Submillimeter Wave Spectrum of $HS^{34}SH$

P. Mittler, G. Winnewisser, and K. M. T. Yamada

I. Physikalisches Institut, Universität zu Köln, Köln, Germany

Z. Naturforsch. **44a**, 718–722 (1989); received June 27, 1989

The rotational spectrum of ^{34}S-substituted disulfane, $HS^{34}SH$, has been measured between 60 and 420 GHz, yielding for the first time the rotational constants $A = 146694.949$ MHz, $B = 6779.018$ MHz and $C = 6776.339$ MHz, together with a complete set of J^4 and J^6 distortion constants.

Introduction

The rotational spectrum of disulfane, HSSH has been studied in a series of papers [1–6] and recently work has been resumed with the aim of understanding some of the subtle details of the HSSH spectrum, its barrier to internal rotation and its isotopic species [7], [8]. In addition it is now highly desirable and possible to have a full substitution structure of disulfane available, which can be compared with the ongoing theoretical chemistry ab-initio structural calculations.

In the present paper we report the spectrum of $HS^{34}SH$ in the frequency range between 60 and 420 GHz, greatly extending the earlier $^rQ_0$-branch measurements of Winnewisser et al. [1]. The values of the rotational and centrifugal distortion parameters of this molecule in the ground state have been significantly improved. All of the 15 parameters up to the J^6 terms have been determined by a least squares analysis.

Experimental

The disulfane spectrum was recorded with the Cologne digitized millimeter wave spectrometer which has recently been described by Bester et al. [9] and Mauer et al. [10]. A 4-m-long free-space cell made of pyrex glass with a 10 cm inner diameter was used as an absorption cell, both ends of which were sealed with PTFE windows. As for all sulfane work it is important to use an acidified glass absorption cell to increase the lifetime up to several hours of the otherwise rather unstable molecule. The R- and P-branches as well as the $K = 2 - 1$ Q-branch of $HS^{34}SH$ in natural abundance were recorded by our millimeter wave spectrometer with significantly higher S/N ratios than the early measurements of Winnewisser and Helminger. The samples of HSSH were prepared in the Institute for Inorganic Chemistry of our University by Hahn [11] according to the preparation schemes outlined by Fehér and Baudler [12–17].

Reprint request to Dr. K. M. T. Yamada, I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, D-5000 Köln 41, FRG.

Rotational Spectrum

In a previous series of papers describing the rotational spectrum of HSSH [1–6] in the millimeter and submillimeter wave region, only the $^rQ_0$-branch of $HS^{34}SH$ was reported. The outstanding spectral characteristics for the symmetric species $HS^{34}SH$ are the perpendicular type spectrum of the molecule with a typical intensity alternation of 3:1 for adjacent J rotational lines (see Figure 1). From the interpretation of the HSSH spectra, the electric dipole moment is aligned with the C_2 symmetry axis, which is the c-axis, bisecting the dihedral angle between the two SH-bonds. For a single substitution such as for $HS^{34}SH$, $DS^{34}SD$ or HSSD the C_2 symmetry of the molecule is lost: consequently no effect of nuclear spin statistics on the intensity of the rotational spectrum is observable, and in principle the perpendicular spectrum could produce both c- and b-type transitions, depending on the rotation of the principal axis system with respect to the direction of the electric dipole moment. For $HS^{34}SH$ this effect is very small and therefore not observable. However both c- and b-type spectra have been observed for HSSD [7] and very recently also for $DS^{34}SD$ which will be discussed elsewhere.

The spectrum of $HS^{34}SH$ follows closely that of $H^{32}S^{32}SH$ and posed therefore no assignment problem. In Fig. 1 we show the $^rQ_1$-branch near 419.6 GHz

0932-0784 / 89 / 0800-0718 $ 01.30/0. – Please order a reprint rather than making your own copy.

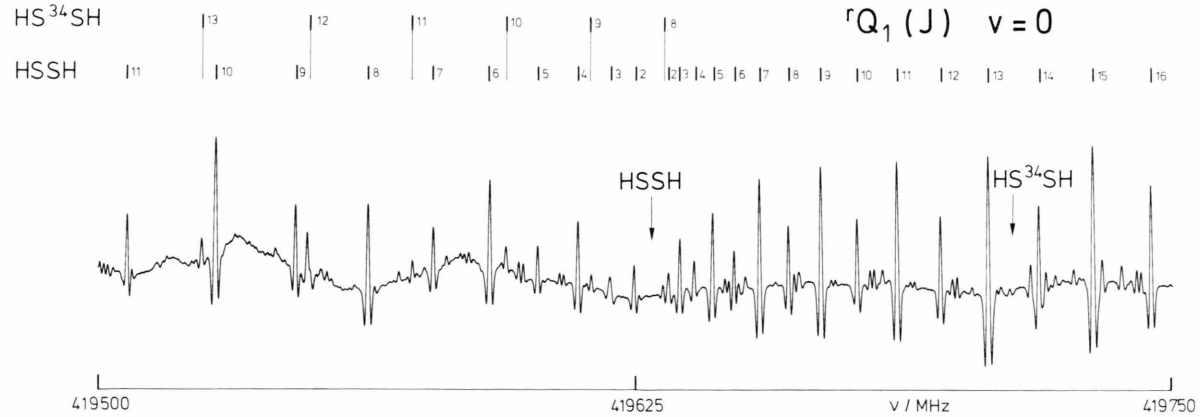

Fig. 1. $^rQ_1$-branch of $HS^{34}SH$ and HSSH. The assignment is indicated for HSSH. For $HS^{34}SH$ the lower frequency transitions. $J_{2,J-1}-J_{1,J-1}$ of the $^rQ_1$-branch have been identified between $J=13$ and 8. The lower J lines fall into the congested part of the spectrum. The subband origins of these Q branches are indicated by arrows.

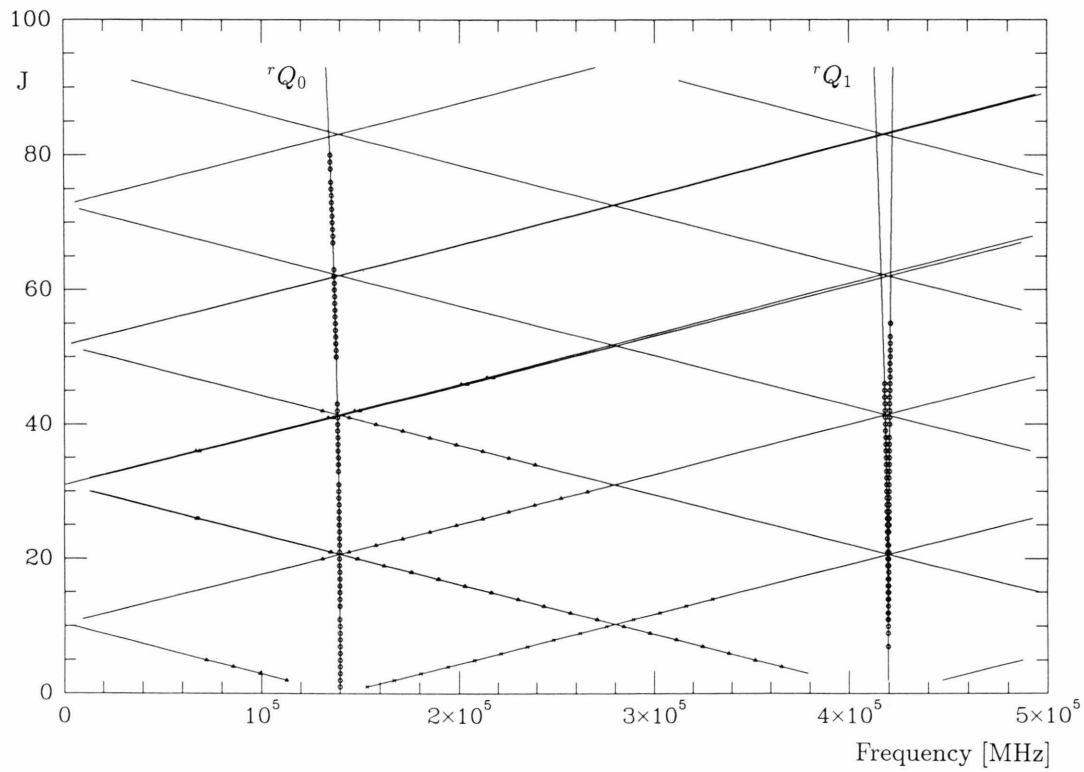

Fig. 2. Fortrat-Diagram of $HS^{34}SH$. Measured transitions are denoted by points, the calculated positions are represented by lines.

recorded with high sensitivity. This recording might be compared to Fig. 1 of Winnewisser and Helminger [4] in 1972, indicating the considerably improved sensitivity, which made the detection of the $^rQ_1$-$HS^{34}SH$ submillimeter spectrum possible.

The Fortrat diagramm shown in Fig. 2 presents an overview of the measured transition frequencies, which are summerized in Table 1. As in the analysis of the HSSH spectra, the recorded $HS^{34}SH$ lines were fit to the Watson S-reduced Hamiltonian up to sextic

Table 1. Observed and Calculated Frequencies of $HS^{34}SH$ in MHz.

J	K_a	K_c	<-	J	K_a	K_c	observed	calculated	o−c
4	1	3	<-	5	0	5	72152.419	72152.400	0.0193
20	0	20	<-	19	1	18	130803.456	130803.511	-0.0550
21	0	21	<-	20	1	19	144309.136	144309.202	-0.0662
22	0	22	<-	21	1	20	157811.030	157811.087	-0.0572
25	0	25	<-	24	1	23	198292.591	198292.625	-0.0335
26	0	26	<-	25	1	24	211777.928	211778.003	-0.0751
28	0	28	<-	27	1	26	238735.215	238735.286	-0.0711
29	0	29	<-	28	1	27	252206.834	252206.932	-0.0980
1	1	1	<-	1	0	1	139913.333	139913.356	-0.0233
2	1	2	<-	2	0	2	139910.335	139910.351	-0.0161
3	1	3	<-	3	0	3	139905.833	139905.843	-0.0098
4	1	4	<-	4	0	4	139899.835	139899.831	0.0040
5	1	5	<-	5	0	5	139892.315	139892.315	-0.0001
6	1	6	<-	6	0	6	139883.261	139883.294	-0.0330
7	1	7	<-	7	0	7	139872.764	139872.767	-0.0030
8	1	8	<-	8	0	8	139860.715	139860.733	-0.0176
9	1	9	<-	9	0	9	139847.190	139847.190	0.0003
10	1	10	<-	10	0	10	139832.113	139832.137	-0.0237
11	1	11	<-	11	0	11	139815.562	139815.572	-0.0099
13	1	13	<-	13	0	13	139777.897	139777.899	-0.0024
14	1	14	<-	14	0	14	139756.809	139756.787	0.0216
15	1	15	<-	15	0	15	139734.151	139734.155	-0.0042
16	1	16	<-	16	0	16	139710.006	139710.000	0.0057
17	1	17	<-	17	0	17	139684.310	139684.320	-0.0100
18	1	18	<-	18	0	18	139657.090	139657.111	-0.0213
19	1	19	<-	19	0	19	139628.340	139628.371	-0.0313
20	1	20	<-	20	0	20	139598.062	139598.097	-0.0347
21	1	21	<-	21	0	21	139566.249	139566.284	-0.0352
22	1	22	<-	22	0	22	139532.895	139532.930	-0.0353
23	1	23	<-	23	0	23	139498.022	139498.031	-0.0092
24	1	24	<-	24	0	24	139461.581	139461.583	-0.0020
25	1	25	<-	25	0	25	139423.603	139423.582	0.0212
26	1	26	<-	26	0	26	139384.018	139384.023	-0.0052
27	1	27	<-	27	0	27	139342.901	139342.903	-0.0019
33	1	33	<-	33	0	33	139063.100	139063.118	-0.0180
34	1	34	<-	34	0	34	139010.907	139010.929	-0.0215
35	1	35	<-	35	0	35	138957.104	138957.136	-0.0322
36	1	36	<-	36	0	36	138901.720	138901.735	-0.0150
37	1	37	<-	37	0	37	138844.721	138844.719	0.0022
38	1	38	<-	38	0	38	138786.072	138786.081	-0.0095
39	1	39	<-	39	0	39	138725.796	138725.817	-0.0205
40	1	40	<-	40	0	40	138663.887	138663.917	-0.0303
50	1	50	<-	50	0	50	137953.460	137953.467	-0.0173
51	1	51	<-	51	0	51	137873.101	137873.107	-0.0057
52	1	52	<-	52	0	52	137791.032	137791.019	0.0127
55	1	55	<-	55	0	55	137534.365	137534.307	0.0585
56	1	56	<-	56	0	56	137445.289	137445.222	0.0675
57	1	57	<-	57	0	57	137354.427	137354.364	0.0633
58	1	58	<-	58	0	58	137261.785	137261.723	0.0617
59	1	59	<-	59	0	59	137167.228	137167.291	-0.0625
60	1	60	<-	60	0	60	137071.109	137071.055	0.0537
67	1	67	<-	67	0	67	136346.000	136346.057	-0.0567
68	1	68	<-	68	0	68	136234.945	136235.018	-0.0731
69	1	69	<-	69	0	69	136122.033	136122.079	-0.0455
70	1	70	<-	70	0	70	136007.202	136007.226	-0.0241
71	1	71	<-	71	0	71	135890.415	135890.449	-0.0338
72	1	72	<-	72	0	72	135771.713	135771.735	-0.0215
73	1	73	<-	73	0	73	135651.072	135651.071	0.0012
74	1	74	<-	74	0	74	135528.482	135528.445	0.0370
75	1	75	<-	75	0	75	135403.824	135403.845	-0.0205
76	1	76	<-	76	0	76	135277.285	135277.256	0.0286
2	1	1	<-	1	0	1	167028.926	167028.941	-0.0151
5	1	4	<-	4	0	4	207706.687	207706.747	-0.0596
6	1	5	<-	5	0	5	221267.263	221267.309	-0.0459
8	1	7	<-	7	0	7	248389.641	248389.645	-0.0035
14	2	12	<-	15	1	14	216243.175	216243.208	-0.0335
14	2	13	<-	15	1	15	216567.652	216567.727	-0.0752
15	2	13	<-	16	1	15	202673.531	202673.573	-0.0418
15	2	14	<-	16	1	16	203041.800	203041.865	-0.0651
18	2	17	<-	19	1	19	162481.564	162482.312	-0.7478
19	2	17	<-	20	1	19	148396.562	148396.588	-0.0262
19	2	18	<-	20	1	20	148968.879	148968.927	-0.0479
20	2	18	<-	21	1	20	134828.260	134828.281	-0.0205
20	2	19	<-	21	1	21	135458.927	135459.005	-0.0778
25	2	23	<-	26	1	25	66997.755	66997.763	-0.0078
25	2	24	<-	26	1	26	67966.177	67966.229	-0.0517
36	1	35	<-	35	2	33	68566.479	68566.477	0.0019
36	1	36	<-	35	2	34	66677.923	66677.855	0.0677
41	1	40	<-	40	2	38	136275.066	136275.065	0.0014
41	1	41	<-	40	2	39	133792.320	133792.286	0.0341
42	1	42	<-	41	2	40	147196.162	147196.134	0.0278
46	1	45	<-	45	2	43	203918.592	203918.594	-0.0016
46	1	46	<-	45	2	44	200742.878	200742.872	0.0062
47	1	46	<-	46	2	44	217438.468	217438.473	-0.0050
47	1	47	<-	46	2	45	214111.574	214111.601	-0.0272
10	2	9	<-	10	1	9	419615.207	419615.196	0.0107
11	2	10	<-	11	1	10	419595.151	419595.172	-0.0206
11	2	9	<-	11	1	11	419771.493	419771.467	0.0261

Table 1. (continued)

J	K_a	K_c	<-	J	K_a	K_c	observed	calculated	o−c
12	2	11	<-	12	1	11	419573.392	419573.344	0.0475
12	2	10	<-	12	1	12	419781.594	419781.577	0.0168
14	2	13	<-	14	1	13	419524.317	419524.303	0.0145
14	2	12	<-	14	1	14	419804.282	419804.264	0.0181
15	2	14	<-	15	1	14	419497.074	419497.098	-0.0243
16	2	15	<-	16	1	15	419468.133	419468.113	0.0201
16	2	14	<-	16	1	16	419830.237	419830.206	0.0306
17	2	16	<-	17	1	16	419437.380	419437.353	0.0273
18	2	17	<-	18	1	17	419404.730	419404.824	-0.0942
18	2	16	<-	18	1	18	419859.375	419859.362	0.0134
19	2	18	<-	19	1	18	419370.607	419370.535	0.0724
19	2	17	<-	19	1	19	419875.140	419875.129	0.0110
20	2	19	<-	20	1	19	419334.491	419334.491	-0.0002
20	2	18	<-	20	1	20	419891.693	419891.681	0.0121
21	2	20	<-	21	1	20	419296.724	419296.702	0.0221
21	2	19	<-	21	1	21	419908.997	419909.010	-0.0133
22	2	21	<-	22	1	21	419257.198	419257.175	0.0231
22	2	20	<-	22	1	22	419927.129	419927.110	0.0191
23	2	22	<-	23	1	22	419215.926	419215.919	0.0073
24	2	23	<-	24	1	23	419172.990	419172.942	0.0477
24	2	22	<-	24	1	24	419965.632	419965.589	0.0425
25	2	24	<-	25	1	24	419128.263	419128.255	0.0080
25	2	23	<-	25	1	25	419985.999	419985.953	0.0458
26	2	25	<-	26	1	25	419081.868	419081.866	0.0015
26	2	24	<-	26	1	26	420007.047	420007.055	-0.0078
27	2	26	<-	27	1	26	419033.805	419033.787	0.0180
27	2	25	<-	27	1	27	420028.869	420028.886	-0.0165
28	2	27	<-	28	1	27	418984.015	418984.027	-0.0118
28	2	26	<-	28	1	28	420051.446	420051.436	0.0100
29	2	28	<-	29	1	28	418932.595	418932.597	-0.0019
29	2	27	<-	29	1	29	420074.702	420074.697	0.0051
30	2	28	<-	30	1	30	420098.635	420098.658	-0.0232
31	2	29	<-	31	1	31	420123.287	420123.310	-0.0227
32	2	31	<-	32	1	31	418768.405	418768.402	0.0027
32	2	30	<-	32	1	32	420148.628	420148.641	-0.0132
33	2	32	<-	33	1	32	418710.411	418710.409	0.0020
33	2	31	<-	33	1	33	420174.654	420174.642	0.0124
34	2	33	<-	34	1	33	418650.826	418650.806	0.0203
35	2	34	<-	35	1	34	418589.585	418589.605	-0.0203
36	2	35	<-	36	1	35	418526.833	418526.821	0.0116
37	2	36	<-	37	1	36	418462.466	418462.468	-0.0015
38	2	37	<-	38	1	37	418396.562	418396.558	0.0040
38	2	36	<-	38	1	38	420314.276	420314.282	-0.0055
39	2	38	<-	39	1	38	418329.098	418329.107	-0.0092
40	2	39	<-	40	1	39	418260.137	418260.130	0.0070
40	2	38	<-	40	1	40	420374.402	420374.410	-0.0084
41	2	40	<-	41	1	40	418189.661	418189.641	0.0195
41	2	39	<-	41	1	41	420405.351	420405.340	0.0113
42	2	41	<-	42	1	41	418117.675	418117.657	0.0177
42	2	40	<-	42	1	42	420436.816	420436.828	-0.0119
43	2	42	<-	43	1	42	418044.205	418044.193	0.0117
43	2	41	<-	43	1	43	420468.874	420468.861	0.0127
44	2	42	<-	44	1	44	420501.425	420501.426	-0.0011
45	2	43	<-	45	1	45	420534.449	420534.508	-0.0590
46	2	44	<-	46	1	46	420568.120	420568.093	0.0273
47	2	45	<-	47	1	47	420602.154	420602.165	-0.0114
48	2	46	<-	48	1	48	420636.707	420636.711	-0.0043
49	2	47	<-	49	1	49	420671.703	420671.715	-0.0122
50	2	48	<-	50	1	50	420707.189	420707.162	0.0273
51	2	49	<-	51	1	51	420743.041	420743.035	0.0058
52	2	50	<-	52	1	52	420779.322	420779.320	0.0021
53	2	51	<-	53	1	53	420816.002	420816.000	0.0024
54	2	52	<-	54	1	54	420853.123	420853.058	0.0648
35	3	32	<-	36	2	34	211943.183	211943.204	-0.0208
36	3	33	<-	37	2	35	198445.743	198445.757	-0.0139
36	3	34	<-	37	2	36	198352.484	198352.482	0.0023
40	3	37	<-	41	2	39	144498.679	144498.668	0.0106
40	3	38	<-	41	2	40	144358.908	144358.898	0.0100
41	3	38	<-	42	2	40	131023.309	131023.295	0.0137
41	3	39	<-	42	2	41	130869.599	130869.601	-0.0019

terms yielding a set of rotational and centrifugal constants which are summerized in Table 2. From the previous measurements essentially only the values of $A-B$ and $C-B$ were known. As expected, a comparison between the molecular constants of HSSH and $HS^{34}SH$ bears out the close similarity of the two species.

In addition to the ground state measurements we have also observed the first excited torsional state

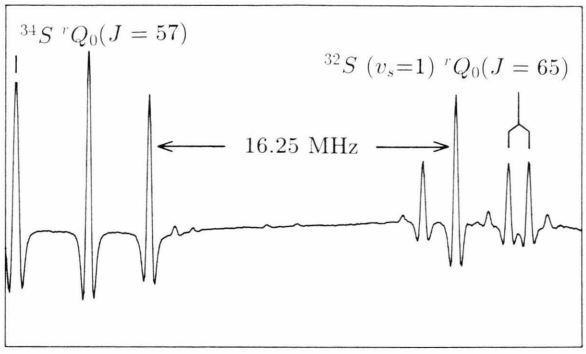

Fig. 3. A 16 MHz-doublet of the first excited state $v_t=1$ of $HS^{34}SH$, $^{r}Q_0$ (25). The lines without indication are the unidentified ones.

Table 2. Comparison of the Ground State Constants of $H^{32}S^{34}SH$[a].

Constant	$HS^{34}SH$[b]	Unit	HSSH[c]	Unit
A	146694.94953(78)	MHz	146858.138(41)	MHz
B	6779.01852(49)	MHz	6970.4272(36)	MHz
C	6776.33936(49)	MHz	6967.6862(35)	MHz
D_J	5.11835(46)	kHz	5.39849(25)	kHz
D_{JK}	81.459(10)	kHz	85.5254(64)	kHz
D_K	2.4148(22)	MHz	2.42354(93)	MHz
d_1	8.2000(61)	Hz	8.892 (19)	Hz
d_2	−24.558(10)	Hz	−27.2835(58)	Hz
H_J	−1.26(12)	mHz	−1.533(31)	mHz
H_{JK}	−21.9(34)	mHz	−19.6(16)	mHz
H_{KJ}	1.7(13)	Hz	1.48(87)	Hz
H_K	−0.68(22)	kHz	−0.207(94)	kHz
h_1	0.00479(76)	mHz	0.0890(57)	mHz
h_2	0.0470(53)	mHz	−0.0277(32)	mHz
h_3	−0.009(37)	mHz	−0.0573(25)	mHz

[a] The numbers in the parentheses are one standard deviation in units of the last digit quoted.
[b] This work.
[c] Derived from recent millimeter wave measurements [18].

Table 3. Observed Transition Frequencies of $HS^{34}SH$ in the $v_t=1$ state.

J	Lower Component (MHz)	Higher Component (MHz)
1	139116.271	
2	139105.360	139121.161
3	139089.009	139104.856
4	139067.331	139083.139
5		
6	139007.582	139023.394
7	138969.583	138985.386
8	138926.106	138941.953
9	138877.248	138893.105
10	138822.977	138838.826
11		
12	138698.159	138714.072
13	138627.661	138643.576
14		138567.643
15	138470.398	138486.365
16	138383.704	
17	138291.573	138307.582
18	138194.091	138210.134
19	138091.232	
20		137999.088
21	137869.376	137885.456
22	137750.414	137766.563
23	137626.100	137642.276
24	137496.436	137512.649
25	137361.425	137377.675
26	137221.093	137237.378
27	137075.440	137091.773
28	136924.468	136940.839
29	136768.205	136784.617
30	136606.639	136623.099
31	136439.782	136456.285
32	136267.651	
33	136090.252	136106.859
34		
35	135719.730	135736.418
36	135526.591	135543.329
37	135328.236	
38	135124.695	135141.577
39	134915.919	134932.845
40	134702.009	134718.986
41	134482.868	134499.938
42	134258.613	
43	134029.167	134046.364
44	133794.597	133811.853
45		133572.205

($v_t=1$) for the $^{r}Q_0$-branch as listed in Table 3. By fitting the data by a least squares method we have obtained the torsional energy splitting ΔE, rotational constants $A-(B+C)/2$ and $(B-C)$, and the centrifugal distortion constant D_{JK}. Because of the correlation among the ΔE and two $A-(B+C)/2$, we have constained in the first procedure the $A-(B+C)/2$ value of the upper state of the torsional doubling to be identical to that of the lower component. There is no significant effect on the observed torsional splitting upon substitution: The observed splitting ΔE of $HS^{34}SH$ due to tunneling is 7.8904 MHz, which is very close to that of the normal species. Recently the barriers to internal rotation have been determined for HSSH to be 2840 cm^{-1} and 2040 cm^{-1} for the cis- and trans-configurations respectively, which lead to the relatively small splitting observed here for the first excited torsional state (see Figure 3).

Table 4. Molecular Constants of $HS^{34}SH$ in the First Excited Torsional State[a].

Constant	Predicted Value	Unit
ΔE	7.8904(57)	MHz
Higher Component		
$A-(B+C)/2$[b]	139129.5260(57)	MHz
$B-C$	8.8134(34)	MHz
D_{JK}	0.51318(84)	MHz
Lower Component		
$A-(B+C)/2$[b]	139129.5260(57)	MHz
$B-C$	8.8134(35)	MHz
D_{JK}	0.51245(88)	MHz

[a] The numbers in the parentheses are one standard deviation in units of the last digit quoted.
[b] Constrained to be identical for the lower and the upper component.

Conclusion

In the process of our ongoing work on the disulfanes with the aim of understanding in detail their spectra and structure we have measured for the first time the complete $HS^{34}SH$ spectrum, i.e. P-, Q- and R-branch transitions, which resulted in a complete set of molecular constants. It is our intention to supplement the existing data with further measurements on HSSD and DSSD to an extend that it will be possible to derive a full substitution structure. If sufficient excited state transitions can be measured we might finally derive an equilibrium structure, important for testing ab-initio calculations of the structure.

Acknowledgement

The disulfane sample was kindly provided by Dr. Hahn, Institut für Anorganische Chemie, Universität zu Köln. This work was supported by the Deutsche Forschungsgemeinschaft, special grant SFB 301.

[1] G. Winnewisser, M. Winnewisser, and W. Gordy, J. Chem. Phys. **49,** 3465 (1968).
[2] G. Winnewisser, J. Chem. Phys. **56,** 2944 (1972).
[3] G. Winnewisser and P. Helminger, J. Chem. Phys. **56,** 2954 (1972).
[4] G. Winnewisser and P. Helminger, J. Chem. Phys. **56,** 2967 (1972).
[5] G. Winnewisser, J. Chem. Phys. **57,** 1803 (1972).
[6] G. Winnewisser, J. Chem. Phys. **41,** 534 (1972).
[7] S. Urban, E. Herbst, P. Mittler, G. Winnewisser, and K. M. T. Yamada, J. Mol. Spectrosc. in press.
[8] E. Herbst and G. Winnewisser, Chem. Phys. Lett. **155,** 572 (1989).
[9] M. Bester, M. Tanimoto, B. Vowinkel, G. Winnewisser, and K. M. T. Yamada, Z. Naturforsch. **38a,** 64 (1983).
[10] D. Mauer, G. Winnewisser, and K. M. T. Yamada, J. Mol. Struc. **190,** 457 (1989).
[11] J. Hahn, Z. Naturforsch., Teil B, **40,** 263 (1965).
[12] F. Fehér and M. Baudler, Z. Elektrochem. **47,** 844 (1941).
[13] F. Fehér and M. Baudler, Z. Anorg. Chem. **253,** 170 (1947).
[14] F. Fehér and M. Baudler, Z. Anorg. Chem. **254,** 251 (1947).
[15] F. Fehér and M. Baudler, Z. Anorg. Chem. **254,** 289 (1947).
[16] F. Fehér and M. Baudler, Z. Anorg. Chem. **258,** 132 (1949).
[17] F. Fehér in „Handbuch der Präparativen Anorganischen Chemie" (G. Brauer Ed.), 3rd ed., Vol. 1, Stuttgart 1975.
[18] P. Mittler, Diplomarbeit (Master Thesis), Universität zu Köln 1989.