Detection of Gas-Phase Hydrogentsulsulfide, 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 unambiguously 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 C₃ 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 C₂ or C₃, 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 H₂Sₙ dates back as far as 1777. The knowledge of the persulfides and disulfane, H₂S₂, is thus 40 years older than its oxygen analogue hydrogen-peroxid, 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 H₂Sₙ (n = 2, ..., 6) display similar spectroscopic features [3–6]. From the close resemblance of these features with those of the H₂O₂ 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 H₂S₂ [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 H₂S₃.

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% (H₂S₂ and H₂S are present only in traces) [10,11]. Additional amounts of H₂S₃ as well as H₂S₂ 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 H₂S, H₂S₂ and H₂S₃ distill off from the species of higher molecular weight and can be isolated in different traps at temperatures of 0°C (H₂S₂), −78°C (H₂S) and −196°C (H₂S). 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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The observed rotational spectrum of H$_2$S$_3$ 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 $^1$Q$_7$-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 $^1$Q$_7$-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$_2$S$_3$ 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

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**Table 1. Rotational Parameters of H$_2$S$_3$.**

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>14099.8962 (10)</td>
<td>MHz</td>
</tr>
<tr>
<td>$B$</td>
<td>2749.4456 (26)$^b$</td>
<td>MHz</td>
</tr>
<tr>
<td>$C$</td>
<td>2370.5544 (26)$^b$</td>
<td>MHz</td>
</tr>
<tr>
<td>$D_{ij}$</td>
<td>0.0$^c$</td>
<td></td>
</tr>
<tr>
<td>$D_{ijk}$</td>
<td>-11.6826 (28)</td>
<td>kHz</td>
</tr>
<tr>
<td>$B_{ij}$</td>
<td>126.422 (14)</td>
<td>kHz</td>
</tr>
<tr>
<td>$d_1$</td>
<td>-0.2094 (14)</td>
<td>kHz</td>
</tr>
<tr>
<td>$d_2$</td>
<td>-0.0129399</td>
<td>kHz</td>
</tr>
<tr>
<td>$H_{ij}$</td>
<td>0.0$^c$</td>
<td></td>
</tr>
<tr>
<td>$H_{ijk}$</td>
<td>-0.0078 (16)</td>
<td>Hz</td>
</tr>
<tr>
<td>$H_{ikj}$</td>
<td>-0.426 (14)</td>
<td>Hz</td>
</tr>
<tr>
<td>$H_k$</td>
<td>3.652 (56)</td>
<td>Hz</td>
</tr>
<tr>
<td>$h_1$</td>
<td>0.27 (32)</td>
<td>mHz</td>
</tr>
<tr>
<td>$h_2$</td>
<td>-0.08 (81)</td>
<td>mHz</td>
</tr>
<tr>
<td>$h_3$</td>
<td>0.18 (30)</td>
<td>mHz</td>
</tr>
</tbody>
</table>

$^a$ Numbers in the parentheses are one standard deviations determined by the least-squares fit.

$^b$ The $(B + C)$ 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 probable structures of $\text{H}_2\text{S}_3$ 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-$\text{H}_2\text{S}_3$ conformation with $C_2$-symmetry was assumed by Wieser et al. [14] for assigning the IR- and Raman spectra of $\text{H}_2\text{S}_3$ and $\text{H}_2\text{S}_4$ in solution [14]. However IR-spectra of $\text{H}_2\text{S}_3$ 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 $\text{H}_2\text{S}_n$ ($n=1,...,4$) and obtained under the assumption of a trans-conformer for $\text{H}_2\text{S}_3$ 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 factor 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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