Detection of Gas-Phase Hydrogentrisulfide, HSSSH

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The rotational spectrum of gas phase HSSSH has been recorded for the first time in absorption with the Cologne free-space-cell millimeterwave spectrometer. In the frequency region between 80 and 300 GHz a prominent series of Q-branches has been observed and assigned. The hitherto identified rotational lines unambigously arise from a perpendicular-type spectrum. In addition, successive *J* lines of the compact Q-branches show no indication of the easily detectable intensity alternation which arises when the molecule possesses an axis of symmetry due to nuclear spin statistical weights. Therefore the geometrical structure of the molecule does not have a C_2 axis of symmetry. The present data are not complete enough for a unique structure determination. However on the basis of the present data we can definitely rule out conformations with C_2 or C_{2v} symmetry to be responsible for the strongest observed transitions of the spectrum. The molecule is not floppy as predicted from semi empirical MO calculations. On the contrary the conformation observed is rather rigidly locked into one position with no sign of possible internal rotation. We consider a sulfur triangle with the two hydrogen atoms sticking out symmetrically to the same side of the SSS-plane to be the most likely structure.

Introduction

The chemistry and spectroscopy of sulfanes has a long and rich history. The first chemical evidence of the sulfanes H_2S_n dates back as far as 1777. The knowledge of the persulfides and disulfane, H_2S_2, is thus 40 years older than its oxygen analog hydrogenperoxid, HOOH. The first detailed characterisation of disulfane and the higher sulfanes was given by Bloch and Höhn in 1908 [1]. In the 40's the pioneering work of Fehér and Baudler lead in a series of papers [2–6] to a clear separation of the individual sulfanes with chain lengths up to 6. The Raman-spectra of these sulfanes $H_2S_n (n = 2, \ldots, 6)$ display similar spectroscopic features [3–6]. From the close resemblance of these features with those of the H_2O_2 spectrum Fehér and Baudler concluded correctly that the sulfanes possess chain structure. Due to the relative chemical instability of the sulfanes, earnest high resolution spectroscopic work both in the millimeter- and infrared region was held back to the mid 60's. With the advent of the free-space glass absorption cells for microwave spectroscopy [7] the inherent instability of the sulfanes towards cell walls (especially metal walls) could be overcome, since glass can be especially well acidified to handle sulfane molecules. Despite this technical advance all high resolution spectroscopic investigations remained limited to H_2S_2 [8]. In our renewed effort to understand the spectra of sulfanes and the structure of the sulfur chain we have been able to detect for the first time the rotational spectrum of gas phase H_2S_3.

Chemical Preparation

The content of trisulfane in crude sulfane mixtures prepared by acid decomposition of sodium polysulfide [9] may vary between 11 and 15 mol% (H_2S_2 and H_2S are present only in traces) [10, 11]. Additional amounts of H_2S_3 as well as H_2S_2 are formed when the crude sulfane oil is passed through a cracking column at a temperature of 130 °C and reduced pressure (15 Torr). Under these conditions the volatile sulfanes H_2S, H_2S_2 and H_2S_3 distill off from the species of higher molecular weight and can be isolated in different traps at temperatures of 0 °C (H_2S_3), −78 °C (H_2S_2) and −196 °C (H_2S). The cracking apparatus first described by Fehér and Baudler [3] was only modified by using an electrically heated column with a temperature controller. From 260 g of a crude sul-

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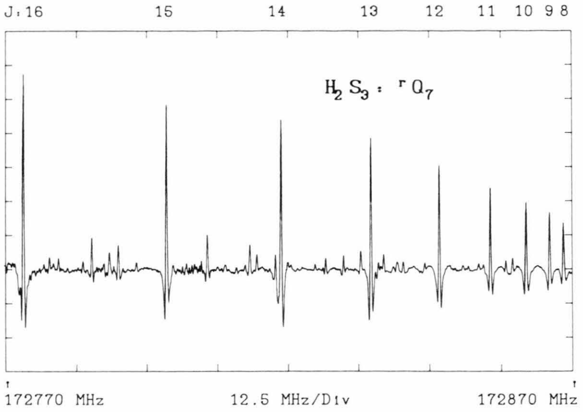

Fig. 1. The low J-transitions of the $^rQ_7$-branch exhibit the typical behaviour of a perpendicular-type spectrum. The lines do not show any splitting due to torsional motion.

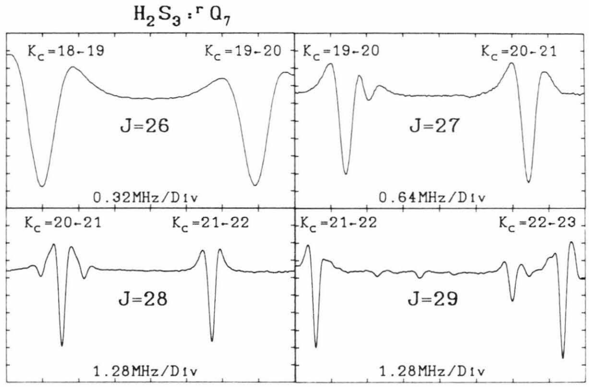

Fig. 2. The four high J-lines of the $^rQ_7$-branch of cis-H_2S_3 are split by the effects of inertial asymmetry (K-splitting). These lines do not exhibit the typical intensity alternation observed in all spectra arising from asymmetric rotors with C_2-symmetry. For trans-H_2S_3 the expected intensity ratio would be 3:1.

fane mixture typically 40 g of H_2S_3 are obtained. After purification by vacuum distillation [9] the trisulfane was transferred into the sample tube from which it was allowed to evaporate into the spectrometer cell.

Observations

The millimeter-wave spectrometer used has been described in its essential parts by Bester et al. [12] although the present spectrometer version employs several new additions both in electronics and data handling which will be described elsewhere.

Table 1. Rotational Parameters of H_2S_3 [a].

Constant	Value	Unit
A	14 099.8962 (10)	MHz
B	2749.4456 (26) [b]	MHz
C	2370.5544 (26) [b]	MHz
D_J	0.0 [c]	
D_{JK}	−11.6826 (28)	kHz
D_K	126.422 (14)	kHz
d_1	−0.2494 (14)	kHz
d_2	−0.01293 (99)	kHz
H_J	0.0 [c]	
H_{JK}	−0.0078 (16)	Hz
H_{KJ}	−0.426 (14)	Hz
H_K	3.652 (56)	Hz
h_1	0.27 (32)	mHz
h_2	−0.08 (81)	mHz
h_3	0.18 (30)	mHz

[a] Numbers in the parentheses are one standard deviations determined by the least-squares fit.
[b] The $\frac{1}{2}(B + C)$ was assumed to be 2560 MHz on the basis of a predicted molecular structure.
[c] Undeterminable at the present and assumed to be zero.

The observed rotational spectrum of H_2S_3 is dense, but consists of several series of regularly spaced (about every 23 GHz) compact and therefore conspicuous Q-branches. The individual J lines in the Q-branches are readily assigned and are analysed on the basis of the Watson S-reduced Hamiltonian. The molecule is a slightly asymmetric but prolate rotor. The rotational parameters are given in Table 1 and have been determined from more than 300 assigned Q-branch transitions. Figure 1 reproduces a plot of one of the 7 measured ground-state Q-branches, the $^rQ_7$-branch. All Q-branches reveal three important features:

(i) successive J lines do not exhibit an intensity alternation. The missing intensity alternation can only be seen for those high J-transitions for which the K-degeneracy can be resolved. In Fig. 2 we present for the $^rQ_7$-branch four successive J-lines for which the K-type splitting is resolved. It is the equal intensity of those lines and of other observed high J lines of different Q-branches which indicate that the H_2S_3 molecule associated with these spectra does not feature a C_2 axis of symmetry.

(ii) The ground state Q-branch lines as well as excited state Q-branch lines do not exhibit any resolvable splitting due to torsional motion. On the basis of the assigned lines we conclude that the observed molecule must be locked into one conformation which is the cis-conformer. However the failure to detect any torsional splitting infers that the barrier to internal

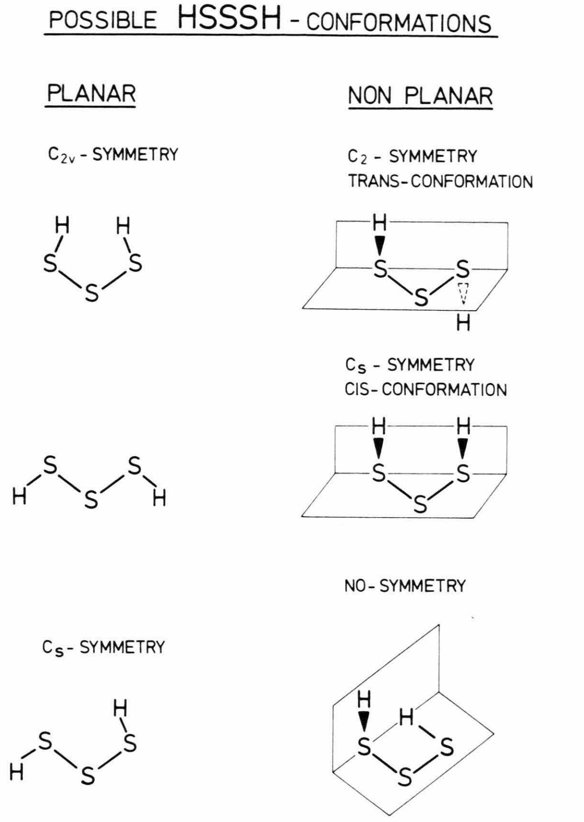

Fig. 3. Possible conformers of HSSSH. For the conformers which have no symmetry at all only one example is illustrated.

rotation (i.e. tunneling to the trans-conformation) is at least as high as or higher than for H_2S_2 [7].

(iii) All main characteristics of the spectrum clearly arise from a permanent electric dipole moment oriented perpendicular to the rotor-axis. From a better fit to the observed spectra a *c*-type spectrum is inferred rather than a *b*-type. Unambiguous proof will come from the observation of Q-branches with low *K*-values.

Discussion

Force field calculations and semiempirical MO studies suggested that H_2S_3 consists of a mixture of two conformers rapidly interconverting with each other [13]. The possible conformations discussed in the literature for H_2S_3 are summarized in Fig. 3, where we have also included one out of many possible H_2S_3 structures which display no symmetry. Amongst the probable structures of H_2S_3 semiempirical MO calculations predict that two non-planar conformers are relatively stable: the trans-form which exhibits C_2 symmetry and the cis-form with C_s symmetry. At ambient temperatures rapid interconversion is suggested.

A trans-H_2S_3 conformation with C_2-symmetry was assumed by Wieser et al. [14] for assigning the IR- and Raman spectra of H_2S_3 and H_2S_4 in solution [14]. However IR-spectra of H_2S_3 in solution can never be obtained with sufficiently high resolution to differentiate between the two possible conformers.

Our spectra clearly indicate that the molecule has no axis of symmetry and must be tightly locked into one conformation. On the basis of the present spectroscopic evidence we favour the cis-form (see Fig. 3) for the molecule: a bend SSS chain with the two hydrogen atoms attached to the end-sulfur-atoms and both H-atoms sticking out of the SSS-plane in the same directional sense. The cis-conformation can account for all observed and hitherto assigned spectroscopic features.

MNDO-Calculations show that the permanent electric dipole moment in the cis-form is about 2.5 Debye whereas for the trans-conformation the dipole moment is considerably smaller (0.4 Debye) which makes the trans-form difficult to detect.

Trsic and Laidlaw [15] used an ab initio Hartree-Fock-Slater calculation for describing the polysulfanes H_2S_n $(n = 1, \dots, 4)$ and obtained under the assumption of a trans-conformer for H_2S_3 an electric dipole moment of 0.62 D, which is in approximate agreement with our MNDO-results. Our present experimental data clearly establish the cis-conformer, but we can not completely rule out the presence of the trans-conformer in the gas phase. On the basis of the smaller dipole moment (neglecting for the moment the probable energy difference between the cis- and the trans-conformer) we expect the rotational spectra of the trans-conformer to be weaker by a faktor of $(\mu_{\text{cis}}/\mu_{\text{trans}})^2 \approx 40$.

Detailed information on the structure will come from observation of isotopically substituted species. Especially D replacement is expected to help locating the positions of the hydrogen nuclei.

Conclusion

The reported spectrum is the first gas-phase spectrum obtained for a sulfur chain molecule where the chain length exceeds two. In contrast to the linear carbon chain the sulfur chain is bent. It will be of considerable chemical, spectroscopic and astrophysical interest to understand the structure and the formation of sulfur chain molecules.

Acknowledgement

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