Rotational Spectrum of cis-HS_3D

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The rotational spectrum of HS_3D in the vibrational ground state has been measured in the frequency range between 75 and 293 GHz. Up to now, about 180 Q-, 30 P-, and 70 R-branch *c*-type transitions have been identified. The preliminary rotational constants of the species observed support the cis-conformation established earlier from the H_2S_3 rotational spectrum.

I. Introduction

In our pursuit of understanding the structure of sulfur chain molecules we have extended our investigations on the rotational spectrum of HSSSH [1, 2] to the partially deuterated species HSSSD. The rotational spectrum of HSSSH was found to be dense, and the carrier of the strongest absorption lines assigned at that time was the cis-conformer of HSSSH, displaying a strong *c*-type spectrum.

Since the non-planar cis-conformation, in which the two hydrogen atoms are attached to end-sulfur-atoms of the bend sulfur chain, exhibits C_S symmetry [1, 2], one expects a perpendicular-type spectrum consisting of both *c*- and *b*-type transitions with one of them carrying the stronger component of the dipole moment. A similar situation is predicted for cis-HSSSD and has now been found: The assigned rotational spectrum consists of strong *c*-type and weak *b*-type transitions, confirming the structure shown in Figure 1.

The purpose of this communication is to present a preliminary analysis of the observed cis-HSSSD transitions with a comparison to HSSD [3].

II. Experimental

The HS_3D spectrum was measured in part by using the millimeter-wave spectrometer described in its essential parts by Bester et al. [4] and Mauer et al. [5]. Two backward wave oscillators (Carcinotrons, Thomson-CSF) are newly implemented as millimeter wave sources. These Carcinotrons deliver radiation in the frequency ranges 200–250 GHz and 256–300 GHz with a power level between 10 and 150 mW. They are phase locked to an atomic clock. In addition, standing waves in the radiation path of the free space absorption cell were suppressed to a considerable extent by a tilted arrangement of the cell's teflon windows. These modifications result in an enhanced sensitivity of our spectrometer; a detailed description will be given elsewhere [6]. The spectra were recorded in the second derivative form with source frequency modulation.

The HS_3D sample has been prepared by deuteration of H_2S_3 with gaseous DCl according to a procedure which has already been used for the preparation of HS_2D [7]. H_2S_3 has been obtained by cracking

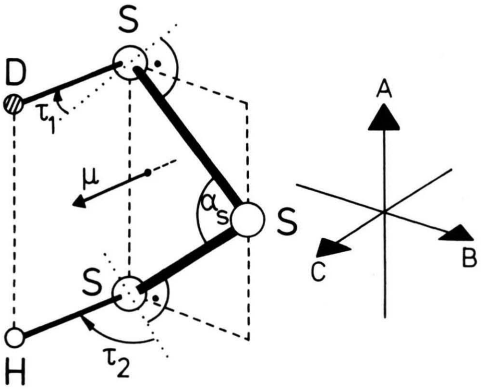

Fig. 1. Structure of cis-HSSSD and orientation of principal axes of inertia.

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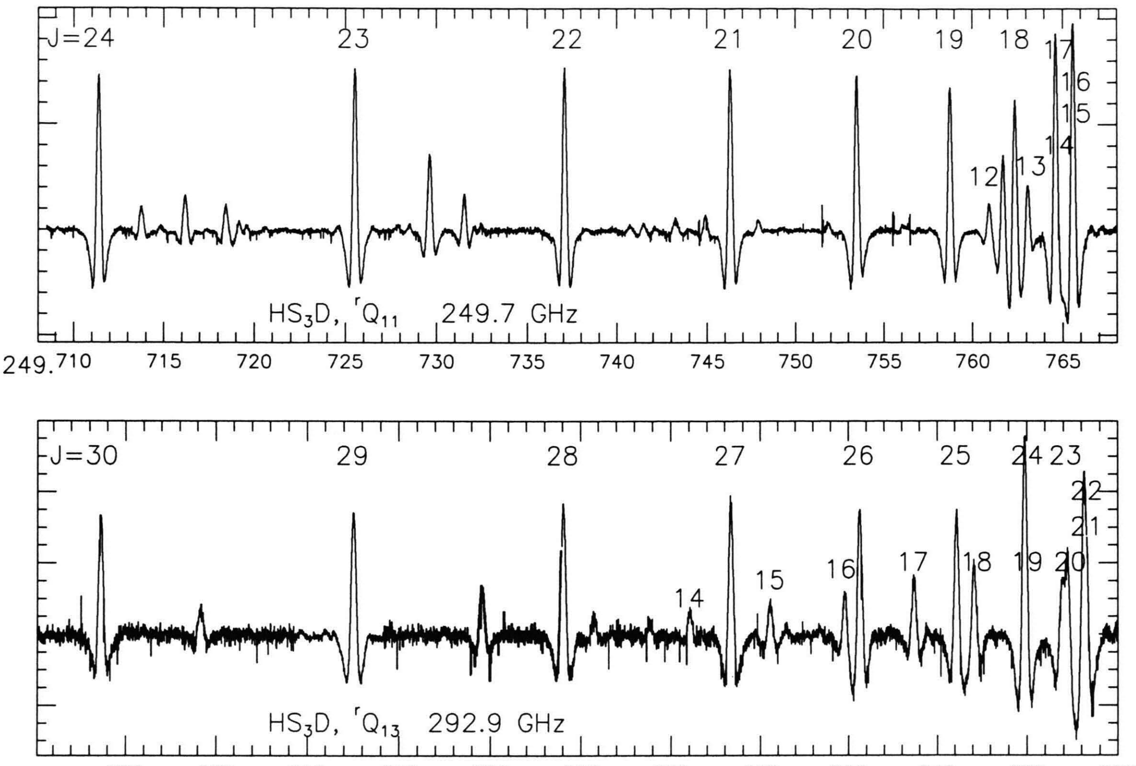

Fig. 2. Recorded $^rQ_{11}$ and $^rQ_{13}$ branches of HS_3D. The spectra shown were obtained by using two Carcinotrons.

crude sulfane oil under reduced pressure (1.5 mbar) at a temperature of 80 °C in a modified rotary evaporator [7]. The separation of H_2S_3 from the lower homologues has been achieved by a multiple coil condensor cooled to -20 °C. The sample thus obtained was only contaminated by H_2S_4. Purification by subsequent distillation resulted in a probe containing about 98% trisulfane, which has been used for deuteration. The deuterated sample used for the measurement of its rotational spectrum showed a concentration ratio [HSSSD]/[HSSSH] of about 0.4 as judged by NMR measurements. The cell has been deuterated and conditioned by introducing DCl gas with a pressure of 0.1 mbar prior to the measurements. The spectra were obtained at pressures between 20 and 40 μbar.

III. Observed Spectra: Assignment

The observed rotational spectrum of HSSSD is dense, but in analogy to the HSSSH spectrum [1, 2] it is dominated by a series of regularly spaced but conspicuous Q-branches. Figure 2 shows two Q-branches of HSSSD with its characteristic *J*-pattern. Because of the larger moment of inertia I_a the Q-branch origins of HS_3D are shifted towards lower frequencies in comparison to the appropriate HS_3H positions.

After assignment of seven $^rQ_{K_a}$-branches, for $K_a=4$, 6, 9 to 13 and J up to $J=25$, which allowed to fit $\left(A-\frac{B+C}{2}\right)$, $(B-C)$ and some centrifugal parameters, the *K*-doublet splitting of the R-branches could be predicted precisely. Scanning the spectrum in a frequency range of ±400 MHz at 163 GHz, the first R-branch *K*-doublet could be identified, which in turn led to the measurement and assignment of further R-branch and P-branch lines, thus securing the assignment.

The preliminary rotational constants *A*, *B*, and *C* of cis-HS_3D, together with the corresponding rotational constants of H_2S_3, are shown in Table 2. The observed transitions are assigned and analysed on the

Table 1. Measured frequencies in MHz of the two Q-branches shown in Figure 1. The frequency accuracy for not overlapped lines is better than 30 kHz.

J	$^rQ_{11}$	$^rQ_{13}$
12	249 760.953	–
13	249 763.085	–
14	249 764.615	292 930.995
15	249 765.553	292 935.516
16	249 765.553	292 939.756
17	249 764.615	292 943.660
18	249 762.378	292 947.061
19	249 758.750	292 949.880
20	249 753.570	292 951.941
21	249 746.302	292 953.146
22	249 737.078	292 953.146
23	249 725.520	292 952.191
24	249 711.374	292 949.880
25		292 946.077
26		292 940.596
27		292 933.298
28		292 923.989
29		292 912.445
30		292 898.528

Table 2. Molecular constants of cis-H_2S_3 and cis-HS_3D.

Parameter	H_2S_3 [5]	HS_3D
A [MHz]	14 103.20962 (25)	13 395.4648 (6)
B [MHz]	2 752.75945 (11)	2 682.1826 (5)
C [MHz]	2 373.86989 (12)	2 334.7892 (5)
$\varkappa$	−0.93539456 (2)	−0.93718405 (10)

basis of the Watson S-reduced Hamiltonian. The complete analysis of the cis-HSSSD spectrum will be published elsewhere. In comparing the HSSSD Q-branch behaviour with HSSD, one notices that the HSSD spectrum consists of two almost equally intense *c*- and *b*-type transitions [8, 3], whereas for cis-HSSSD the *c*-type transitions are much stronger. The nearly 45 degree rotation of the molecule fixed axes upon deuteration for HSSD produces the observed equally intense *b*- and *c*-type spectra [8]. For cis-HSSSD the dipole moment vector almost coincides with the *c*-axis. Axis rotation in cis-HSSSD caused by deuteration is very small and no significant additional contribution to the *b*-dipole moment is expected, leaving the *b*-dipole moment component very small. HS_3D turns out to come somewhat closer to an accidental prolate symmetric top than H_2S_3, as the respective values of Ray's asymmetry parameter $\varkappa$ show. For H_2S_2 the reverse situation is found: $\varkappa(H_2S_2) = -0.9999608118$ (29) and $\varkappa(HS_2D) = -0.8642430601$ (36) from [3].

IV. Discussion and Conclusion

With the unambiguous detection of the rotational spectrum of the HSSSD cis-conformer, we have renewed our efforts to search for the trans-conformer of the parent species HSSSH, whose existence is suggested by all quantum chemical calculations. In fact MO-calculations have the trans-conformer to be lower in energy than the cis-species, however due to the opposite direction of the two SH-bonds a relatively low resultant dipole moment is expected, which makes the assignment rather difficult. The C_2-symmetry of the molecule [1] will impose on the spectrum the characteristic 3:1 intensity alternation as observed for disulfane [8]. We therefore also expect for HSSSD a trans-conformer to exist, but its spectrum has not yet been identified.

In deriving a complete structural determination of HSSSH we plan to extend our measurements to DSSSD and the ^{34}S isotopomers.

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[1] D. Mauer, G. Winnewisser, and Koichi M. T. Yamada, J. Mol. Structure **190,** 457 (1988).
[2] D. Mauer, G. Winnewisser, K. M. T. Yamada, J. Hahn, and K. Reinartz, Z. Naturforsch. **43a,** 617 (1988).
[3] J. Behrend, P. Mittler, G. Winnewisser, and K. M. T. Yamada, J. Mol. Spectrosc. **150,** 90 (1991).
[4] M. Bester, M. Tanimoto, B. Vowinkel, G. Winnewisser, and K. M. T. Yamada, Z. Naturforsch. **38a,** 64 (1983).
[5] D. Mauer, G. Winnewisser, and K. M. T. Yamada, J. Mol. Spectrosc. **136,** 380 (1989).
[6] M. Liedtke, R. Schieder, and G. Winnewisser (to be published).
[7] J. Hahn, P. Schmidt, K. Reinartz, J. Behrend, G. Winnewisser, and K. M. T. Yamada, Z. Naturforsch. **46b,** 1338 (1991).
[8] G. Winnewisser, J. Mol. Spectrosc. **41,** 534 (1972).