H₂³⁴S.

In this work we present new experimental measurements of the spectrum of hydrogen sulfide in the region 1.4 – 10.5 THz (45 – 360 cm⁻¹). This work is a byproduct of our work in order to produce a complete hot line list of H₂S [30]. The following section gives experimental details. Section 3 presents the analysis of our new frequencies. In Section 4 a comprehensive comparison with the previous measurements is presented.

2. Experiments

The Fourier transform FIR absorption spectrum of gas phase H₂S in natural abundance was recorded using a globar source available on the Bruker IFS125 interferometer of the AILES beamline at the SOLEIL synchrotron [31]. A resolution of 0.005 cm⁻¹ was used to record the spectrum in the spectral range 45 – 360 cm⁻¹. A pressure of 0.16 mbar of H₂S was injected in a room-temperature White-type cell aligned for an optical path length of 150 m. The interferometer was pumped to a pressure below 10⁻⁴ mbar using a turbomolecular pump; two polypropylene windows were used to separate the interferometer from the absorption cell. The resulting spectrum is the coaddition of 1020 scans (about 12 hours of acquisition time). Fig-

Figure 1 shows an overview of the recorded spectrum, while Figure 2 gives an illustrative region containing newly observed lines.

Spectral calibration was performed using the residual water transitions and the accurate transition frequencies of Refs. [32] and [33]. A calibration curve was prepared to facilitate correction of the recorded frequencies for H₂S. Figure 3 shows the dispersion of the water transitions before and after the calibration. The accuracy of the line position is thus estimated to be 0.0005 cm⁻¹.

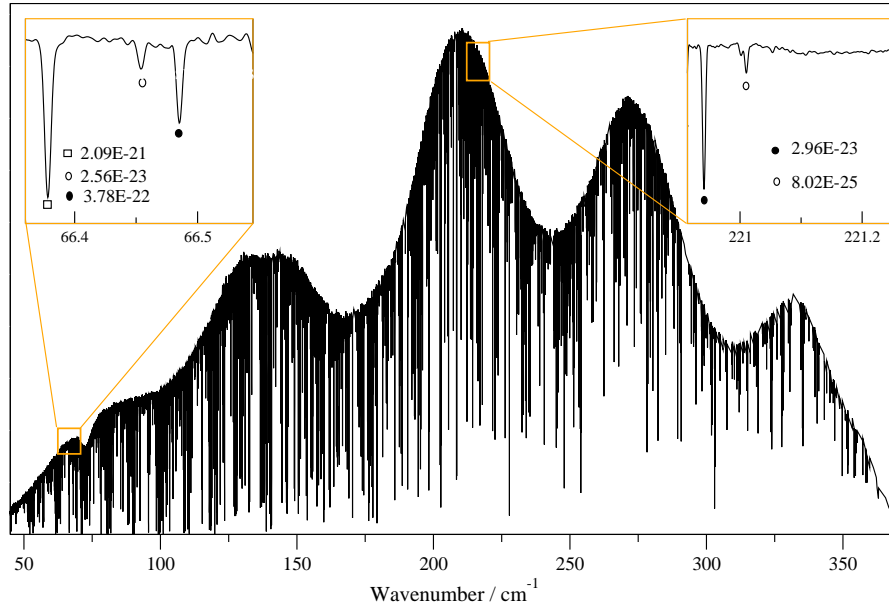


Figure 1: Room temperature absorption spectrum of H₂S recorded at AILES beamline. The insets illustrate detection of different line intensities for two sample regions of the spectrum. The numbers next to the symbols give the intensities of the lines in cm⁻¹/(molecule×cm⁻²) according to HITRAN [21].

3. Spectral analysis

Lines for H₂S molecule with intensities above 10⁻²⁵ cm⁻¹/(molecule×cm⁻²) were detected for the region above 80 cm⁻¹. In the region below 50 cm⁻¹ only lines with intensity above about 10⁻²³ cm⁻¹/(molecule×cm⁻²) were detected as a consequence of the nature of the spectrum

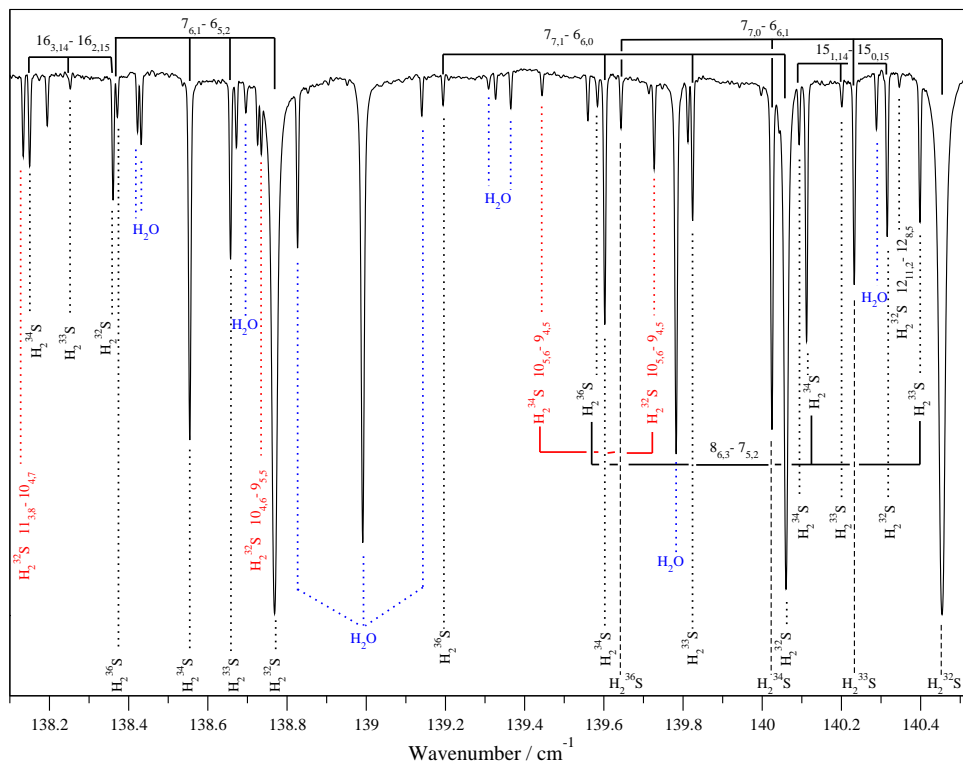


Figure 2: A portion of the absorption spectrum of H_2S recorded at SOLEIL, showing some rotational transitions in both ground and bending vibrational states $v_2 = 1$. The pure rotational transitions of the vibrational bending state $v_2 = 1$ are illustrated in red color.

obtained from the blackbody radiator: the low intensity of the light leads to a limited signal-to-noise ratio which fast decreases below 50 cm^{-1} as seen in Figure 1. Examples of rge line detections with different intensities in the different regions of the spectrum are given in the same figure.

The absorption spectrum was analysed manually by matching lines with the available data in the HITRAN database [21] and the CDMS database [23, 24] for the main isotopologue for the vibrational ground state transitions. While for H_2^{33}S and H_2^{34}S in their vibrational ground state, the HITRAN database was used. For the H_2^{36}S isotopologue, many transitions were identified and assigned manually by extrapolating the line positions of the three other isotopologues for given quantum numbers, see Figure 2. The pure rotational transitions of the vibrational

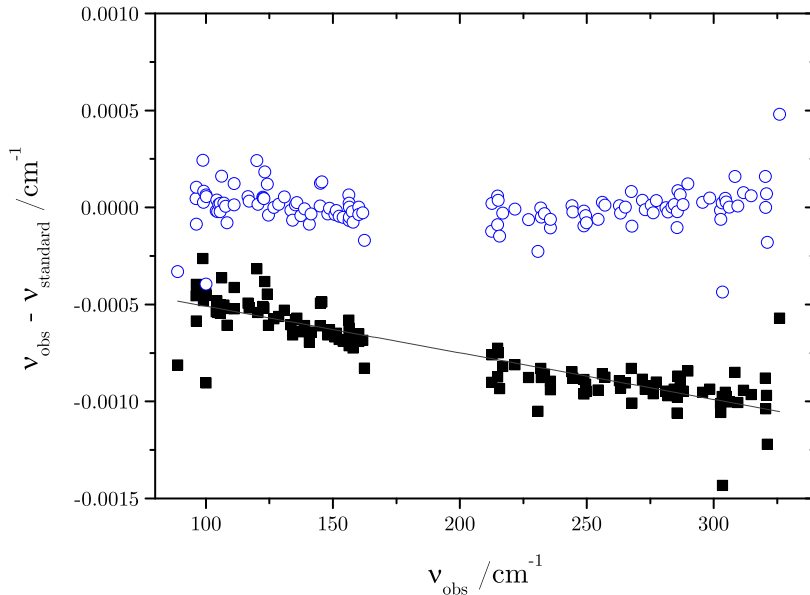


Figure 3: Calibration of the FIR Fourier transform spectrum recorded in this work. Water line positions before calibration (■) and after calibration (○) based in the accurate water line positions of Refs. [32] and [33]. The line equation in cm^{-1} is $d = -2.40(12)\nu - 2.69(26)$, where d is the dispersion and ν is the transition frequency. The standard deviation after calibration is $1.05 \times 10^{-4} \text{ cm}^{-1}$.

state $\nu_2 = 1$ of H_2^{32}S were initially assigned using a variational line list calculated using the DVR3D variational nuclear motion program [34]. This line list will be published elsewhere [30]. Experimental upper energy levels belong to ν_2 band given by Ulenikov et al. [29] were used to calculate the pure rotational transitions in the $\nu_2 = 1$ state for H_2^{32}S and H_2^{34}S . These calculated transitions were used to confirm the assignments for H_2^{32}S and to identify rotational transitions for H_2^{34}S .

Pickett's program CALPGM [35] was used to fit the observed spectra for each of the four isotopologues in both states of this molecule studied in this work. Table 1 summarises the number of the fitted parameters and the number of the spectral lines used in the fit for each isotopologues in both vibrational states. For H_2^{32}S in the ground vibrational state, the 926 newly-recorded lines were combined with 462 lines of Helminger et al. [13], Belov et al. [15], Yamada and Klee

[19]. The resulting fit parameters were used to predict 2919 transitions for H₂³²S in the ground vibrational state up to $J = 30$ and $K_a = 20$. 576 lines of our measurements were combined with 40 lines Saleck et al. [16], Huiszoon and Dymanus [36] available in the literature for H₂³⁴S to fit 41 parameters. Using the fitted parameters, a pure rotational spectrum was predicted up to around 600 cm⁻¹. This predicted spectrum contains 2554 lines with J up to 28 and K_a up to 19. For H₂³²S, 320 newly-recorded pure rotational transitions of the vibrational state $v_2 = 1$ were used in the fittings together with 743 rotational transitions calculated from the ν_2 experimental energy levels of Ulenikov et al. [29]. For H₂³⁴S, the 86 newly-recorded transitions were combined with 240 rotational transitions calculated from the ν_2 experimental energy levels from the same paper, see Table 2. For H₂³³S, 433 of our measured lines were used together with 155 microwave lines measured by Saleck et al. [16] to fit 31 rotational constants and 3 electric quadrupole hyperfine constants for the ³³S nucleus. The predicted spectrum was calculated using the fitted rotational constants only, *i.e.* neglecting the hyperfine structure. This spectrum contains 2471 lines with J up to 32 and K_a up to 20. Because of the the lower abundance of the isotopologue H₂³⁶S, we were able to detect only 91 transitions, with highest J and K_a values of 15 and 11 respectively. These transitions were combined with a single microwave line published by Saleck et al. [16] to fit 24 rotational parameters.

The presence of the H₂S *ortho* – *para* doublets with the 3 to 1 intensity ratio was taken into account in the line assignment process. A value of $\mu = 0.9783$ D [37] for the permanent dipole moment was used in our intensity calculations. For H₂³²S, H₂³³S and H₂³⁴S, the partition function values 503.07, 503.725 and 504.35 [38], respectively, were used in our calculations. For H₂³⁶S, the partition function $Q = 506.51$ was calculated by the CALPGM program. For the intensities of the pure rotational transitions of H₂³²S and H₂³⁴S within their first excited vibrational states $v_2 = 1$, the vibrational band origins from Ref. [29] were used in order to correct the intensity produced by the CALPGM program as given by:

$$I = aI_{\text{CALPGM}}e^{-c_2E_{\text{BO}}/T}, \quad (1)$$

where a is the isotopologue abundance, E_{BO} is the band origin in cm⁻¹, c_2 is the second radiation

constant and T is the temperature in K.

The constants obtained from the fits are presented in Tables 3 and 4. The predicted transitions of H_2^{32}S and H_2^{34}S in its ground and $v_2 = 1$ vibrational states, as well as these for H_2^{33}S and H_2^{36}S in their ground vibrational states, are given in the supplementary material.

4. Results and Discussion

In this work, more than 2400 lines are recorded for the four isotopologues of H_2S in the ground vibrational state, and for H_2^{32}S and H_2^{34}S in the first excited bending state. Table 1 summarises the measurements of the H_2S rotational spectra from this work and from previous studies. Detailed results for the rotational transitions of H_2^{32}S and H_2^{34}S in their ground and first excited bending state, as well as H_2^{33}S and H_2^{36}S in their ground states are given in the supplementary material. After a description of the available data used for comparison with this work, results will be detailed.

4.1. Available data

The line positions of the rotational band spectrum collected in HITRAN were originally obtained by Flaud et al. [18] in 1983, who recorded a hydrogen sulfide spectrum between 50 and 310 cm^{-1} with a Fourier transform spectrometer at a resolution of 0.005 cm^{-1} . In this experiment the three isotopic species H_2^{32}S , H_2^{33}S , H_2^{34}S were observed in natural abundance. Flaud et al. [18] have measured 631 lines in this region and combined them with 42 previously published microwave transitions in a least squares fit. Rotational constants for each isotopologue were calculated using the $A-I'$ representation of the Watson Hamiltonian. These constants were used to predict the positions of the absorption of the natural abundance hydrogen sulfide in the FIR region and intensities using $\mu = 0.974\text{ D}$ for the permanent dipole moment [10].

In 1994 Yamada and Klee [19] recorded a pure rotational spectrum for H_2^{32}S in the FIR region using a Fourier transform infrared spectrometer. They detected more than 370 transitions in the region 30 to 260 cm^{-1} with a resolution of 0.0017 cm^{-1} . These lines were combined with

Table 1: Summary of the fits for the four isotopologues of H₂S in the ground and first bending vibrational states with a comparison with the previous works for the same molecule.

	Used method	Vib. state	ISO	MW lines		IR lines		parameters		σ^c cm ⁻¹		
				Previous	Recorded	Previous	Recorded	MW(MHz)	IR(cm ⁻¹)		RMS	
Fland et al. [18]	A-I ^r	000	H ₂ ³² S	39 [9, 10, 12, 13]	—	—	387	29	0.25	0.00035	0.0008	
			H ₂ ³³ S	1 [9, 12]	—	—	71	8	—	—	0.00031	0.0008
			H ₂ ³⁴ S	2 [9, 12]	—	—	173	15	—	—	0.00025	0.0010
Yamada and Klee [19]	S-I ^r	000	H ₂ ³² S	40 [13, 14]	—	—	376	30	82	0.000213	0.0007	
			H ₂ ³² S	29 [13, 14]	64	376 [19]	30	24	366	0.000265	0.0003	
Belov et al. [15]	Padé-I ^r	000	H ₂ ³² S	—	155	71 [18]	—	37 ^a	—	—	—	
Saleck et al. [16]	A-I ^r	000	H ₂ ³³ S	—	38	173 [18]	—	28	—	—	—	
			H ₂ ³⁴ S	2 [12]	—	380 [15, 19]	926	44	0.339	0.00046	—	
This work	S-I ^r	000	H ₂ ³² S	82 [13, 15]	—	—	433	34 ^a	0.258	0.00046	—	
			H ₂ ³³ S	155 [16]	—	—	576	41	0.063	0.00047	—	
			H ₂ ³⁴ S	40 [16, 36]	—	—	91	24	0.002	0.00051	—	
			H ₂ ³⁶ S	1 [16]	—	743 ^b	320	43	—	—	0.00043	—
			H ₂ ³² S	—	—	240 ^b	86	23	—	—	0.00044	—

^a Including hyperfine constants.

^b Calculated from experimental energy levels given by Ulenikov et al. [29].

^c Standard deviation between our measurements and the recorded transitions for each work.

Table 2: Summary of available data for H₂S pure rotational transitions.

Vib. state	Data source		Number of lines				Max. J		Max. K_a		σ^b cm ⁻¹
			Total	M		P	M	P	M	P	
				Microwave	Infrared						
000	HITRAN [18]	H ₂ ³² S	1540	39 [9, 10, 12, 13]	387 [18]	1114	22	27	15	19	0.0062
		H ₂ ³³ S	808	1 [9, 12]	73 [18]	734	15	22	10	13	0.0008
		H ₂ ³⁴ S	1048	2 [9, 12]	173 [18]	873	18	24	12	15	0.0019
	CDMS [23, 24]	H ₂ ³² S	1501	82 [11–13, 15]	441 [15, 18, 19]	978	22	25	15	19	0.0037
		H ₂ ³³ S	4759 ^a	155 [16]	73 [18]	4531	15	22	10	15	—
		H ₂ ³⁴ S	990	40 [12, 16]	173 [18]	777	18	24	12	16	0.0009
	JPL [22]	H ₂ ³² S	1525	82 [13, 15, 39]	379 [15, 19]	1064	16	21	13	18	0.0168
	This work	H ₂ ³² S	2919	82 [11–13, 15]	1306	1531	26	30	17	20	
		H ₂ ³³ S	2471	155 [16]	433	2038	21	32	14	20	
		H ₂ ³⁴ S	2554	40 [12, 16]	576	1938	24	28	16	19	
H ₂ ³⁶ S		1004	1 [16]	91	912	15	17	11	13		
010	This work	H ₂ ³² S	1813		1064	749	22	23	13	15	
		H ₂ ³⁴ S	1011		326	685	14	18	10	12	

^a Including hyperfine structure.

^b The standard deviation is calculated using the frequencies measured in this work relative to the results of fits, denoted P for Predicted in each database. M for measured.

the available 40 millimetre and sub-millimetre wave transition frequencies to test several forms of Watson’s reduced Hamiltonian extended up to powers of J^{10} .

Ground state pure rotational transitions of H₂³²S were studied by Belov et al. [15] in 1995. They measured rotational transitions frequencies up to 36 cm⁻¹ in Cologne and up to 85 cm⁻¹ in Lille. The 84 measured lines were analysed together with the existing microwave and IR data recorded by Yamada and Klee [19] to test the Watson-type Hamiltonian and a Hamiltonian with a Padé formulation [40].

Yamada and Klee’s measurements [19] were subsequently combined with the measurements by Helminger et al. [13], Belov et al. [15], Helminger et al. [39] to predict the H₂³²S pure rotational lines which are in the JPL catalog [22] for J up to 21 using $\mu = 0.974$ D [10]. The data published in CDMS catalog was predicted for H₂³²S up to $J = 25$, H₂³³S up to $J = 22$, and H₂³⁴S up to $J = 24$ using the measurements from Refs. [11–13, 15, 18, 19] and $\mu = 0.9783$ D [37].

The most accurate study of lines positions in the ν_2 band of H₂S was performed by Ulenikov et al. [29]. In this work, lines were assigned to H₂³²S and its isotopologues H₂³³S and H₂³⁴S with a resolution of 0.0020 cm⁻¹. 226 upper state energy levels were obtained with $J \leq 17$ and

Table 3: Parameters in MHz for the (000) vibrational state of H_2^{32}S , H_2^{33}S , H_2^{34}S and H_2^{36}S .

	Parameter		H_2^{32}S	H_2^{33}S	H_2^{34}S	H_2^{36}S	
1	10000 ^a	A	310583.5798(106)	310025.7737(197)	309502.3997(103)	308559.20(34)	
2	20000	B	270367.6824(121)	270367.1693(224)	270366.9368(98)	270354.74(174)	
3	30000	C	141820.0415(69)	141702.4070(174)	141591.8242(93)	141395.80(93)	
4	200	Δ_J	20.861771(261)	20.87749(84)	20.90496(56)	20.6197(151)	
5	1100	Δ_{JK}	-76.23237(64)	-76.33674(232)	-76.48005(180)	-73.937(98)	
6	2000	Δ_K	117.72636(68)	117.58223(196)	117.49020(147)	115.559(126)	
7	40100	δ_J	8.865995(99)	8.863831(281)	8.866950(141)	8.5716(195)	
8	50000	δ_K	-0.641960(33)	-0.654477(112)	-0.666993(74)	-0.7067(38)	
9	300	H_J	0.01022690(312)	0.0100421(84)	0.0102278(111)		
10	1200	H_{JJK}	-0.0903531(127)	-0.089668(58)	-0.091210(55)		
11	2100	H_{JKK}	0.155866(35)	0.154950(126)	0.157519(49)	0.0576(33)	
12	3000	H_K	-0.0338364(300)	-0.033831(117)	-0.035149(42)		
13	40200	h_J	10^{-03} 2.88144(151)	2.8209(39)	2.8646(35)	-3.639(194)	
14	50100	h_{JK}	10^{-03} -0.96339(71)	-0.97261(229)	-0.98017(188)	-1.1850(286)	
15	60000	h_K	10^{-03} 1.24685(33)	1.25103(125)	1.26596(65)	1.1179(110)	
16	400	L_J	10^{-06} -5.6700(186)	-4.0663(291)	-5.551(71)	103.98(288)	
17	1300	L_{JJJK}	10^{-03} 0.072865(181)	0.058824(298)	0.07417(49)	-0.9742(215)	
18	2200	L_{JJKK}	10^{-03} -0.22325(78)	-0.18567(146)	-0.20564(95)	1.173(42)	
19	3100	L_{JKKK}	10^{-03} 0.27447(96)	0.23823(310)	0.23350(146)	-0.5454(194)	
20	4000	L_K	10^{-03} -0.16145(53)	-0.14806(233)	-0.13911(68)		
21	40300	l_J	10^{-06} -1.0205(81)	-0.6487(138)	-1.0517(280)	57.95(177)	
22	50200	l_{JK}	10^{-06} -0.2743(37)	-0.2523(93)	-0.2579(98)		
23	60100	l_{Jkk}	10^{-06} -1.7256(50)	-1.5518(71)	-1.6312(56)		
24	70000	l_K	10^{-06} 0.39780(137)	0.4483(58)	0.4605(37)		
25	500	M_J	10^{-09} 4.801(60)		3.712(147)	-364.4(167)	^a Pickett's
26	1400	M_{JJJK}	10^{-06} -0.06825(128)		-0.04173(149)	3.847(148)	
27	2300	M_{JJJKK}	10^{-06} 0.2466(58)			-3.981(205)	
28	3200	M_{JJKKK}	10^{-06} -0.4541(77)	-0.0936(105)		1.756(130)	
29	4100	M_{JKKKK}	10^{-06} 0.4151(40)	0.1808(240)	0.2908(127)		
30	5000	M_K	10^{-06} -0.09827(255)	-0.0538(151)	-0.1882(95)		
31	40400	p_J	10^{-09} 0.8269(141)		0.941(64)	-187.8(86)	
32	60200	p_{JJJK}	10^{-09} 0.7954(275)				
33	70100	p_{JKKK}	10^{-09} -0.6732(104)	-0.7882(203)	-1.0281(192)	4.074(302)	
34	80000	p_K	10^{-09} 0.33763(256)	0.3172(123)	0.2162(38)		
35	600	S_J	10^{-09} -0.003664(90)				
36	1500	S_{JK}	10^{-09} 0.07339(253)		-0.02754(260)	-2.857(188)	
37	2400	S_{JJK}	10^{-09} -0.2464(111)		0.3880(168)		
38	3300	S_{KKJ}	10^{-09} 0.2604(134)		-0.954(39)		
39	5100	S_{KJ}	10^{-09} -0.1150(63)		0.2930(165)		
40	50400	s_{JJK}	10^{-12} 0.9302(190)	0.5108(216)	0.571(60)		
41	60300	s_{KKJJ}	10^{-12} -0.509(48)		1.175(57)		
42	70200	s_{KKJ}	10^{-12} 0.2140(203)		0.7967(281)		
43	80100	s_{KJ}	10^{-12} -0.4382(77)	-0.549(34)			
44	90000	s_K	10^{-12} 0.02109(147)		0.0954(46)		
45	3400	T_{KJ}	10^{-12}		1.205(70)		
46	3500	U_{KJ}	10^{-15}		-1.633(65)		
	110010000	X_{aa1}		-32.841(78)			
	110020000	X_{bb1}		-8.635(98)			
	10020000	C_{bb1}		0.0281(77)			
		σ_{rms}	0.93487	0.93345	0.95080	1.01830	

program CALPGM notations [35]

Table 4: Parameters in MHz for the (010) vibrational state of H_2^{32}S and H_2^{34}S .

	Parameter		H_2^{32}S	H_2^{34}S
1	10000 ^a	A	321448.00(92)	320320.70(93)
2	20000	B	276539.09(59)	276527.92(58)
3	30000	C	139968.49(45)	139745.45(33)
4	200	Δ_J	22.7889(120)	22.9990(92)
5	1100	Δ_{JK}	-83.055(36)	-84.175(41)
6	2000	Δ_K	138.498(49)	138.140(56)
7	40100	δ_J	10.3437(43)	10.4004(46)
8	50000	δ_K	-0.12951(55)	-0.14990(69)
9	300	H_J	0.008815(134)	0.011775(75)
10	1200	H_{JJK}	-0.09011(63)	-0.10151(42)
11	2100	H_{JKK}	0.19188(124)	0.16602(110)
12	3000	H_K	-0.02368(114)	-0.01116(144)
13	40200	h_J	10^{-03} 2.551(58)	3.670(36)
14	60000	h_K	10^{-03} 1.7950(59)	1.5654(50)
15	400	L_J	10^{-03} 0.02418(66)	
16	1300	L_{JJJK}	10^{-03} -0.0569(49)	
17	2200	L_{JJKK}	10^{-03} -0.4467(94)	
18	3100	L_{JKKK}	10^{-03} 0.5360(251)	
19	4000	L_K	10^{-03} -0.4698(183)	
20	40300	l_J	10^{-06} 9.21(32)	
21	50200	l_{JJK}	10^{-06} -8.560(127)	-4.340(79)
22	60100	l_{Jkk}	10^{-06} -5.399(79)	
23	500	M_J	10^{-06} -0.10405(155)	
24	1400	M_{JJJK}	10^{-06} 0.3766(132)	
25	2300	M_{JJKK}	10^{-06} 1.625(71)	
26	3200	M_{JJKKK}	10^{-06} -1.798(196)	1.930(140)
27	5000	M_K	10^{-06} 2.674(109)	-4.338(228)
28	40400	p_J	10^{-06} -0.02665(64)	
29	50300	p_{JJJK}	10^{-06} 0.04927(104)	
30	60200	p_{JJKK}	10^{-06} 0.02644(45)	
31	70100	p_{JKKK}	10^{-06} 0.004057(58)	0.01145(71)
32	80000	p_K	10^{-09} 0.4954(111)	-4.28(37)
33	600	S_J	10^{-09} 0.10009(282)	
34	2400	S_{JJK}	10^{-09} -5.056(245)	
35	3300	S_{KKJ}	10^{-09} 5.98(52)	-9.99(59)
36	6000	S_K	10^{-09} -0.000010520(279)	0.00002790(127)
37	50400	s_{JJK}	10^{-09} -0.10802(238)	
38	60300	s_{KKJJ}	10^{-09} -0.06970(114)	-0.07184(225)
39	70200	s_{KKJ}	10^{-09} -0.014413(295)	-0.1020(49)
40	90100		10^{-15} 7.904(239)	
41	100000		10^{-15} 5.208(237)	
42	7100		10^{-12} -0.07457(239)	
43	8000		10^{-12} 0.12992(202)	
	σ_{rms}		0.85759	0.87911

^a Pickett's program CALPGM notations [35]

$K_a \leq 13$ for H_2^{32}S . 181 of these energy levels up to $J \leq 17$ and $K_a \leq 10$ were fitted with a standard deviation of $9.96 \times 10^{-2} \text{ cm}^{-1}$. For H_2^{34}S , 126 energy levels with $J \leq 14$ and $K_a \leq 10$ were obtained, 80 of them up to $J \leq 12$ and $K_a \leq 7$ were used to fit the constants for the $v_2 = 1$ vibrational state of this isotopologue. Ulenikov et al. [29] used the ground state energies for the three isotopologues from Ref. [18].

4.2. Rotational transitions in the ground vibrational state

As can be seen from Table 1, we were able to extend significantly the number of the experimental infrared lines for all of four isotopologues of H_2S considered. For instance, for the transitions within the ground vibrational state of H_2^{32}S , we recorded 926 lines, while only 387 lines from the same spectral region were reported by Flaud et al. [18]. Our spectrum contains lines with J up to 26 and K_a up to 17, which also significantly extends the coverage of the energy levels probed, see Table 1. This table also shows standard deviations between our measured line positions and the previously measured line positions. Our analysis suggests that while we get very good agreement with the previous measurements, there are problems with the predicted line positions tabulated in the databases, see Table 2. Figure 4 illustrates some of these errors in the prediction of the lines positions in the HITRAN and CDMS databases; Table 6 summarises these problems. Figures 5 and 6 give general idea about the accuracy of the line positions available in these databases and that from our fit.

Rotational transitions of the H_2^{36}S isotopologue in its ground vibrational state are detected in this work up to $J = 15$ and $K_a = 11$. Over 50 lines were identified and assigned manually by extrapolation method mentioned above. As a result, 91 lines were assigned as H_2^{36}S lines with a root mean square error of 0.00051 cm^{-1} .

Saleck et al. [16] published three recorded microwave lines as H_2^{36}S rotational transitions. From these lines, only the transitions $2_{0,2} - 1_{1,1}$ line at 686766.635 MHz. could be added to our fit without destroying it. These three transitions are listed in Table 5 and compared to the predicted line positions resulting from our fit.

Table 5: Three H_2^{36}S rotational transitions published by Saleck *et al.* [16] and their counterparts calculated in this work. The numbers in parentheses next to Saleck *et al.* and This work transition values are the experimental uncertainty and the fitting estimated error, respectively. Δ is the difference between the transitions in the two works.

$J'_{K_a, K_c} - J''_{K_a, K_c}$	Saleck <i>et al.</i> (MHz)	This work (MHz)	Δ (MHz)
$3_{3,1} - 3_{2,2}$	559250.950(0.100)	559796(27)	-546
$4_{4,1} - 4_{3,2}$	636677.520(0.100)	637643(37)	-966
$2_{0,2} - 1_{1,1}$	686766.635(0.100) ^a	686772(24)	-6

^a Line is included in our fit.

4.3. Rotational transitions in the bending vibrational state $v_2 = 1$ of H_2^{32}S and H_2^{34}S

We were able to assign initially 214 pure rotational transitions associated with the vibrational state $v_2 = 1$ of H_2^{32}S covering energy levels up to $J = 20$ and $K_a = 14$ using the variationally calculated line list. Then 181 experimental energy levels up to $J \leq 17$ and $K_a \leq 10$ from Ref. [29] were used to calculate 759 rotational transitions in the first excited bending state for H_2^{32}S . 559 of these calculated transitions are in the region $45 - 360 \text{ cm}^{-1}$. The calculations were performed using the combination differences method. As a result, 216 transitions could be matched to transitions in our spectrum with the standard deviation of 0.0004 cm^{-1} . Eight lines were found to have much higher errors in their calculated positions (all close to 0.3 cm^{-1}). All of these lines belong to the energy levels $12_{2,11}$ and $12_{1,11}$, and all the calculated transitions involving these energy levels showed the same problem. We suspect this is a typographical problem in the corresponding table of Ref. [29]. However these transitions were excluded from the fit and these lines are tabulated in the supplementary material. Our spectrum contains 104 transitions that cannot be calculated from Ulenikov *et al.*'s experimental energy levels. These new recorded transitions have quantum numbers up to $J = 22$ and $K_a = 13$. Figure 7 shows the accuracy of the fit performed in this work for H_2^{32}S rotational spectrum in the $v_2=1$ state as well as the calculated rotational transitions using the experimental energy levels of Ulenikov *et al.* [29] and the variationally calculated line list.

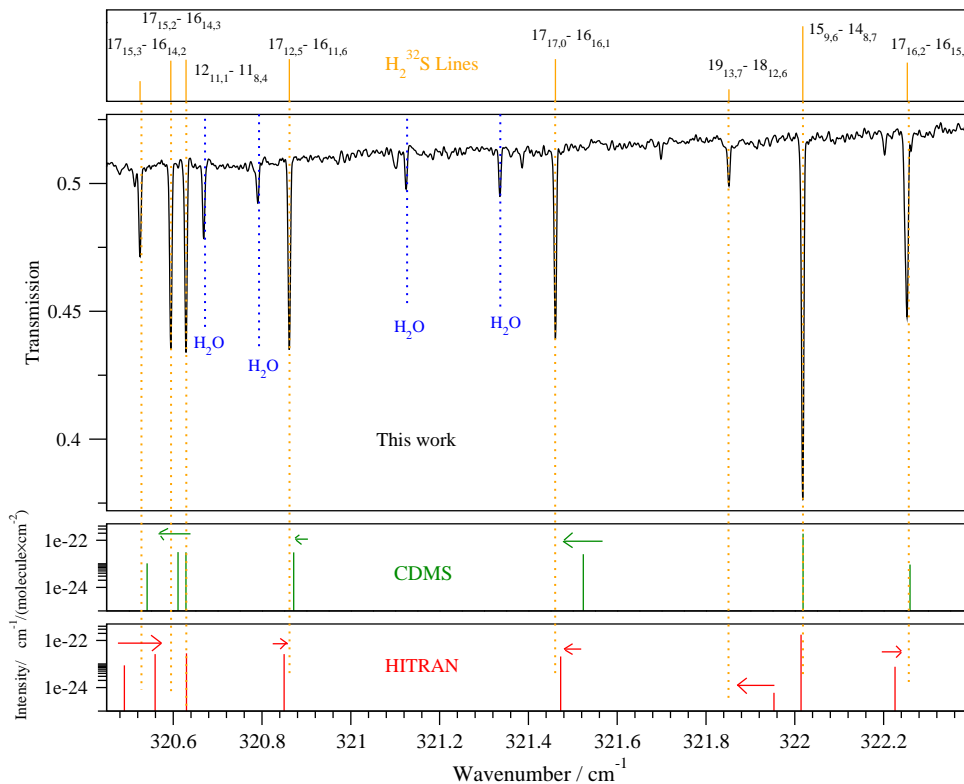


Figure 4: A portion of the absorption spectrum of H_2S recorded at SOLEIL, showing the errors in the line positions predicted in HITRAN and CDMS databases.

For H_2^{34}S , 240 rotational transitions up to $J = 12$ and $K_a = 7$ were calculated using the 80 experimental energy levels published by Ulenikov et al. [29]. 177 lines of these calculated transitions are in the region $45 - 360 \text{ cm}^{-1}$. 42 lines could be assigned in our spectrum using these calculated transitions for $J \leq 10$ and $K_a \leq 6$. After fitting the effective Hamiltonian's constants, 44 extra lines were assigned up to $J = 14$ and $K_a = 10$. Figure 7 shows the accuracy of the fit for H_2^{34}S rotational spectrum in the $v_2 = 1$ state and the calculated rotational transitions using the experimental energy levels of Ulenikov et al. [29].

Figure 2 shows a portion of the assigned spectrum which includes transitions for the four isotopologues of H_2S with the same quantum numbers and some pure rotational $v_2 = 1$ transitions of H_2^{32}S and H_2^{34}S .

Table 6: Summary of the differences in the predicted line positions, in cm^{-1} , in different databases compared to the measured line positions of this work.

Vib. state transition	ISO	Data source	Max. absolute error	error > 0.001 cm^{-1}		Number of lines errors > 0.001 cm^{-1}
				Min. J	Min. K_a	
000-000	H_2^{32}S	HITRAN	0.0687	3	1	213
		CDMS	0.0626	3	2	139
		JPL	0.2141	3	2	238
		This work	0.0025	4	0	105
		Line list [30]	0.0848	3	3	780
	H_2^{33}S	HITRAN	0.0056	2	0	124
		This work	0.0023	6	1	30
	H_2^{34}S	HITRAN	0.0202	6	1	62
		CDMS	0.0087	6	1	40
		This work	0.0022	6	1	35
	H_2^{36}S	This work	0.0014	10	1	3
010-010	H_2^{32}S	This work	0.0023	9	2	18
		Line list [30]	0.3695	2	1	203
	H_2^{34}S	This work	0.0032	7	0	17

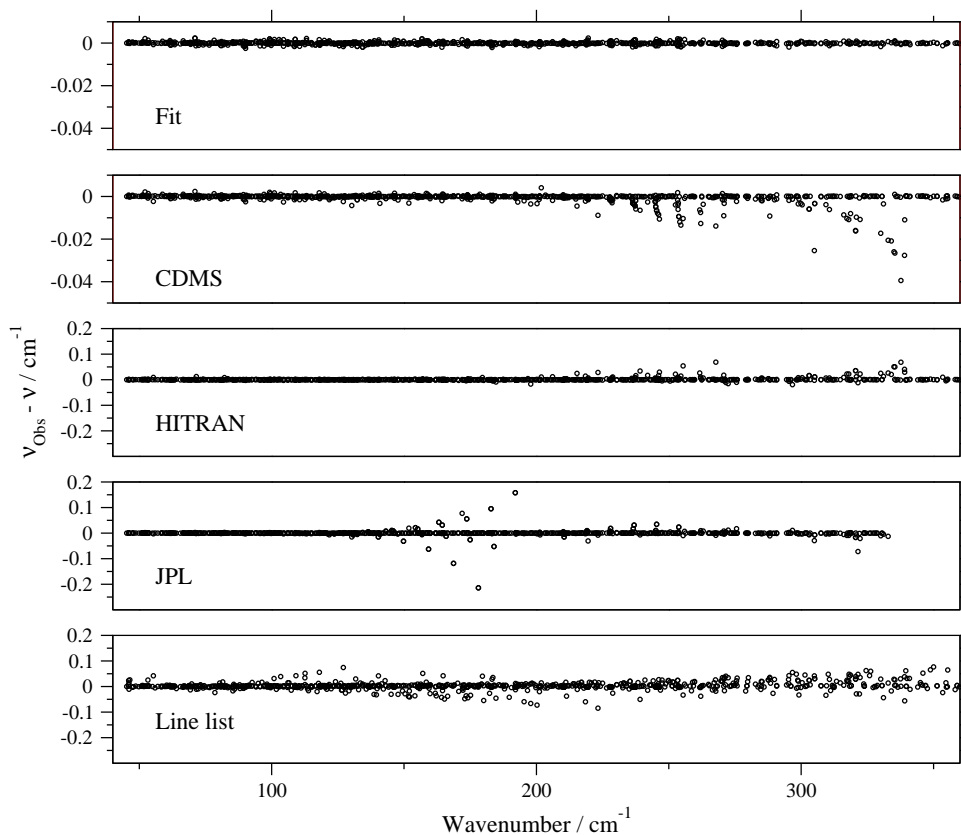


Figure 5: Accuracy of the ground vibrational state rotational transitions of H_2^{32}S in different databases compared to our measurements. $\nu_{\text{Obs}} - \nu$ represents the deviations of the line positions measured here from that of CDMS [23], HITRAN [21], JPL [22] and variational calculations [30]. Note the magnified scale for our fit and CDMS.

5. Conclusions

More than 1300 new lines in the pure rotational band of the absorption spectrum for H_2^{32}S , H_2^{33}S , H_2^{34}S , and H_2^{36}S are detected and assigned in the ground vibrational state as well as in the first excited bending vibrational state for H_2^{32}S and H_2^{34}S . Using these newly detected lines, the effective rotational constants for the four isotopologues of H_2S in the two vibrational states have been fitted. Problems in predicted lines positions from CDMS, and JPL databases made on the basis previous studies were identified. Our new data has been submitted for inclusion in the 2012 update of the HITRAN database [41].

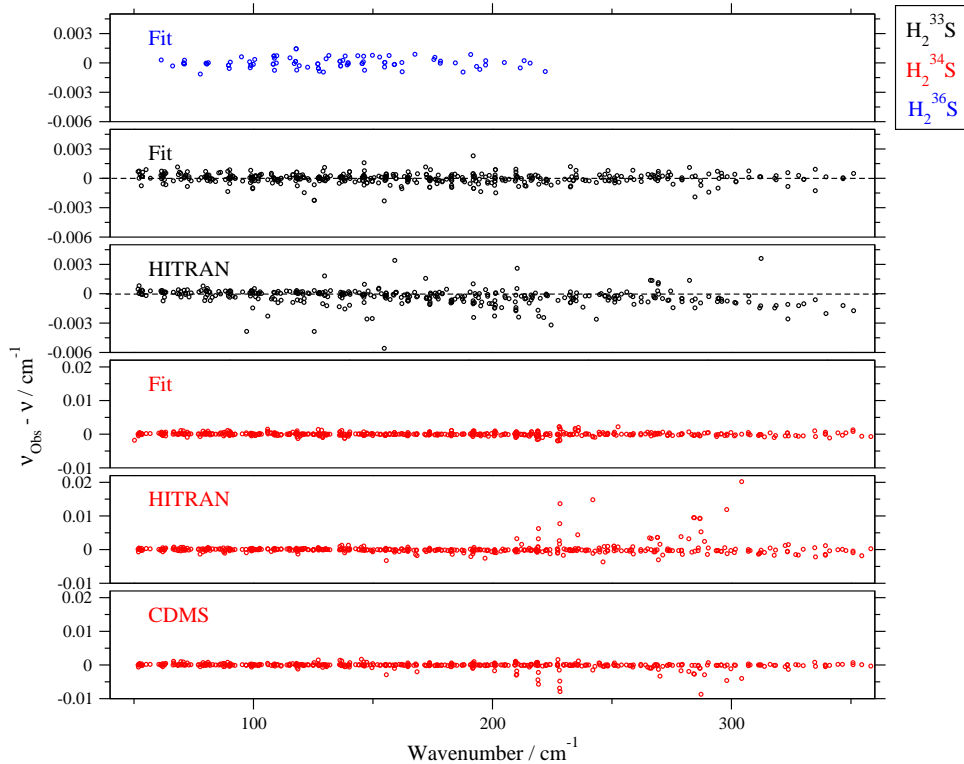


Figure 6: Accuracy of the ground vibrational state rotational transitions of H_2^{33}S and H_2^{34}S in our fit and HITRAN [21] compared to our measurements. $\nu_{\text{Obs}} - \nu$ are given as our observed frequency minus our fit and HITRAN [21]. Note the plots for H_2^{34}S are on a different vertical scale.

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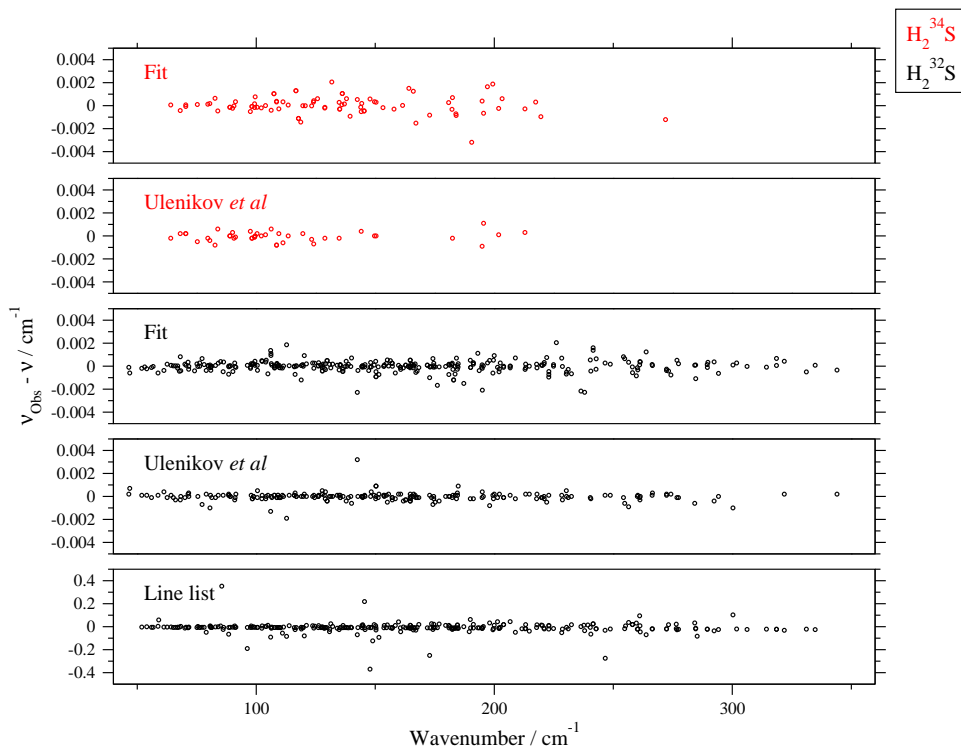


Figure 7: Accuracy of the first bending vibrational state rotational transitions of H_2^{32}S and H_2^{34}S in our fit, and the transitions calculated from the experimental energy levels published by Ulenikov *et al.* [29] compared to our measurements. Also the variational calculations [30] compared to our measurements for H_2^{32}S . $\nu_{\text{Obs}} - \nu$ given as our observed frequency minus our fit, Ulenikov *et al.*'s transitions, and the variational calculations. Note the reduced scale for the line list.

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