LETTERS TO THE EDITOR

The $^rQ_4$ Branch of HSSH at 1.25 THz

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The rotational structures of the Q branches of disulfane. HSSH, provide impressive examples for high-resolution spectroscopy, which are used to demonstrate the broadband tunability of the Cologne terahertz spectrometer (*1, 2*). The chain structure of the HSSH molecule has been well established (*3*). The most conspicuous features of the molecule's geometry are the two nearly right angles, the $\angle$SSH = 97.88(5)° angle and the dihedral angle η = 90.3(2)°. This special geometrical structure makes HSSH an almost accidental prolate symmetric top. The permanent electric dipole moment lies perpendicular to the S–S axis and is collinear with the C_2 symmetry axis, which is necessarily one of the principal axes. It is this nearly right angle geometry of the molecule which, by chance, makes the two moments of inertia I_b and I_c almost equal. Thus the HSSH molecule is an almost perfect symmetric top molecule, but with asymmetric rotor selection rules. For a dihedral angle η = 90.26°, the molecule would be an exact accidental symmetric top and distinguishing the b and c axes would have no meaning, because the K-doubling structure would be degenerate. However, as a consequence of the actual size of the dihedral angle η = 90.3(2)°, the axis of largest moment of inertia is the c axis, which is coincident with the symmetry axis. This fact leads to a pure perpendicular c-type rotational spectrum, which is dominated by regularly spaced $\sim[2\{A - (B + C)/2\}] \cong [2\{A - B\}]$, but very prominent Q branches. Combined with the small difference between the two rotational constants ($B - C$) $\sim$ 2.7 MHz, the Q branches become very compact, enhancing their prominence and adding to their unusual spectroscopic beauty.

It is the J spacing of the Q branches which can be used advantageously to test the high spectral resolution of the employed spectrometer. For the first time we can report in the present Letter the completely resolved rotational structure of the $^rQ_4$ branch of HSSH near 1.25 THz. This advance in high-resolution spectroscopy was achieved by using a frequency- and phase-stabilized backward wave oscillator (BWO). Finally, we compare the observed $^rQ_4$ branch with the highest resolution Fourier transform recording available to date.

The entire rotational band has been measured by either millimeter-wave techniques or high-resolution Fourier transform (FT) spectroscopy in the far-infrared region. By millimeter- and sub-millimeter-wave techniques the lower K_a Q branches were measured to high precision and in Doppler-limited resolution, i.e., the $^rQ_{K_a}$ with K_a = 0, 1, 2, 3. For the $^rQ_0$ branch several J transitions were recorded with sub-Doppler resolution, which revealed the small torsional splitting associated with the torsional motion of the two SH bars relative to each other (*4*). Commencing at $\sim$30 cm^{-1}, all higher K_a ($\geq$3) Q branches were recorded by FT spectroscopy. With the recent recording and precise measurement of the $^rQ_3$ branch by Belov *et al.* (*2*), we have succeeded for the first time in achieving overlap near
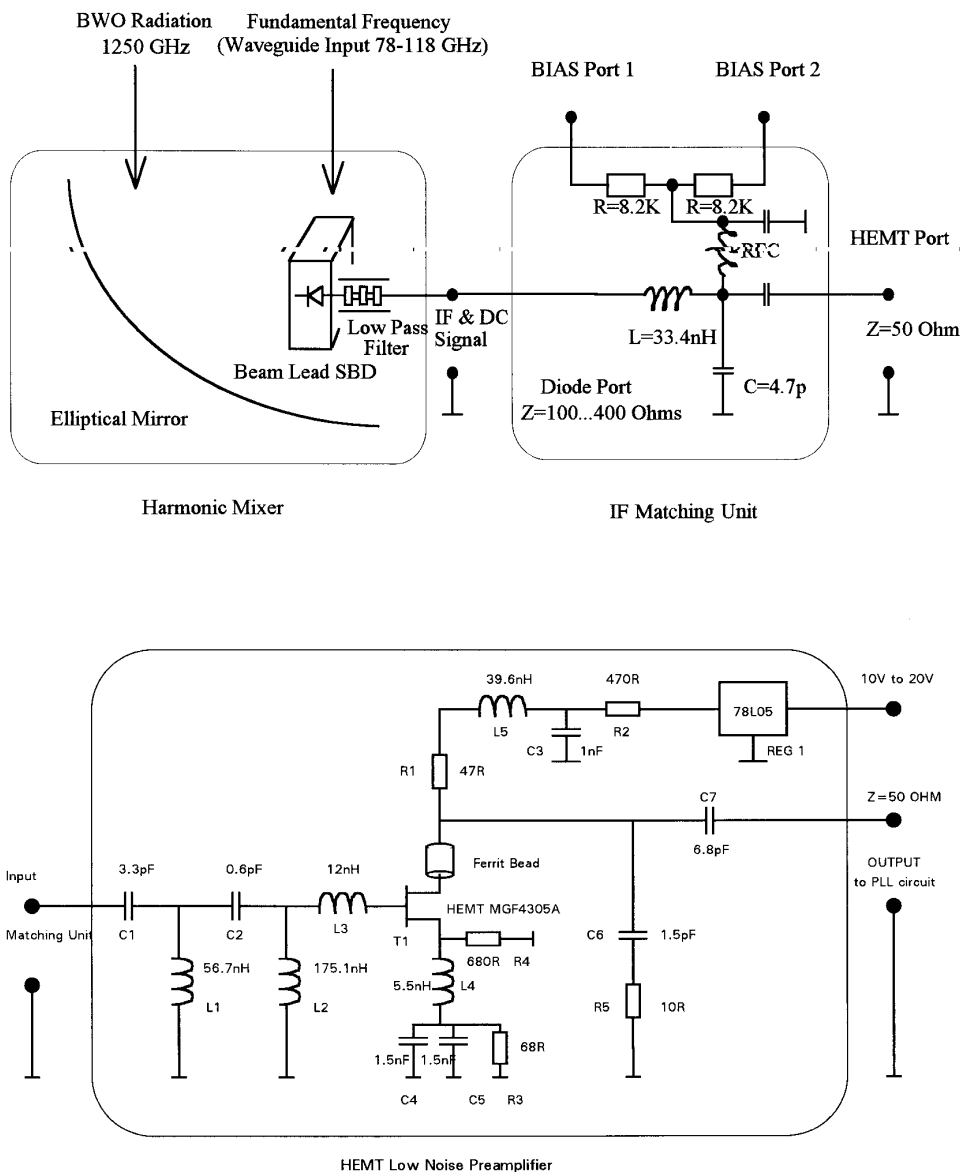
FIG. 1. Block diagram of the harmonic mixer, and circuit diagram of the matching unit and of the low-noise HEMT preamplifier. For the matching unit and HEMT preamplifier unit operating at room temperature the noise figure was determined to be 36 K.

980 GHz between the submillimeter-wave measurements and the existing Fourier transform data around 32.65 cm^{-1}, obtained in 1987 at the Giessen molecular spectroscopy laboratory (7). The present high-resolution recording of the $^rQ_4$ branch serves yet as another example for the continued widening overlap of the two techniques, as the terahertz spectroscopy is pushed toward higher frequencies. At the far-infrared wavelength end of the spectrum, the wavelength resolution of the FT recorded spectra is instrument limited rather than Doppler limited. The latter is the case for the spectra obtained with the broadband submillimeter-wave scanning techniques.

The Cologne terahertz spectrometer has been described in some detail by Winnewisser et al. (5).
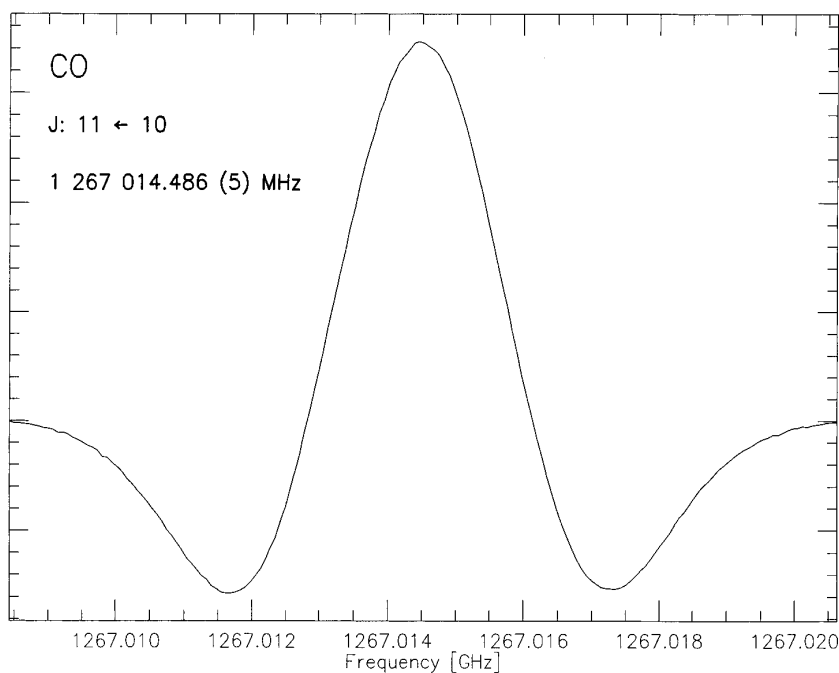
FIG. 2. Recorder tracing of the $J = 11 \leftarrow 10$ transition of CO. The absorption line is displayed in second derivative form. The measurement accuracy of the absorption peak is estimated to be 5 kHz.
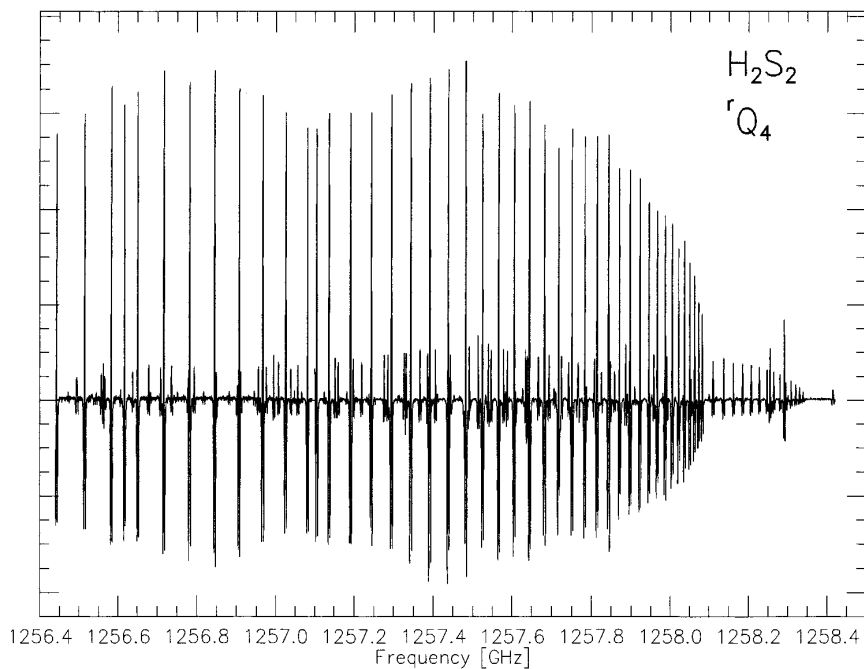

FIG. 3. Display of a 2-GHz spectral scan of the ground state of the $^rQ_4$ branch of HSSH. In comparison to the main isotopomer, the bandhead of the ^{34}S isotopomer is displaced toward higher frequencies. For higher J values ($J \geqslant 19$) the two Q branches overlap. In the center of the spectrum one notices in addition the congestion of weak lines pertaining to the Q branch of the first excited S=S stretching state. The spectra are in second derivative form and are Doppler limited.

TABLE I

Comparison between Calculated (Evenson) and Cologne Measured Transition
Frequencies of CO

$J' \leftarrow J''$	K. Evenson [6]			Cologne	
	ν_{calc} [a]	$\Delta\nu$ [b]	σ_{exp} [c]	ν_{obs} [d]	$\Delta\nu$ [e]
	/MHz	/kHz	/kHz	/MHz	/kHz
1 ← 0	115 271.203 (0)	1	5		
2 ← 1	230 538.001 (0)	−1	1		
3 ← 2	345 795.992 (1)	−1	1	345 795.989 (5)	−3
4 ← 3	461 040.770 (1)	−1	2		
5 ← 4	576 267.934 (1)	−12	32	576 267.931 (5)	−3
6 ← 5	691 473.080 (1)	11	12	691 473.075 (5)	−5
7 ← 6	806 651.805 (2)	1	10		
8 ← 7	921 799.709 (2)	2	10	921 799.700 (5)	−9
9 ← 8	1 036 912.390 (2)	11	10	1 036 912.393 (5)	3
10 ← 9	1 151 985.449 (2)	3	11		
11 ← 10	1 267 014.488 (2)	12	10	1 267 014.486 (5)	−2
12 ← 11	1 381 995.109 (2)	−4	13		

[a] The values in brackets are the 1σ standard errors of the calculated transitions in units of the last quoted digits.

[b] Differences between the measured frequencies used by Evenson and ν_{calc} [6]. The transitions commencing with $J : 5 \leftarrow 4$ at 576 GHz were measured with tunable FIR laser techniques.

[c] Estimated 1σ uncertainties of the observed frequencies [6].

[d] The values in brackets are the estimated 1σ uncertainties of the measured frequencies in units of the last quoted digits.

[e] Differences between Cologne measurements and ν_{calc} from K. Evenson [6].

The heart of the spectrometer is furnished by continuously tunable BWOs. the frequency output signal of which has now been frequency and phase stabilized up to 1.3 THz. The high frequency BWOs are supplied by the ISTOK Research and Production Co. (Fryazino, Moscow region). The portion of the terahertz radiation which is transmitted through the free space absorption cell was focused onto a newly installed, magnetically tuned, hot electron InSb detector, supplied by Queen Mary College, UK. The sensitivity of the InSb detector is specifically optimized for the region 1 to 2 THz, with an average NEP (noise equivalent power) of 3 pW Hz$^{-1/2}$. This detector sensitivity results in a spectrometer sensitivity of $\sim 10^{-8}$ cm^{-1}, which was checked with spectra measured for CH$_3$CN at 1 THz.

The precision of the frequency measurements with the Cologne terahertz spectrometer is estimated to be about ± 5 kHz for single, well-isolated transitions. The output of the 1.2-THz BWO (type OB-84) was locked via a frequency mixer–multiplier chain to the 11th and 12th harmonics of a 78- to 118-GHz synthesizer, supplied by the KVARZ Co. In turn this synthesizer was locked to the 5-MHz signal output of a rubidium frequency standard (Rhode und Schwarz Co.), which provides a short-term accuracy of 1 part in 10^{-11} sec. At frequencies above 1 THz phase locking of the BWOs becomes increasingly difficult, due to several adverse factors: since both the output power of the BWOs decreases with frequency and since higher harmonics of the synthesizer are required, extreme low-noise amplification of the intermediate frequency (IF) signal is of utmost importance. In addition,
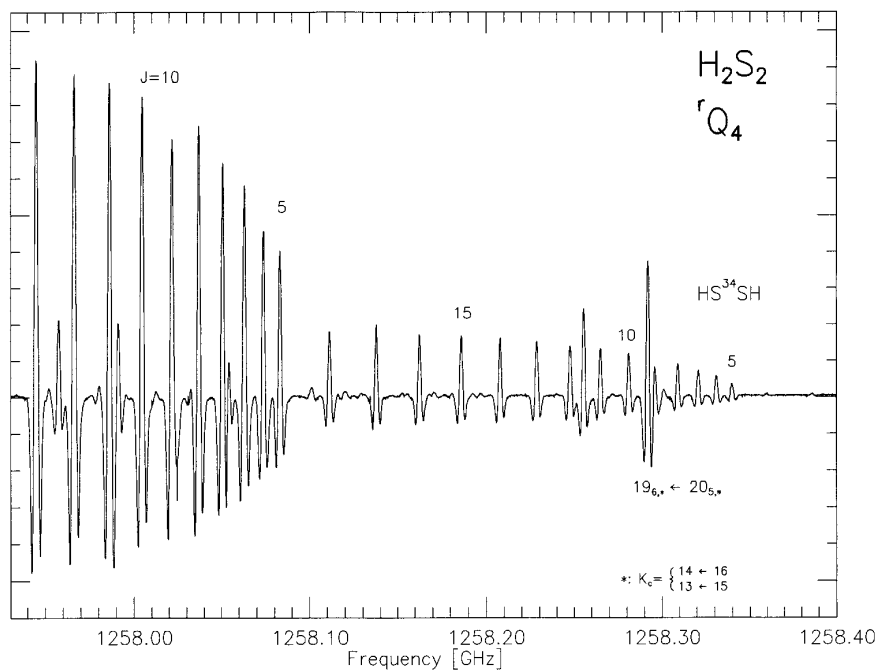
FIG. 4. Detail of the $^rQ_4$ bandhead displaying the superposition of the spectra of the main and ^{34}S isotopomers. This recording should be compared with Fig. 3 of our previous paper (2). The BWO is source modulated at a frequency of 10 kHz and recorded in the 2f mode. The resolution of the terahertz spectra is Doppler limited.

the portion of the terahertz signal, which travels through air, i.e., between the BWO and the mixer, is further decreased by absorption due to the moisture in the air. The phase lock loop (PLL) circuit needs a signal-to-noise ratio of more than 30 dB in order to provide a stable lock signal. Therefore the harmonic mixer conversion loss has to be minimized due to reducing the input return loss at the IF port. A matching unit was added to transform the high diode impedance to the 50 Ω standard impedance, as is shown in Fig. 1. The input return loss of the harmonic mixer was reduced to < -12 dB in the IF range between 310 and 390 MHz.

Special attention was paid to the sensitivity of the PLL-IF preamplifier. With the help of an computer-aided design tool (Microwave Harmonica, V4.11 from Compact Software) an optimum embedding network was found to match simultaneously the scattering and noise parameters of the high electron mobility transistor, the HEMT device. As a result, at ambient room temperature, we measured with a network analyzer a flat gain of 21 dB over the entire IF band (310–390 MHz) with an average noise figure of 0.51 dB, which corresponds to 36 K noise temperature. This noise figure represents a significant improvement in comparison to previous IF amplifiers with noise temperatures around 250 K.

The frequency accuracy and reproducibility of our spectrometer has been cross-checked by measuring the rotational transitions of CO. The highest rotational transition of CO presently measured with the Cologne terahertz spectrometer is $J = 11 \leftarrow 10$ at 1 267 014.486(5) MHz, shown in Fig. 2. Our complete measurements on CO are listed in Table I and are compared with the appropriate transitions taken from the frequency list provided by Evenson (6). These latter line positions represent calculated values based on a large set of experimentally measured line frequencies recorded with a tunable far-infrared laser spectrometer (TuFIR). It is seen that in the region of overlap with the submillimeter-wave measurements, the transition frequencies obtained with the two different techniques agree very well with each other. Within the experimentally estimated error limits (<5 kHz), the Cologne measurements match the calculated frequencies quoted by Evenson and derived by him from a least-squares fit to a complete data set including all rotational transitions up to $J = 38 \leftarrow 37$ at 4.3 THz.

TABLE II

Observed Frequencies for the Bandhead Region of the $'Q_4$ Branches of HSSH and HS^{34}SH in their Ground Vibrational States

	HSSH		HS^{34}SH	
J	$\nu_{exp}/$MHz	$\Delta\nu_{exp}$[a]	$\nu_{exp}/$MHz	$\Delta\nu_{exp}$
5	1258083.269	0.050	1258339.806	0.050
6	1258073.888	0.050	1258331.082	0.050
7	1258063.138	0.050	1258320.805	0.050
8	1258050.794	0.050	1258309.073	0.050
9	1258037.005	0.050	1258296.064	0.150[b]
10	1258021.662	0.050	1258281.261	0.050
11	1258004.717	0.050	1258265.146	0.050
12	1257986.266	0.050	1258247.575	0.050
13	1257966.287	0.050	1258228.542	0.050
14	1257944.775	0.050	1258208.038	0.050
15	1257921.752	0.050	1258186.049	0.050
16	1257897.114	0.050	1258162.627	0.050
17	1257870.967	0.050	1258137.796	0.050
18	1257843.244	0.050	1258111.386	0.050

[a] $\Delta\nu_{exp}$ represents the estimated 1σ uncertainties of the measured frequencies.
[b] Line partly covered by a P–branch transition of HSSH.

For example, the Cologne measurement of the $J = 11 \leftarrow 10$ transition agrees within 2 kHz of the calculated best fit value quoted by Evenson (6).

In the present Letter we report precisely measured line positions of the $'Q_4$ in the ground vibrational state. Figure 3 presents a ~2-GHz sweep over the bandhead region of the $'Q_4$ branch. It is clearly recognized that aside from the dominating ground state band, there is absorption seen from the ^{34}S-substituted species, the line positions of which are displaced toward slightly higher frequencies. The additional absorption due to the S=S stretching state commences at slightly lower frequencies than the ground state band but overlaps with it. These findings are in agreement with the assignment of the previously measured but lower K_a (=0, 1, 2, 3) Q branches. In Fig. 4 the detail of the bandhead region of the $'Q_4$ branch is depicted. It is strikingly similar to the bandhead region of the $'Q_3$ branch shown in Fig. 3 by Belov *et al.* (2). Although we have measured the $'Q_4$ branch to high J number (~46) no splitting due to K-doubling has been resolved. A measurable contribution to the splitting is expected for values of $J \sim 90$, which will then reveal whether the K-doubling of the $K = 4$ levels is also anomalous, as observed for the $K = 2$ and 3 levels (see, e.g., Ref. 2). In Table II we present the precisely measured transition frequencies of the bandhead region. As soon as the measurements of the $'Q_4$ branch are complete, in the sense that the line positions of the high $J > 50$ transitions are determined, they will be used in a global fitting procedure with all the existing ground state data.

The $'Q_4$ branch has also been recorded with the Giessen FT spectrometer (7). The transmittance spectrum near 42 cm^{-1} is displayed in Fig. 5. It is seen that the resolution of the FT spectrum is still instrument limited, but the shapes of the Q-branch profiles agree well with the present Doppler-limited Cologne terahertz spectra. The achieved overlap in the spectral ranges of the Cologne terahertz and Giessen FT spectrometer has contributed toward absolute calibration of the FTIR spectrometers on an absolute frequency scale. For the purpose of frequency calibration of FT spectrometers, CO and H$_2$S (8) are very useful molecules, since their rotational spectra are now precisely measured in the FIR region.
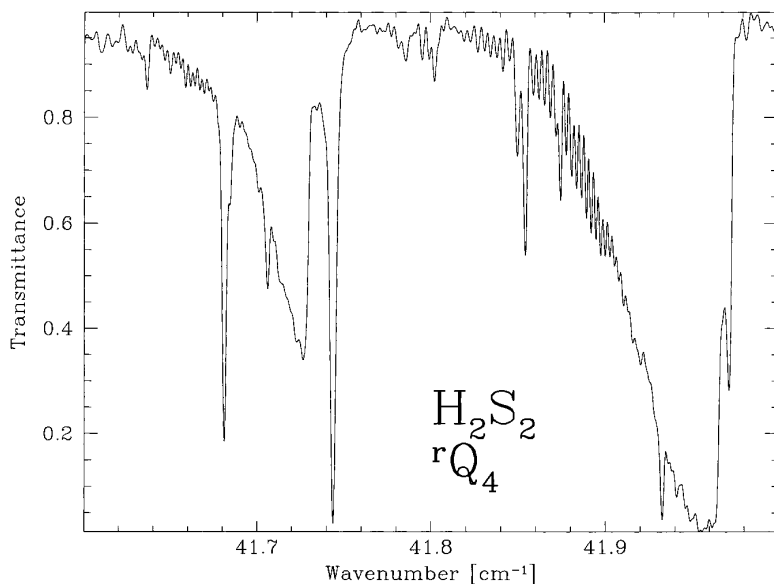
FIG. 5. $^rQ_4$ branch recorded with the Giessen Fourier transform spectrometer. The ground state rotational transitions are located at ~41.96 cm^{-1}, whereas those of the first excited torsional state appear at ~41.73 cm^{-1}. The FT spectrum is instrument limited.

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