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LETTER TO THE EDITOR

Precision Measurement of the $^rQ_2$ Branch at 700 GHz and the $^rQ_3$ Branch at 980 GHz of HSSH

S. P. BELOV,[1] M. LIEDTKE,† TH. KLAUS,† R. SCHIEDER,† A. H. SALECK,† J. BEHREND,† K. M. T. YAMADA,† G. WINNEWISSER,† AND A. F. KRUPNOV ‡

† I. Physikalisches Institut, Universität zu Köln, D-50937 Cologne, Germany; and ‡ Microwave Spectroscopy Laboratory, Institute of Applied Physics, Nizhnii Novgorod, Russia 603024

Recently we reported the observation of the $^rQ_3$ branch of HSSH with a bandhead near 980 GHz by using the newly designed Cologne submillimeter spectrometer (*1*). The rotational spectrum in the ground state was obtained by employing a broadband backward wave oscillator (BWO) operated at that time in the free-running mode. One essential feature of these BWOs, which became evident in these preliminary scans in the free-running mode, is their broadband and continuous tunability in single-mode performance. Figure 1 presents a comparison between a survey scan of the ground state spectrum of the complete $^rQ_3$ branch of HSSH with the presently available highest resolution FT-far-infrared spectrum recorded in the Giessen laboratory. All individual features recognizable in the FTIR spectrum are clearly resolved in the terahertz spectrum. Among these are some accidentally superimposed R and P branches, and in particular the shoulder at the bandhead of the main isotope turned out to be caused by the bandhead ($J < 18$) of the $HS^{34}SH$ isotopomer.

Very recently, we succeeded to frequency and phase stabilize the BWOs up to 1.1 THz (*2*), which allows high-resolution scanning spectroscopy in the terahertz region to be conducted routinely with microwave accuracy and with an achieved sensitivity unparalleled by other techniques. This breakthrough in high-resolution scanning spectroscopy became possible by the opening of the borders between the East and the West and subsequently by the immediate start of collaborative efforts essentially between the University of Cologne, Germany, and the Institute of Applied Physics, Nizhnii Novgorod, Russia.

[1] On leave of absence from the Microwave Spectroscopy Laboratory, Nizhnii Novgorod, Russia.

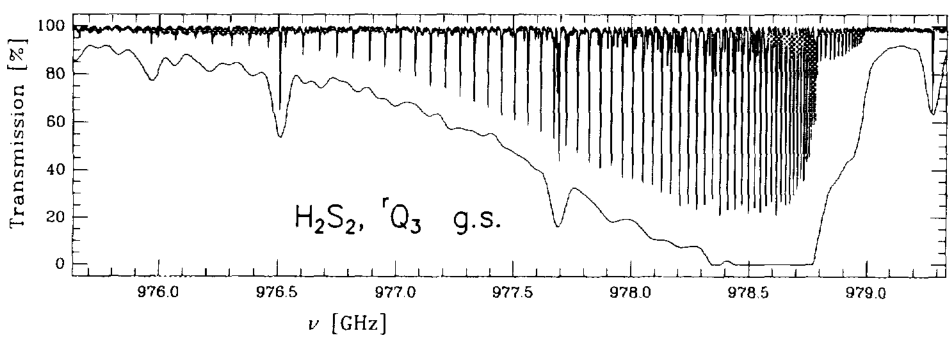

FIG. 1. The submillimeter-wave spectrum of HSSH over the complete $^rQ_3$ branch region (upper trace) is compared with the FTIR recording (lower trace) obtained in the Giessen molecular spectroscopy laboratory. The upper trace was recorded by scanning the BWO in the free-running mode. It should be noted that the wavelength resolution of the FT tracing is instrument limited, whereas the terahertz spectrum is Doppler limited. This figure is essentially the same as Fig. 2 of our previous paper (*1*), except that the slowly changing 100% transmission level has been corrected here to be flat by a digital data manipulation.

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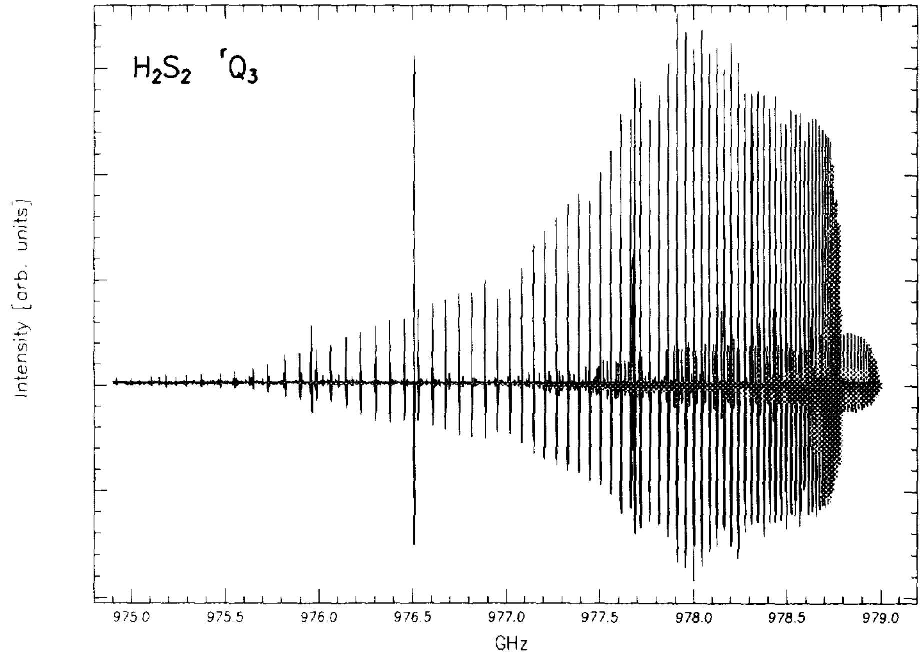

FIG. 2. The $^rQ_3$ transitions measured with the BWO phase-locked to a millimeter-wave synthesizer with source frequency modulation. The second derivative spectrum was obtained by demodulating the detector signal with a phase-sensitive detector in the $2f$ mode in all other Q branches. The ground state $^rQ_3$ branch of HSSH coincides with several weaker Q branches and some P and R branch lines.

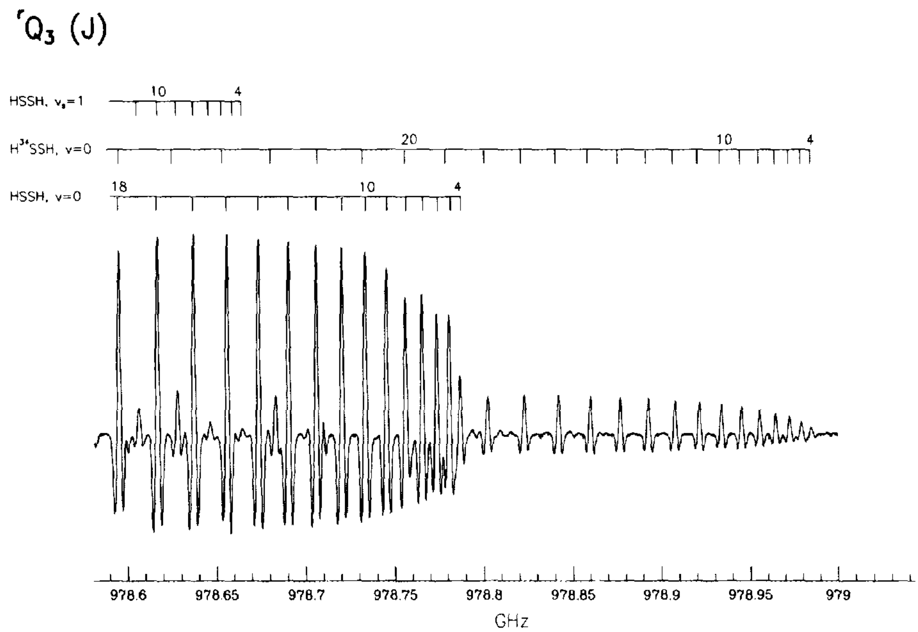

FIG. 3. Detail in the $^rQ_3$ bandhead showing a superposition of the spectra of the ground state main isotopomer, HSSH, and its ^{34}S isotopomer, $HS^{34}SH$, as well as Q-branch lines of the first excited S–S stretching state. The extremely good signal-to-noise ratio, high sensitivity, and high frequency precision have been realized by the phase-locked BWO spectrometer with source frequency modulation. This figure should be compared with Fig. 3 of our previous paper (*1*).

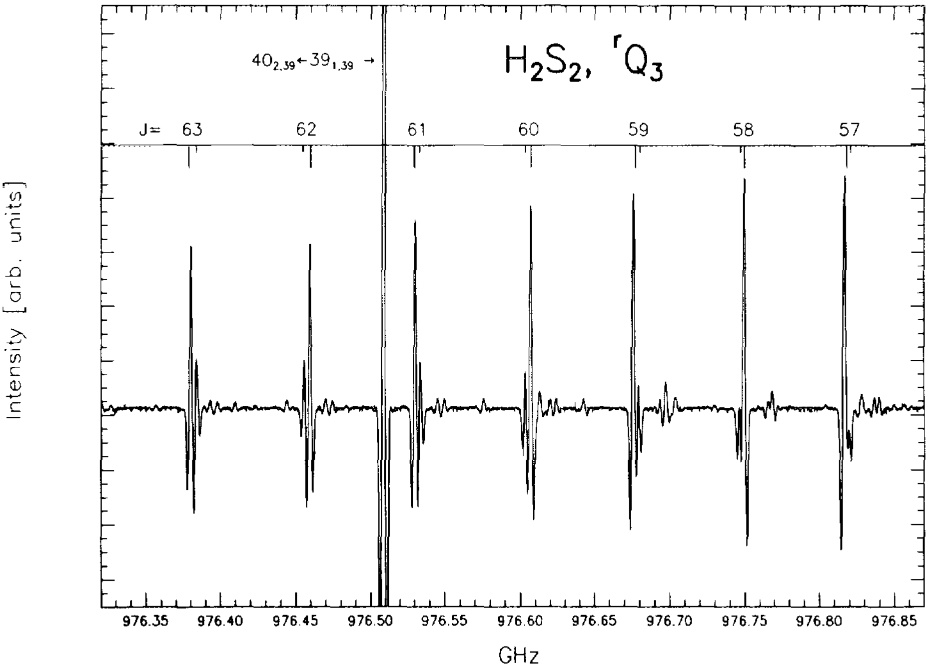

FIG. 4. The observed K-doubling in high-J transitions of the $^rQ_3$ in HSSH. This figure should be compared with Fig. 5 of our previous paper (*1*); the improvement of the signal-to-noise ratio compared to the previous work is obvious. The 3:1 intensity alternation due to the hydrogen nuclear spin statistics allowed us to correctly assign the K-doublets, leading to the anomalous K-doubling of the $K_a = 3$ rotational state.

The pure rotational spectra of simple chain molecules such as HSSH and HOOH in the ground and various vibrationally excited states together with their different isotopomer spectra are particularly amenable to broadband high-resolution spectroscopy, both in the Doppler-limited and in the sub-Doppler domains. The beauty of the perpendicular band spectra exhibited by near-prolate tops and the wealth of information contained in these spectra is revealed particularly impressively by this new technique. We have measured the $^rQ_{K_a}$ branches for higher K_a values of HSSH and HOOH for two purposes: (i) To obtain new spectroscopic information on high-J and high-K transitions, on the anomalous K-doubling of near-prolate tops, and on the mass dependence of the torsional problem. For DSSD our measurements in close agreement with theoretical predictions for the third excited torsional state, a torsional splitting of 17 MHz. (ii) We also wish to demonstrate the hitherto unknown wide tunability of the employed BWOs and the high sensitivity of the new Cologne terahertz spectrometer (see Figs. 2–4).

The essential components of the Cologne system (*2*) consist of the high-frequency and broadband tunable BWOs supplied by the ISTOK Research and Production Co. (Fryazino, Moscow region), a newly designed multiplier-mixer with low-noise HEMT amplifier circuitry, two precision tunable millimeter-wave synthesizers (78 to 118 GHz and 118 to 178 GHz, from the Institute of Electronic Measurement, KVARZ, Nizhnii Novgorod), and He-cooled InSb detectors. A more detailed description of the apparatus is in preparation and will be published elsewhere.

In the present Letter we concentrate exclusively on the fitting of $^rQ_2$ and $^rQ_3$ branches and report precisely measured line positions of the ground vibrational state, although we have succeeded in measuring the rotational spectra of the various excited torsional and SS-stretching states for HSSH, HSSD, and DSSD.

The $^rQ_3$ branch has been characterized in our first paper (*2*). However, at that time we were not yet in a position to report the precise line frequencies which are now summarized in Table I. A preliminary fit has been carried out for these newly measured submillimeter-wave transitions together with those reported earlier (*3*) using Watson's S-reduced Hamiltonian (*4*):

$$\begin{aligned}\hat{H} = {} & (B+C)\hat{J}^2 + \{A - \tfrac{1}{2}(B+C)\}\hat{J}_z^2 - D_J\hat{J}^4 - D_{JK}\hat{J}^2\hat{J}_z^2 - D_K\hat{J}_z^4 + H_J\hat{J}^6 + H_{JK}\hat{J}^4\hat{J}_z^2 + H_{KJ}\hat{J}^2\hat{J}_z^4 \\ & + H_K\hat{J}_z^6 - L_{JK}\hat{J}^4\hat{J}_z^4 - L_{KJ}\hat{J}^2\hat{J}_z^6 - L_K\hat{J}_z^8 + \tfrac{1}{4}(B-C)(\hat{J}_+^2 + \hat{J}_-^2) \\ & + d_1\hat{J}^2(\hat{J}_+^2 + \hat{J}_-^2) + d_2(\hat{J}_+^4 + \hat{J}_-^4) + h_1\hat{J}^4(\hat{J}_+^2 + \hat{J}_-^2) + h_2\hat{J}^2(\hat{J}_+^4 + \hat{J}_-^4) + h_3(\hat{J}_+^6 + \hat{J}_-^6). \qquad (1)\end{aligned}$$

TABLE I

Observed Frequencies of $^rQ_2(J)$ and $^rQ_3(J)$ of HSSH in the Ground Vibrational State[a]

J	$^rQ_2$ $K_c'' = J - K_a''$ Observed	O−C	$^rQ_2$ $K_c'' = J - K_a'' + 1$ Observed	O−C	$^rQ_3$ $K_c'' = J - K_a''$ Observed	O−C	$^rQ_3$ $K_c'' = J - K_a'' + 1$ Observed	O−C
4	699278.805	11	699278.805	30	978786.274	1	978786.274	1
5	699274.528	−4	699274.528	40	978780.228	−63	978780.228	−63
6	699269.365	−60	699269.365	28				
7	699263.452	−24			978764.758	17	978764.758	17
8	699256.644	−45			978755.199	28	978755.199	28
9					978744.417	13	978744.417	13
11	699231.323	−37						
12			699219.981	−27				
13	699210.436	40			978689.374	1	978689.374	2
14	699198.751	38	699196.399	0	978672.626	4	978672.626	4
15	699186.222	−17	699183.197	−16	978654.672	−2	978654.672	−1
16	699173.007	20	699169.084	−12	978635.563	31	978635.563	32
17	699158.953	−10	699153.967	−68	978615.227	36	978615.227	37
18	699144.054	−126	699138.019	−3	978593.589	−62	978593.589	−60
19	699128.640	−10	699121.042	0	978570.917	−0	978570.917	2
20	699112.394	9	699103.086	0	978547.021	37	978547.021	41
21			699084.143	5	978521.847	−7	978521.847	−1
22			699064.181	−5	978495.496	−29	978495.496	−21
23			699043.179	−36				
24	699040.206	−6						
25					978409.321	−33	978409.321	−17
26	699000.125	63	698974.029	−13	978378.232	−2	978378.232	17
27			698948.837	−6	978345.894	−22	978345.894	2
28	698957.369	2			978312.397	−3	978312.397	28
29	698935.093	−12			978277.670	−15	978277.670	23
30	698912.248	−14	698866.593	13				
31			698836.856	−16	978204.624	−35	978204.624	22
32					978166.319	−28	978166.319	41
33	698840.400	−15	698773.906	−8	978126.777	−60	978126.777	23
34	698815.413	−15			978086.106	−21	978086.106	78
36	698764.030	12	698670.286	−6	978001.079	−31		
37			698633.201	−12				
39	698656.116	23	698555.129	23			977864.401	37
41	698628.170	−16	698471.543	−22				
42	698599.905	−52	698427.686	−8	977717.188	−81	977716.967	48
43	698571.433	−1	698382.367	−19			977665.428	68
44	698542.630	−13	698335.707	94	977612.958	−99		
45			698287.308	−39				
46	698484.374	10						
48			698133.295	−8				

[a] Frequencies are listed in MHz and the observed − calculated values are given in the column of O−C in kHz.

In the course of the fitting procedure we have detected in our previous paper (*3*) a few misassignments or poor measurements for the *P*- and *R*-branch transitions. The new fit is now carried out without those erroneous lines, yielding a standard deviation of 39 kHz. The best fit parameters have been determined as listed in Table II purely from the millimeter- and submillimeter-wave transitions.

It is now undoubtedly concluded that the *K*-type doublet for the $K_a = 3$ rotational levels are inverted in HSSH as well as those for $K_a = 2$; see Fig. 6 of Ref. (*1*). The revision of the *P*- and *R*-branch assignments in the millimeter/submillimeter-wave region and global fit together with the far-infrared transitions measured

TABLE I—*Continued*

	${}^{r}Q_2$		${}^{r}Q_2$		${}^{r}Q_3$		${}^{r}Q_3$	
	$K_c'' = J - K_a''$		$K_c'' = J - K_a'' + 1$		$K_c'' = J - K_a''$		$K_c'' = J - K_a'' + 1$	
J	Observed	O–C	Observed	O–C	Observed	O–C	Observed	O–C
49			698078.763	−10				
50			698022.591	−8				
51			697964.746	−5				
52	698306.031	10	697905.186	−8				
53	698276.086	−16						
54	698246.227	11	697780.821	−4				
55	698216.371	−17	697715.936	−10				
56					976886.942	−30		
57	698157.045	−10					976816.532	30
58	698127.608	−11						
59			697437.630	6			976675.761	−34
60	698069.370	−12	697363.165	5				
61	698040.642	−12						
62	698012.249	14	697208.105	−4				
63	697984.145	−18	697127.434	−8			976379.738	27
64	697956.466	−11	697044.632	0			976302.581	−43
65	697929.195	−20	696959.671	38			976224.334	25
66			696872.393	−13			976144.769	7
67	697876.094	−28			976069.705	33		
68			696691.131	29	975988.198	12	975981.991	22
69	697825.273	65					975898.735	16
70	697800.648	−21					975814.187	−43
71	697776.833	31	696401.396	24	975736.496	−55		
72	697753.633	−12	696299.859	−22	975650.330	45	975641.560	30
73	697731.237	−7	696195.896	38			975553.380	67
74	697709.627	−16	696089.282	26	975474.247	81	975463.841	−9
75	697688.879	−8	695980.085	55	975384.213	−103	975373.127	−10
76			695868.164	31	975293.330	53		
77			695753.479	−35				
78	697632.151	11	695636.071	−59	975107.609	−12	975093.437	−41
79			695515.874	−56	975013.005	−3	974997.728	−14
80	697599.388	18	695392.796	−68			974900.664	−79
87					974213.368	−1		
88			694299.075	−13	974108.127	38	974078.961	49
90			693993.366	−7	973893.968	−18		
91			693835.396	19				
92					973675.097	−79		
93					973564.069	59		
94			693340.096	−64				
95			693167.870	46				
96			692991.798	40				

by the Giessen high-resolution FTIR spectrometer are in progress, employing more parameters than those given in Eq. (1); the results will be presented elsewhere.

Since the presently measured spectral range just overlaps the FTIR spectrum at its low-wavenumber end, it will be very interesting to check the consistency between the submillimeter-wave spectra and the FTIR spectra which have been calibrated independently. This overlap of the two methods in the terahertz spectral range now opens the possibility to calibrate FTIR spectrometers on an absolute frequency scale.

TABLE II

Molecular Parameters of HSSH in the Ground Vibrational State

Parameter	Value
A /MHz	146 858.1173(78)
B /MHz	6 970.42815(44)
C /MHz	6 967.68729(44)
D_J /kHz	5.39984(46)
D_{JK}/kHz	85.5336(31)
D_K /MHz	2.4085(26)
d_1 /Hz	9.0162(40)
d_2 /Hz	−27.33764(82)
H_J /mHz	−1.47(13)
H_{JK}/mHz	−22.24(46)
H_{KJ}/Hz	4.29(42)
H_K /kHz	−3.32(30)
h_2 /μHz	41.57(14)
h_3 /μHz	3.442(30)
L_{JK} /μHz	226.5(205)
L_{KJ} /mHz	33.8(167)
L_K /Hz	−127.4(102)
σ^d /kHz	38.6

[a] The numbers in parentheses are one standard deviation in the unit of the last digit quoted.

[b] Standard deviation of the fit.

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