

Terahertz Rotational Spectrum of H₂SS. P. BELOV,^{*,1} K. M. T. YAMADA,^{*,2} G. WINNEWISSER,^{*,3} L. POTEAU,[†]
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The rotational transition frequencies of H₂S in the terahertz region were measured precisely up to 1.08 THz by a BWO-based scanning spectrometer at Cologne, Germany, and up to 2.56 THz by a laser sideband spectrometer at Lille, France. The data obtained were analyzed together with the available mmW, sub-mmW, and FIR data using the Watson-type Hamiltonian with the power series expansion of 35 parameters up to J^{10} terms and with the Padé approximation of 24 parameters up to J^8 terms. The results of the two different fits are compared and discussed. The present measurements are compared with those obtained with a FTIR spectrometer at its low-frequency limit, for the purpose of providing H₂S lines in the terahertz region as an absolute calibrator for FIR FT spectroscopy. © 1995 Academic Press, Inc.

I. INTRODUCTION

Similarly to the rotational spectrum of water, H₂O, hydrogen sulfide, H₂S, represents a very light asymmetric top molecule. In terms of Ray's asymmetry parameter, $\kappa(\text{H}_2\text{S}) = 0.5234$ and $\kappa(\text{H}_2\text{O}) = -0.4362$, both molecules are almost in between the two limiting cases of a prolate and an oblate top and are thus very asymmetric. The spectra of both molecules are beset with interactions, which presumably arise from their asymmetry and the large-amplitude motions of the hydrogen atoms. Experimentally, their rotational spectra show no obvious "coherent" line pattern as can be expected for molecules in the prolate or oblate limiting cases. The lines are rather spread out over the entire millimeter-wave (mmW) and submillimeter-wave (sub-mmW) region. Theoretically, sizable difficulties exist in fitting and predicting the line positions, particularly those of high J and K values. Thus, any highly accurate new measurements are of great value in testing the existing different Hamiltonians by the quality of the fits to the experimental data.

The pure rotational spectrum of H₂S has been the subject of numerous investigations and we cite only the most recent papers which also summarize the previous work. Flaud *et al.* (1) measured the far-infrared spectrum with a Fourier transform spectrometer at a resolution of 0.005 cm^{-1} and analyzed the observed 387 line positions in the range from 50 to 300 cm^{-1} together with the 39 mmW and sub-mmW lines

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listed by Helminger *et al.* (2). Very recently, Yamada and Klee (3) remeasured the far-infrared spectrum of H₂S with a FTIR spectrometer in Giessen at a slightly higher resolution of 0.0017 cm⁻¹. From the combined analysis of the available mmW and sub-mmW data and their far-infrared data, they obtained results similar to those of Flaud *et al.*

The molecule H₂S is one of the most promising candidates for the experimental observation of the fourfold clustering effect in high- J , high- K_a rotational levels, which is expected to be observable in the terahertz region. This effect was observed in the H₂Se molecule (4–7) and calculated for H₂S using the potential energy surface fitted to the experimental data (8). The high-precision measurement of transitions with higher rotational quantum numbers could be very useful for the assignment of intra-cluster transitions.

We report in this paper highly accurate new measurements taken with the Cologne terahertz spectrometer and with the Lille sideband laser system. These new data are analyzed together with the existing data and serve as a test for the employed Hamiltonians, i.e., for the power series expanded Watson-type Hamiltonian and the Hamiltonian with the Padé formulation.

II. EXPERIMENTAL PROCEDURES

The new H₂S spectra up to 1.08 THz were obtained with the Cologne terahertz spectrometer, whereas the data higher in frequency, i.e., up to 2.56 THz, were recorded with the laser sideband spectrometer at Lille.

At Cologne, high-resolution scanning spectroscopy in the terahertz region has recently been accomplished by frequency and phase stabilization of high-output frequencies of backward wave oscillators (BWO) (9, 10). The BWOs were supplied by the ISTOK Research and Production Co., located in Fryazino, Moscow Region. The accuracy in measurement for single lines, as monitored by reference measurements on CO, is estimated to be better than 20 kHz, whereas the sensitivity of the spectrometer at 1 THz has been determined to reach 10⁻⁷ cm⁻¹ in fortunate cases. Since the wavelength region or the frequency coverage of the terahertz spectrometer overlaps with the long wavelength range of FTIR spectrometers, absolute calibration of the data of the latter instruments may now be achieved. For the ground state of the main isotopomer H₂³²S, we have measured 57 transitions between 535 and 1076 GHz and some lines in the mmW region.

At Cologne, these measurements are part of a program recently started to measure and analyze the spectra of molecules with astrophysical relevance up into the terahertz region. Airborne, satellite, and ground-based interstellar sub-mmW observations, together with advances in receiver development, have raised the interest and the need for highly precise line positions in the terahertz region. We have therefore expanded the present measurements for the main isotope to the rare isotopomers H₂³⁴S and H₂³³S (11).

In Lille, a far-infrared laser microwave single sideband spectrometer was used in the sub-mmW region. It is an improved version of the spectrometer described in Refs. (12, 13). The output of an optically pumped sub-mmW laser and that of a tunable microwave synthesizer are mixed in a Schottky diode. The tunability of the sideband radiation is ±18 GHz around the laser frequency. A heterodyne receiver is used to detect the sideband signal, with the unmodulated part of the primary laser power being used as a local oscillator. This enables us to keep the sideband propagation losses at a very low level, and thus to optimize the sensitivity. The reproducibility of the mea-

TABLE I
Observed Line Positions in MHz Used in the Analysis

Transition	Observed MHz	σ_{obs} kHz	$\Delta(W)$ kHz	$\Delta(P)$ kHz	Transition	Observed MHz	σ_{obs} kHz	$\Delta(W)$ kHz	$\Delta(P)$ kHz
$3_{3,1} - 4_{0,4}$	35028.150	70.0	26.0	161.8	$7_{3,2} - 7_{4,3}$	555253.972(K)	70.0	31.8	165.3
$7_{1,6} - 6_{4,3}$	89497.990	70.0	34.7	177.9	$6_{4,2} - 6_{3,3}$	567079.618(K)	70.0	28.6	8.8
$4_{2,2} - 5_{1,5}$	119664.420	70.0	9.1	38.1	$3_{3,1} - 3_{2,2}$	568050.557(K)	70.0	36.1	12.4
$10_{2,8} - 9_{5,5}$	131463.479(K)	70.0	37.7	78.8	$5_{5,0} - 5_{4,1}$	579799.042(K)	70.0	8.6	81.8
$10_{3,8} - 9_{4,5}$	149662.617(L)	50.0	28.4	426.2	$8_{6,2} - 8_{5,3}$	593170.000(K)	70.0	6.5	69.2
$10_{3,8} - 9_{4,5}$	149662.619(K)	70.0	26.4	428.2	$5_{3,2} - 5_{2,3}$	611441.629(K)	70.0	35.2	124.1
$10_{4,6} - 11_{3,9}$	150964.861(K)	70.0	28.7	93.7	$7_{6,1} - 7_{5,2}$	626474.625(K)	70.0	40.9	114.6
$10_{5,6} - 11_{2,9}$	155595.799(K)	70.0	11.7	320.0	$4_{4,1} - 4_{3,2}$	650374.186(K)	70.0	51.6	24.5
$7_{3,4} - 8_{2,7}$	161438.450	70.0	43.1	5.2	$8_{2,6} - 7_{5,3}$	657148.801(K)	70.0	0.9	95.8
$1_{1,0} - 1_{0,1}$	168762.762	10.0	10.8	29.7	$4_{2,2} - 4_{1,3}$	665393.738(K)	70.0	16.4	101.8
$7_{2,6} - 6_{3,3}$	175009.580	70.0	35.2	219.1	$2_{0,2} - 1_{1,1}$	687303.468(K)	70.0	15.1	149.3
$7_{4,4} - 8_{1,7}$	185099.880	70.0	2.5	246.8	$9_{7,2} - 9_{6,3}$	689120.170	70.0	17.7	503.4
$4_{1,4} - 3_{2,1}$	204140.170	70.0	23.9	121.1	$3_{1,2} - 3_{0,3}$	708470.430	70.0	257.0	252.2
$2_{2,0} - 2_{1,1}$	216710.435	10.0	3.2	30.6	$10_{7,3} - 10_{6,4}$	733032.813(K)	100.0	104.8	537.3
$4_{3,2} - 5_{0,5}$	228556.270	70.0	22.3	153.9	$2_{1,2} - 1_{0,1}$	736034.096(K)	70.0	11.6	170.0
$11_{5,7} - 10_{8,2}$	270489.520(N)	100.0	39.4	70.5	$3_{2,2} - 3_{1,3}$	747301.890	70.0	19.7	15.1
$9_{7,2} - 10_{4,7}$	293967.090(N)	100.0	17.8	337.2	$6_{6,0} - 6_{5,1}$	748241.490	70.0	84.9	74.1
$3_{3,0} - 3_{2,1}$	300505.560	70.0	34.1	47.5	$5_{5,1} - 5_{4,2}$	749432.280	70.0	5.8	10.2
$6_{1,5} - 5_{4,2}$	314437.790	70.0	11.1	22.1	$4_{3,2} - 4_{2,3}$	765937.910	70.0	53.9	76.7
$8_{4,5} - 7_{7,0}$	325325.170(N)	100.0	23.6	299.2	$9_{4,6} - 10_{1,9}$	768445.471(K)	100.0	64.9	83.5
$3_{2,1} - 3_{1,2}$	369101.450	70.0	61.0	59.9	$6_{2,4} - 7_{1,7}$	777907.970(K)	100.0	16.1	65.5
$4_{3,1} - 4_{2,2}$	369126.912	70.0	12.9	29.8	$11_{8,3} - 11_{7,4}$	782355.888(K)	100.0	67.6	477.5
$3_{1,3} - 2_{2,0}$	392617.840	70.0	33.1	190.4	$6_{3,4} - 7_{0,7}$	784758.248(K)	100.0	47.1	125.6
$2_{1,1} - 2_{0,2}$	393450.490	70.0	24.2	15.9	$11_{4,8} - 10_{5,5}$	785745.685(K)	100.0	40.3	480.1
$5_{4,1} - 5_{3,2}$	407676.730	70.0	7.7	122.9	$8_{7,1} - 8_{6,2}$	794222.464(K)	100.0	5.0	353.4
$9_{2,7} - 8_{5,4}$	410377.930	500.0	24.2	226.1	$5_{4,2} - 5_{3,3}$	800852.070(K)	100.0	92.8	44.1
$4_{4,0} - 4_{3,1}$	424314.820	70.0	42.1	95.0	$14_{5,10} - 13_{6,7}$	804636.115(K)	100.0	0.4	40.5
$5_{1,4} - 4_{4,1}$	436373.360	70.0	91.3	74.1	$8_{5,3} - 8_{4,4}$	804733.232(K)	100.0	15.8	71.5
$11_{4,7} - 12_{3,10}$	440698.370(N)	100.0	3.4	408.5	$7_{2,5} - 6_{5,2}$	827201.473(K)	100.0	33.8	64.4
$11_{5,7} - 12_{2,10}$	441837.360(N)	100.0	22.8	720.8	$5_{2,4} - 4_{3,1}$	827915.046(K)	100.0	5.9	26.7
$5_{5,0} - 6_{2,5}$	451946.970(N)	70.0	0.4	5.0	$6_{5,2} - 6_{4,3}$	854965.950(K)	100.0	42.7	73.2
$1_{1,1} - 0_{0,0}$	452390.330	70.0	12.6	110.7	$6_{6,1} - 6_{5,2}$	860132.559(K)	100.0	80.0	127.3
$12_{3,9} - 11_{6,6}$	457114.830(N)	100.0	90.3	145.8	$6_{2,4} - 5_{5,1}$	863805.837(K)	100.0	30.1	99.9
$5_{2,3} - 6_{1,6}$	461632.430(N)	200.0	2.0	19.8	$7_{4,3} - 7_{3,4}$	880057.374(K)	100.0	29.7	215.0
$9_{3,7} - 8_{4,4}$	475148.220(N)	200.0	30.1	245.9	$12_{9,3} - 12_{8,4}$	900350.769(K)	100.0	57.0	554.8
$8_{4,5} - 9_{1,8}$	475701.480(N)	200.0	7.6	239.7	$7_{7,0} - 7_{6,1}$	910665.789(K)	100.0	128.4	319.8
$5_{3,3} - 6_{0,6}$	493085.000(N)	200.0	81.5	26.8	$7_{6,2} - 7_{5,3}$	928640.535(K)	100.0	38.8	105.4
$6_{5,1} - 6_{4,2}$	493362.160	70.0	33.4	189.3	$4_{2,3} - 3_{3,0}$	930145.832(K)	100.0	34.9	90.0
$2_{2,1} - 2_{1,2}$	505565.230	70.0	12.8	48.1	$6_{4,3} - 6_{2,4}$	947260.470(K)	100.0	14.1	224.6
$6_{2,5} - 5_{3,2}$	535528.818(K)	70.0	32.7	183.7	$11_{7,4} - 11_{6,5}$	970575.280(K)	100.0	46.8	178.0

measurements is better than 400 kHz. However, since the frequency of the FIR laser is not accurately known, we assumed the experimental uncertainty to be 500 kHz in the present analysis. One mmW transition, $10_{3,8} \leftarrow 9_{4,5}$, was measured with a computer-controlled mmW spectrometer using superheterodyne detection (14). The accuracy of this measurement is better than 50 kHz and agrees within 2 kHz with the independent measurements at Cologne, as listed in Table I; we have included both measurements in the fit. The $10_{7,3} \leftarrow 10_{6,4}$ transition at 733 032.813 MHz was measured independently at the Cologne and Lille laboratories with exactly the same line position, which may be a fortuitous accident.

All mmW and sub-mmW line frequencies used in the present analysis are listed in Table I; they consist of the lines measured in this work in Cologne (marked with "K")

TABLE I—*Continued*

Transition	Observed MHz	σ_{obs} kHz	$\Delta(W)$ kHz	$\Delta(P)$ kHz	Transition	Observed MHz	σ_{obs} kHz	$\Delta(W)$ kHz	$\Delta(P)$ kHz
9 _{8,1} – 9 _{7,2}	973853.486(K)	100.0	14.2	130.0	13 _{10,3} – 13 _{9,4}	1075532.420(K)	100.0	13.5	117.1
7 _{7,1} – 7 _{6,2}	976182.689(K)	100.0	111.7	250.2	7 _{3,4} – 7 _{2,5}	1271191.060(L)	500.0	1334.0	1535.8
10 _{3,7} – 9 _{6,4}	994980.915(K)	100.0	88.7	270.8	4 _{0,4} – 3 _{1,3}	1280325.290(L)	500.0	1002.6	1152.0
3 _{1,3} – 2 _{0,2}	1002778.698(K)	100.0	12.9	169.9	4 _{1,4} – 3 _{0,3}	1281714.080(L)	500.0	1810.0	1958.8
4 _{1,3} – 4 _{0,4}	1018347.230(K)	100.0	18.5	28.2	8 _{5,4} – 8 _{4,5}	1284386.960(L)	500.0	113.5	211.3
8 _{7,2} – 8 _{6,3}	1019453.648(K)	100.0	18.5	263.1	11 _{11,0} – 11 _{10,1}	1378842.460(L)	500.0	219.5	211.9
5 _{3,3} – 5 _{2,4}	1023122.572(K)	100.0	43.8	52.8	10 _{6,5} – 10 _{5,6}	1538414.430(L)	500.0	22.8	234.9
11 _{9,2} – 11 _{8,3}	1024023.115(K)	100.0	9.5	163.8	9 _{4,5} – 9 _{3,6}	1540101.170(L)	500.0	506.8	202.6
6 _{4,3} – 6 _{3,4}	1025884.417(K)	100.0	24.3	21.2	4 _{1,3} – 3 _{2,2}	1551369.730(L)	500.0	101.4	239.0
4 _{2,3} – 4 _{1,4}	1026511.165(K)	100.0	36.0	40.6	9 _{5,5} – 9 _{4,6}	1557067.200(L)	500.0	784.5	607.7
7 _{5,3} – 7 _{4,4}	1040275.600(K)	100.0	36.9	92.0	8 _{3,5} – 8 _{2,6}	1571153.100(L)	500.0	1497.1	1326.4
8 _{8,0} – 8 _{7,1}	1056278.051(K)	100.0	145.3	14.6	6 _{2,5} – 6 _{1,6}	1608602.840(L)	500.0	28.9	116.4
10 _{3,7} – 11 _{2,10}	1059153.358(K)	100.0	11.8	129.3	8 _{3,6} – 8 _{2,7}	1882773.010(L)	500.0	425.5	152.0
10 _{6,4} – 10 _{5,5}	1063111.587(K)	100.0	42.0	502.5	7 _{1,6} – 7 _{0,7}	1900140.870(L)	500.0	251.6	183.8
13 _{4,9} – 12 _{7,8}	1067447.995(K)	100.0	36.4	17.5	7 _{2,6} – 7 _{1,7}	1900177.280(L)	500.0	674.6	-669.0
8 _{6,3} – 8 _{5,4}	1071313.608(K)	100.0	103.2	87.0	6 _{3,3} – 5 _{4,2}	2560498.730(L)	500.0	193.1	477.7
2 _{2,1} – 1 _{1,0}	1072836.548(K)	100.0	25.3	172.8					

Note: The experimental uncertainties assumed in the present analysis are given in the column of σ_{obs} . Observed calculated values are listed in the columns of $\Delta(W)$ and $\Delta(P)$ for the Watson-type and Padé-type Hamiltonians respectively. The frequencies indicated by (K) have been measured in Cologne, (L) in Lille, and (N) in Nizhnii Novgorod. The frequencies with no indications are taken from the literature.

and in Lille (marked with “L”) and of the unpublished data from the Nizhnii Novgorod laboratory (marked with “N”) obtained using a sub-mmW synthesizer and an acoustic cell (15), together with those line positions reported by Helminger *et al.* (2) and by Burenin *et al.* (16).

III. HAMILTONIANS USED FOR THE ANALYSIS

In the analysis of the entire data set now available for H₂³²S we have taken two approaches. First, we intended to obtain a fit to the power series expansion of the Watson-type Hamiltonian, and second, we applied a Padé-type formalism to the data with the aim of finding the most reliable way of predicting new line positions outside the range of the J , K values covered by the fitted data.

Extended Watson-Type Hamiltonian

The Hamiltonian used here is the conventional Watson S -reduced Hamiltonian up to sextic centrifugal distortion terms, extended to include higher than sextic terms in the angular momentum. For the present data set we have included terms up to J^{10} . Extensions of the Watson Hamiltonian have been carried out by several authors. In the present paper we follow the formulation of Yamada and Klee (3); the standard Watson-type S -reduced Hamiltonian for asymmetric tops,

$$\begin{aligned}
\hat{H}_{\text{rot}}^S = & \frac{1}{2} (\tilde{B}_x^{(S)} + \tilde{B}_y^{(S)}) \hat{J}^2 + \{ \tilde{B}_z^{(S)} - \frac{1}{2} (\tilde{B}_x^{(S)} + \tilde{B}_y^{(S)}) \} \hat{J}_z^2 - D_J \hat{J}^4 - D_{JK} \hat{J}^2 \hat{J}_z^2 \\
& - D_K \hat{J}_z^4 + H_J \hat{J}^6 + H_{JK} \hat{J}^4 \hat{J}_z^2 + H_{KJ} \hat{J}^2 \hat{J}_z^4 + H_K \hat{J}_z^6 + \{ \frac{1}{4} (\tilde{B}_x^{(S)} - \tilde{B}_y^{(S)}) \\
& + d_1 \hat{J}^2 + h_1 \hat{J}^4 \} (\hat{J}_+^2 + \hat{J}_-^2) + (d_2 \hat{J}^2 + h_2 \hat{J}^4) (\hat{J}_+^4 + \hat{J}_-^4) + h_3 (\hat{J}_+^6 + \hat{J}_-^6), \quad (1)
\end{aligned}$$

has been extended up to J^{10} terms by adding

$$\begin{aligned} \hat{H}' = & -L_J \hat{J}^8 - L_{62} \hat{J}^6 \hat{J}_z^2 - L_{44} \hat{J}^4 \hat{J}_z^4 - L_{26} \hat{J}^2 \hat{J}_z^6 - L_K \hat{J}_z^8 + S_J \hat{J}^{10} + S_{82} \hat{J}^8 \hat{J}_z^2 \\ & + S_{64} \hat{J}^6 \hat{J}_z^4 + S_{46} \hat{J}^4 \hat{J}_z^6 + S_{28} \hat{J}^2 \hat{J}_z^8 + S_K \hat{J}_z^{10} + (l_1 \hat{J}^6 + s_1 \hat{J}^8)(\hat{J}_+^2 + \hat{J}_-^2) \\ & + (l_2 \hat{J}^4 + s_2 \hat{J}^6)(\hat{J}_+^4 + \hat{J}_-^4) + (l_3 \hat{J}^2 + s_3 \hat{J}^4)(\hat{J}_+^6 + \hat{J}_-^6) \\ & + (l_4 + s_4 \hat{J}^2)(\hat{J}_+^8 + \hat{J}_-^8) + s_5(\hat{J}_+^{10} + \hat{J}_-^{10}). \end{aligned} \quad (2)$$

In this Hamiltonian, the centrifugal terms starting with capital letters represent diagonal terms and those with lowercase letters represent off-diagonal terms. The diagonal centrifugal terms are defined by following the sign convention of alternative polynomials; i.e., D and L terms appear with negative signs in the above equation. The off-diagonal terms are always defined with positive signs.

Inclusion of the newly measured precise sub-mmW line frequencies in the data set gives rise to considerable difficulty in fitting the line positions with the Watson-type Hamiltonian. Yamada and Klee (3), as well as Flaud *et al.* (1), were able to fit 40 (39 in the analysis of Flaud *et al.*) mmW and sub-mmW lines, together with FTIR lines, by using an extended Watson-type Hamiltonian with a full set up to J^8 terms and diagonal J^{10} terms as well. With the currently available mmW and sub-mmW transitions, together with the FTIR data of Ref. (3), more parameters had to be adjusted to obtain an acceptable fit. In the present study we have varied all 35 parameters given in the above Hamiltonian, i.e., with a full set of parameters up to J^{10} terms in the weighted least-squares fitting (17).

The weights were assumed to be reciprocally proportional to the squares of the estimated uncertainties of the line positions listed in the σ_{obs} column in Table I. The lines measured by laser sideband spectroscopy were found to be less accurate than the other sub-mmW lines, and thus they are weighted less in the least-squares analysis. For the FTIR data we used the same weighting scheme as described in Ref. (3).

The best fit parameters for 113 mmW and sub-mmW lines and 350 FTIR lines have been determined using the above Hamiltonian in the I' axis representation as listed in Table II. The deviations of the observed line positions from the calculated ones (obs. – calc. values) are listed in the $\Delta(W)$ column in Table I. The root-mean-square (rms) deviation for the FIR data included in the fit was $0.12 \times 10^{-3} \text{ cm}^{-1}$, which is very close to the limit of experimental uncertainty of the FTIR spectrometer used in the measurement: $0.05 \times 10^{-3} \text{ cm}^{-1}$ (3). The slightly larger rms deviation for the mmW and sub-mmW data of 301 kHz is mainly caused by the less accurate laser sideband measurements. For almost all other lines, the deviations are less than 100 kHz, and they also correspond very well to the experimental uncertainties.

We have tried also to fit the same data with the Watson-type A -reduced Hamiltonian. With the same number of adjusted parameters, i.e., 35 parameters for the full set up to the J^{10} power, we obtained a considerably worse fit for the FIR data than with the S -reduced Hamiltonian: a rms deviation of 365 kHz for mmW and sub-mmW transitions and $0.989 \times 10^{-3} \text{ cm}^{-1}$ for FIR data.

Padé Hamiltonian

As an alternative to the effective Hamiltonian expanded in power series, one can also apply the one-dimensional approximation of the A -reduced Watson-type Hamiltonian in Padé form (18) with I' axis choice

TABLE II

Molecular Parameters of H₂S in the Ground Vibrational State
Determined Using an *S*-Reduced Hamiltonian with an *I'* Axis
Choice^a

Parameter	Value	Unit	Parameter	Value	Unit
\hat{A}	310583.5763(57)	MHz			
\hat{B}	270367.6834(70)	MHz			
\hat{C}	141820.0365(42)	MHz			
D_J	20.86146(23)	MHz			
D_{JK}	-76.22912(46)	MHz	d_1	8.866046(90)	MHz
D_K	117.72209(47)	MHz	d_2	0.641754(30)	MHz
H_J	10.2140(40)	kHz			
H_{JK}	-90.174(17)	kHz	h_1	2.8827(20)	kHz
H_{KJ}	155.615(31)	kHz	h_2	-0.9547(10)	kHz
H_K	-33.816(21)	kHz	h_3	1.24878(26)	kHz
L_J	5.442(29)	Hz			
L_{62}	-69.16(22)	Hz	ℓ_1	1.048(15)	Hz
L_{44}	0.21517(62)	kHz	ℓ_2	-0.383(11)	Hz
L_{26}	0.26752(69)	kHz	ℓ_3	1.7655(49)	Hz
L_K	0.15787(34)	kHz	ℓ_4	0.4094(12)	Hz
S_J	3.097(77)	mHz			
S_{82}	38.4(10)	mHz	s_1	0.996(39)	mHz
S_{64}	0.1548(37)	Hz	s_2	0.427(37)	mHz
S_{46}	-0.3370(54)	Hz	s_3	0.994(23)	mHz
S_{28}	0.3517(41)	Hz	s_4	0.7553(72)	mHz
S_K	-98.7(22)	mHz	s_5	0.3248(19)	mHz
rms(IR)	0.116 × 10 ⁻³	cm ⁻¹			
rms(MW)	301	kHz			

^aNumbers in parentheses are standard deviations (1 σ) in units of the last digit.

$$\hat{H}_{\text{rot}}^{\text{Pade}} = \hat{H}_D + \frac{1}{4} [\hat{J}_+^2 + \hat{J}_-^2, \hat{h}_{\text{off}}], \quad (3)$$

where

$$\hat{H}_D = c_0 + \frac{c_1(c_0c_2 - c_{12}) - c_0(c_1c_3 - c_{22})}{c_0c_2 - c_{12} + c_2c_1 - c_0c_3 + c_1c_3 - c_{22}}, \quad (4)$$

$$\hat{h}_{\text{off}} = b_0 + \frac{b_1(b_0b_2 - b_{12}) - b_0(b_1b_3 - b_{22})}{b_0b_2 - b_{12} + b_2b_1 - b_0b_3 + b_1b_3 - b_{22}}, \quad (5)$$

with

$$c_0 = \frac{1}{2} (B + C) \hat{J}^2 + \left(A - \frac{B + C}{2} \right) \hat{J}_z^2, \quad (6)$$

$$c_1 = -\Delta_J \hat{J}^4 - \Delta_{JK} \hat{J}^2 \hat{J}_z^2 - \Delta_K \hat{J}_z^4, \quad (7)$$

$$c_2 = \Phi_J \hat{J}^6 + \Phi_{JK} \hat{J}^4 \hat{J}_z^2 + \Phi_{KJ} \hat{J}^2 \hat{J}_z^4 + \Phi_K \hat{J}_z^6, \quad (8)$$

$$c_3 = L_J \hat{J}^8 + L_{JK} \hat{J}^6 \hat{J}_z^2 + L_{KJ} \hat{J}^4 \hat{J}_z^4 + L_{KK} \hat{J}^2 \hat{J}_z^6 + L_K \hat{J}_z^8, \quad (9)$$

$$b_0 = \frac{1}{2} (B - C) \hat{J}^2, \quad (10)$$

$$b_1 = -2(\delta_J \hat{J}^2 + \delta_K \hat{J}_z^2), \quad (11)$$

$$b_2 = 2(\phi_J \hat{J}^4 + \phi_{JK} \hat{J}^2 \hat{J}_z^2 + \phi_K \hat{J}_z^4), \quad (12)$$

$$b_3 = 2(l_J \hat{J}^6 + l_{42} \hat{J}^4 \hat{J}_z^2 + l_{24} \hat{J}^2 \hat{J}_z^4 + l_K \hat{J}_z^6). \quad (13)$$

The signs of L terms in c_3 (Eq. (9)) as well as those of l terms in b_3 (Eq. (13)) are defined here to be positive, and are opposite to those defined by Yamada and Klee (3).

Instead of the 35 parameters up to J^{10} terms, we used the full set of the parameters up to J^8 power as given above. All 24 parameters have been adjusted in the fitting procedure.

The best fit parameters determined using the Padé-type Hamiltonian are listed in Table III. They are determined from the same set of data and with the same weighting scheme as in the fit using the Watson-type Hamiltonian. The obs. – calc. values for this fit are listed in the $\Delta(P)$ column in Table I.

For the transition $3_{1,2} \leftarrow 3_{0,3}$ near 708 GHz, a considerable discrepancy was found between the observed and calculated line positions (about 250 kHz), consistently for both Hamiltonians, as listed in Table I. This discrepancy originates presumably from the measurement error, because the line position of such a low- J transition can be well calculated with the parameters obtained in the present work. In due course, this transition will be remeasured with our highly precise spectrometer.

TABLE III

Molecular Parameters of H_2S in the Ground Vibrational State Determined Using an A -reduced Padé Hamiltonian with an I' Axis Choice^a

Parameter	Value	Unit	Parameter	Value	Unit
A	310589.956(97)	MHz			
B	270357.091(89)	MHz			
C	141825.393(76)	MHz			
Δ_J	19.57339(18)	MHz			
Δ_{JK}	68.37075(51)	MHz	δ_J	8.861618(75)	MHz
Δ_K	111.03945(54)	MHz	δ_K	3.96586(18)	MHz
Φ_J	8.2944(29)	kHz			
Φ_{JK}	46.363(16)	kHz	ϕ_J	4.13849(93)	kHz
Φ_{KJ}	38.0638(79)	kHz	ϕ_{JK}	-14.7056(59)	kHz
Φ_K	41.7257(86)	kHz	ϕ_K	37.9664(89)	kHz
L_J	5.500(18)	Hz			
L_{62}	42.82(14)	Hz	ℓ_J	2.9049(45)	Hz
L_{44}	0.11552(40)	kHz	ℓ_{JK}	16.856(53)	Hz
L_{26}	0.177714(50)	kHz	ℓ_{KJ}	23.28(12)	Hz
L_K	0.14107(24)	kHz	ℓ_K	57.35(11)	Hz
rms(IR)	0.265×10^{-3}	cm^{-1}			
rms(MW)	366	kHz			

^aNumbers in parentheses are standard deviations (1σ) in units of the last digit.

IV. DISCUSSION

The comparison of different fits performed with the conventional power series models and with the Padé or Padé–Borel models has quite a long history. One of the obvious possibilities is the comparison of the fits achieved with the two models using the same number of parameters and even with terms of exactly the same order. This was done, e.g., in Ref. (19) for the data on the (010) vibrational state of H₂O. The improvement in the standard deviation for the Padé–Borel model was dramatic: it was 60 times better. In Ref. (20), the ground state H₂S mmW and sub-mmW transitions available in the literature at the time, those measured in Nizhnii Novgorod, and IR transitions measured by the FT spectrometer in Bologna were compared in this manner. The improvement of the standard deviation with the Padé model was much more modest, only 3 times better. This could be explained by the fact that water molecules in the

TABLE IV
Comparison of the Predicted Line Positions (in cm⁻¹) with
Observed Line Positions

Transition	Obs.	Watson	Δ	Padé	Δ
16 _{6,11} – 16 _{5,12}	106.05970	106.0593	0.0004	106.0586	0.0011
16 _{3,14} – 16 _{2,15}	138.36090	138.3611	-0.0002	138.3616	-0.0007
16 _{2,15} – 16 _{1,16}	149.80899	149.8397	-0.0307	149.8026	0.0064
17 _{1,16} – 17 _{0,17}	159.27150	159.3317	-0.0602	159.2626	0.0089
17 _{0,17} – 16 _{1,16}	164.44136	164.4120	0.0294	166.4442	-0.0028
18 _{1,18} – 17 _{0,17}	173.66963	173.6176	0.0520	173.6724	-0.0028
17 _{1,16} – 16 _{2,15}	173.90366	173.9040	-0.0003	173.9042	-0.0005
19 _{0,19} – 18 _{1,18}	182.87143	182.7830	0.0884	182.8739	-0.0025
16 _{4,3} – 15 _{3,12}	183.09412	183.0927	0.0014	183.0931	0.0010
18 _{2,17} – 17 _{1,16}	183.09937	183.1008	-0.0014	183.1000	-0.0006
17 _{2,15} – 16 _{3,14}	183.13941	183.1398	-0.0004	183.1408	-0.0014
20 _{1,20} – 19 _{0,19}	192.04560	191.8998	0.1458	192.0466	-0.0010
17 _{3,14} – 16 _{4,3}	192.20101	192.1989	0.0021	192.2019	-0.0009
19 _{1,18} – 18 _{2,17}	192.26903	192.2711	-0.0021	192.2681	0.0009
18 _{3,16} – 17 _{2,15}	192.28345	192.2859	-0.0025	192.2845	-0.0010
17 _{4,13} – 16 _{5,12}	201.13460	201.1324	0.0022	201.1357	-0.0011
21 _{0,21} – 20 _{1,20}	201.19038	200.9572	0.2332	201.1886	0.0018
18 _{4,15} – 17 _{3,14}	201.27837	201.2748	0.0036	201.2808	-0.0024
19 _{2,17} – 18 _{3,16}	201.39838	201.4047	-0.0063	201.4020	-0.0036
20 _{2,19} – 19 _{1,18}	201.40861	201.4143	-0.0057	201.4054	0.0032
17 _{5,12} – 16 _{6,11}	209.98336	209.9816	0.0018	209.9817	0.0016
22 _{1,22} – 21 _{0,21}	210.30550	209.9402	0.3653	210.2976	0.0079
19 _{3,16} – 18 _{4,15}	210.32470	210.3187	0.0060	210.3310	-0.0063
20 _{3,18} – 19 _{2,17}	210.48233	210.4967	-0.0144	210.4851	-0.0028
17 _{6,11} – 16 _{7,10}	218.78840	218.7882	0.0002	218.7857	0.0027
12 _{12,1} – 11 _{11,0}	235.36471	235.3646	0.0001	235.3648	-0.0001
12 _{12,0} – 11 _{11,1}	235.37188	235.3720	-0.0001	235.3722	-0.0003
13 _{11,3} – 12 _{10,2}	247.49443	247.4946	-0.0002	247.4944	0.0001
13 _{10,3} – 12 _{9,4}	248.47606	248.4761	0.0000	248.4752	0.0009
13 _{11,2} – 12 _{10,3}	248.81075	248.8107	0.0001	248.8104	0.0003
13 _{12,2} – 12 _{11,1}	251.52434	251.5243	0.0000	251.5259	-0.0016
13 _{12,1} – 12 _{11,2}	251.61946	251.6193	0.0002	251.6209	-0.0014
13 _{13,0} – 12 _{12,1}	253.33810	253.3393	-0.0012	253.3386	-0.0005
13 _{9,4} – 12 _{8,5}	258.57861	258.5791	-0.0005	258.5779	0.0008
14 _{11,4} – 13 _{10,3}	259.67261	259.6732	-0.0006	259.6720	0.0006
14 _{11,3} – 13 _{10,4}	265.30249	265.3028	-0.0003	265.3009	0.0016
14 _{12,3} – 13 _{11,2}	266.49139	266.4925	-0.0011	266.4920	-0.0006
14 _{12,2} – 13 _{11,3}	267.13373	267.1350	-0.0013	267.1344	-0.0007
14 _{13,2} – 13 _{12,1}	269.74986	269.7505	-0.0006	269.7530	-0.0031
14 _{13,1} – 13 _{12,2}	269.79392	269.7949	-0.0010	269.7974	-0.0034
14 _{14,1} – 13 _{13,0}	270.92950	270.9323	-0.0028	270.9282	0.0013
15 _{13,3} – 14 _{12,2}	284.94320	284.9540	-0.0108	284.9522	-0.0090
15 _{15,0} – 14 _{14,1}	288.14610	288.1571	-0.0110	288.1431	0.0030

TABLE V

Comparison of the Line Positions (in MHz)
Measured by FTIR and Submillimeter-Wave
Spectroscopy^a

Transition	FTIR	Sub-mmW	Δ
3 _{1,3} – 2 _{0,2}	1002773.6	1002778.698	5.1
4 _{1,3} – 4 _{0,4}	1018344.8	1018347.230	2.4
8 _{7,2} – 8 _{6,3}	1019452.9	1019453.648	0.7
5 _{3,3} – 5 _{2,4}	1023120.0	1023122.572	2.6
11 _{9,2} – 11 _{8,3}	1024024.7	1024023.115	1.6
6 _{4,3} – 6 _{3,4}	1025883.8	1025884.417	-0.6
4 _{2,3} – 4 _{1,4}	1026508.1	1026511.165	-3.1
7 _{5,3} – 7 _{4,4}	1040271.7	1040275.600	3.9
8 _{8,0} – 8 _{7,1}	1056274.8	1056278.051	3.2
10 _{6,4} – 10 _{5,5}	1063109.4	1063111.587	2.2
8 _{6,3} – 8 _{5,4}	1071312.0	1071313.608	1.6
2 _{2,1} – 1 _{1,0}	1072834.8	1072836.548	1.7
13 _{10,3} – 13 _{9,4}	1075525.8	1075532.420	6.6
7 _{3,4} – 7 _{2,5}	1271188.8	1271191.060	2.3
4 _{0,4} – 3 _{1,3}	1280322.3	1280324.900	2.6
4 _{1,4} – 3 _{0,3}	1281711.2	1281714.080	-2.9
8 _{5,4} – 8 _{4,5}	1284385.3	1284386.960	1.7
11 _{11,0} – 11 _{10,1}	1378843.2	1378842.460	0.7
10 _{6,5} – 10 _{5,6}	1538412.8	1538414.430	1.6
9 _{4,5} – 9 _{3,6}	1540099.5	1540101.170	-1.7
4 _{1,3} – 3 _{2,2}	1551368.7	1551369.730	1.0
9 _{5,5} – 9 _{4,6}	1557068.3	1557067.200	1.1
8 _{3,5} – 8 _{2,6}	1571153.3	1571153.100	0.2
6 _{2,5} – 6 _{1,6}	1608601.4	1608602.840	1.4
8 _{3,6} – 8 _{2,7}	1882773.4	1882773.010	0.4
6 _{4,3} – 5 _{4,2}	2560500.5	2560498.730	1.8

^a The difference of ν (FTIR) – ν (sub-mmW) is given in the column Δ . The FTIR line positions measured in units of cm^{-1} are converted to MHz by a factor of $1 \text{ cm}^{-1} = 29\,979.2458 \text{ MHz}$.

(010) excited state are much floppier than hydrogen sulfide molecules. Thus, the advantage of the Padé model, particularly for the less rigid molecules, if one uses the same number of parameters is established. However, the advantage of the conventional model rests in its conventionality. The power series based programs for the effective Hamiltonian are available in every spectroscopic laboratory and they are widely used for the analysis of high-resolution molecular spectra.

In the present study, we found that the extended version of the Watson-type Hamiltonian requires more parameters than the Padé model to reproduce the observed line positions with reasonable discrepancies. This problem in fitting the data indicates that the Watson-type Hamiltonian is less capable of fitting the rotational spectrum of H_2S . The result of a 35-parameter fit with the Watson-type Hamiltonian is only slightly better than that of a 24-parameter fit with the Padé-type Hamiltonian, as shown in the rms deviations listed in Tables II and III. However, it is hardly possible to ascribe physical meaning to the higher-order terms such as J^8 and J^{10} .

In the present fits, we have not included the FTIR data of Flaud *et al.* (1), who measured and assigned several high- J transitions up to $J = 22$. These data allow us to test the capability of the two Hamiltonians, Watson type and Padé type, of predicting line positions. In Table IV, we compare the observed transition wavenumbers of $J >$

15, and some low- J but high- K_a transitions, with those calculated by the two methods, using parameters listed in Tables II and III. It is clearly seen that the extrapolation capability of the Pad  -type expansion is significantly—by an order of magnitude—better than that of the conventional power series expansion. The attempt to include those high- J , K_a transitions results in a significant deterioration of the fit with the extended Watson-type Hamiltonian, and only a slight worsening in the Pad   model. Continuing the comparison of the two models, we think that, in fitting the highly precise H₂S rotational data for the ground state, the conventional power series model reaches the limit of its applicability. As more terahertz data become available, the question of the appropriate fitting procedure may become even more accentuated.

Another implication of the present measurements concerns the absolute calibration of the FTIR data set. As mentioned, the frequency coverage of the present sub-mmW measurements overlaps with the long wavelength range of FTIR spectrometers. In Table V we compare the two independent measurements in units of MHz. The FTIR data taken from Ref. (3) were calibrated with selected water lines (21). The agreement of the two independent measurements is extremely good. Systematic red shifts of the FTIR data in the very low frequency range reflect the diffraction effect in the FTIR spectrometer's optical assembly. Since the diffraction effect depends on the wavelength, it requires a nonlinear calibration of the line positions. Thus, it is very important in FTIR spectroscopy in the FIR to have many reliable calibration lines at the very-low-wavenumber end of the region. The sub-mmW data in the terahertz region as presented in the present study should be appropriate for such a purpose.

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