Microwave Spectrum of (SiH₃)₂X, X = O,S, r₀-Structure, Molecular Electric Dipolemoment and Barrier to Internal Rotation of Disilylsulfide

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The rotational spectrum of SiH₃-S-SiH₃ in its vib-torsional ground state has been investigated in the frequency range between 8 and 40 GHz. From the absolute frequencies and torsional splittings a rigid-top-rigid-frame r₀-structure could be derived. The molecular dipole moment was determined from the second order Stark effect of some AA-species rotational transitions. The analysis of the microwave spectrum of the related molecule SiH₃-O-SiH₃ was yet unsuccessful. However several features of the observed spectrum lend support to the idea of a “quasi-linear” double rotor molecule with a relatively low energy hump for the linear configuration of the Si-O-Si-chain.

Introduction

Over the past years considerable effort has been put into the analysis of the microwave spectra of a group of “two top molecules”, having the general formula (CH₃)₂X with X = O [1], S [2] and Se [3]. From this work we have information on the structure, on the electric dipole moment, and on the barrier to internal rotation for these molecules. In the following we report the results of an investigation of the microwave spectra of the homologous silyl compounds (SiH₃)₂O and (SiH₃)₂S, which was started with the aim to provide experimental data as a basis for a discussion of the bonding situation and of the origin of the barrier to internal rotation.

Experimental

The spectra were recorded with a conventional Stark-modulated (33 kHz zero based square wave) microwave spectrometer equipped with a brass waveguide cell of 8 m length and an inner cross section of 1 by 5 cm. Phase stabilized backward wave oscillators were used as radiation sources. Under typical recording conditions sample pressures were about 10 mTorr at temperatures around −65 °C.

Disiloxane

A sample of (SiH₃)₂O was obtained from Dr. A. Almenningen (Oslo). Once admitted to the cell, its microwave spectrum did not change in the course of a day. It was recorded in the frequency range from 23 to 40 GHz. Within the frame of the standard rigid top-rigid frame model [4] and under the assumption of a Si—O—Si bond angle of about 145° as suggested from the electron diffraction work [5] one would expect to find the lower J-lines of the b-type Q-branch to fall into this frequency range. One would further expect, that the rotational spectra of molecules in the AA-torsional ground state of the SiH₃-torsion should approximately follow a rigid rotor pattern with a second order Stark-effect, requiring higher Stark fields (i.e. E_Stark on the order of 1000 V/cm) for full modulation. However the search for this Q-branch of the AA-species failed. Although a great number of strong absorption lines were observed in the recorded range, all of them were fully modulated at Stark fields as low as 50 V/cm with unresolved low intensity Stark patterns, which indicates, that they all were high J transitions. To our opinion this result gives some support to the idea of a quasi-linear heavy atom chain with a comparatively low hump for the linear configuration, as was recently concluded from the Raman spectrum [6]. In such a molecule only vibration-rotation spectra would be allowed with selection rules ΔJ = 0, ± 1; Δv = ± 1, Δl = ± 1 (v, l = quantum numbers for the bending vibration). With a vibrational energy gap of about 250 GHz [6] for (v₁₁ = 0, l₁₁ = 0) → (v₁₁ = 1, l₁₁ = ± 1)

(the index “11” denotes the Si—O—Si bending vibration), the above mentioned “Q-branch frequencies” should be shifted approximately by this amount, which would explain the failure of our search. Although we have not yet been able to
assign the more than 200 observed absorption lines, we list several strong lines for identification purposes in Table 1.

### Disilylsulfide

Initially we prepared samples of Disilsulfide by two different ways:

\[
2 \text{SiH}_3\text{I} + \text{Hg}_2\text{S} \rightarrow (\text{SiH}_3)_2\text{S} + 2 \text{HgI} \quad [7],
\]

\[
2 \text{SiH}_3\text{Br} + \text{Li}_2\text{S} \rightarrow (\text{SiH}_3)_2\text{S} + 2 \text{LiBr} \quad [8].
\]

The second reaction turned out to be superior to the first, since it gave better yields and avoided the use of expensive iodine and poisonous mercury salts. Because (SiH₃)₂S readily reacts with water to form (SiH₃)₂O and H₂S, great care had to be taken, to remove traces of water adsorbed at the walls of the waveguide cell. Despite these precautions, the sample slowly decayed in the cell and after about two hours its spectrum became obscured by the much stronger lines of the (SiH₃)₂O spectrum (compare Table 1). Among the many lines belonging to either the (SiH₃)₂S or (SiH₃)₂O spectra, there also appeared some other very strong, unidentified lines, which might belong to the SiH₃SH molecule. To obtain the pure spectrum of (SiH₃)₂S the cell was refilled every hour.

The assignment of the spectrum was reported in a previous note [9]. In the following we present a refined analysis which includes centrifugal distortion effects. It is based on the effective rotational Hamiltonian given in Equation (1). This Hamiltonian may be thought of as the result of a second order perturbation treatment within torsio-vibrational states, i.e. a Van Vleck transformation, aiming at the vibrational and torsional groundstate. It is assumed that those matrixelements of the full Hamiltonian which are simultaneously off-diagonal in the torsional and vibrational quantum numbers are sufficiently small to justify their neglect, so that the resulting effective rotational operator may be written as a blend of the standard PAM-Hamiltonian [4, 10] used for molecules with two top internal rotation and of the standard centrifugal distortion Hamiltonian [11] used for asymmetric top molecules.

\[
H_{v_1, \sigma_1, v_2, \sigma_2} = H_r + \sum_{i=1}^{2} \sum_{n=1}^{4} W^{(n)}_{v_1, \sigma_1} \mathcal{P}_n + \sum_{i=1}^{2} W^{(d)}_{v_1, \sigma_1} H_{ID} + H_{CD} \quad (1a)
\]

\[
\mathcal{P}_i = -\frac{\lambda_{a1} I_a}{I_a} - \frac{\lambda_{b1} I_b}{I_b} \quad (i = 1, 2)
\]

The symbols have the following meaning:

\[
v_1, \sigma_1, v_2, \sigma_2 = \text{internal rotation quantum numbers}.
\]

\[
H_r = A_0 \mathcal{P}_a^2 + B_0 \mathcal{P}_b^2 + C_0 \mathcal{P}_c^2,
\]

\[
\mathcal{P}_i = \frac{\lambda_{a1} I_a}{I_a} - \frac{\lambda_{b1} I_b}{I_b} \quad (i = 1, 2)
\]

\[
F = \frac{h}{8\pi^2 I_a} \frac{r^2 - q^2}{r^2} \quad (i = 1, 2)
\]

\[
\lambda_{a1} = -\lambda_{a2} = \cos(\theta) \quad (\text{see Fig. 2}),
\]

\[
\lambda_{b1} = \lambda_{b2} = \sin(\theta),
\]

\[
I_a, I_b, I_c = \text{principal moments of inertia},
\]

\[
I_x = \text{moment of inertia of the SiH₃-top about its symmetry axis which is assumed to coincide with the internal rotation axis}.
\]

\[
\mathcal{P}_a, \mathcal{P}_b, \mathcal{P}_c = \text{components of the overall angular momentum about the a-, b-, and c-principal inertia axis respectively}.
\]

\[
W^{(n)}_{v_1, \sigma_1}, W^{(d)}_{v_1, \sigma_1} = \text{perturbation sums from perturbation treatment within the torsional states}\]

\[
H_{ID} = \frac{1}{2} \left[ [\mathcal{P}_i, H_r], \mathcal{P}_i \right] - \frac{1}{2} H_r \mathcal{P}_i^2 - \frac{1}{2} \mathcal{P}_i^2 H_r;
\]

\[
(i = 1, 2).
\]

\[\triangle\] Stelman's denominator correction to the internal rotation perturbation sums [13].
\[ \mathcal{H}_{\text{CD}} = -D_j \mathcal{P}^4 - D_{jk} \mathcal{P}^2 \mathcal{P}^2 - D_k \mathcal{P}^4 \\
\quad - \delta_j [\mathcal{P}^2 (\mathcal{P}^2 - \mathcal{P}_s^2) + (\mathcal{P}_s^2 - \mathcal{P}_e^2)]^2 \\
\quad - 2 R_k [3 (\mathcal{P}^2 \mathcal{P}_s^2 + \mathcal{P}_s^2 \mathcal{P}_e^2) - \mathcal{P}^4 - \mathcal{P}_e^2] \]

...centrifugal distortion Hamiltonian;

\[ \mathcal{P}^2 = \mathcal{P}_s^2 + \mathcal{P}_e^2; \]

...square of the overall angular momentum.

We note that the torsional part of Eq. (1) is based on a potential for the internal rotation \( V(x_1, x_2) \) which may be described by simple three-fold barriers i.e.

\[ V(x_1, x_2) = V_3 \left( \cos(3x_1) - 1 \right) + \frac{V_2}{2} \left( \cos(3x_2) - 1 \right). \]

Since at present our computer programs did not allow us to fit internal rotation parameters, rotational constants, and centrifugal distortion constants simultaneously, we did proceed as follows.

First centrifugal distortion was neglected and initial values for the rotational constants, \( A, B, C \) and the internal rotation parameters \( V_3, I_x, I_\theta \) were fitted to the absolute frequencies and to the torsional splittings given in Table 4 (the result was published in Ref. [9]). In the second step the centrifugal distortion constants were obtained from the AA-species spectrum. For the AA-species \((v_i = 0, \sigma_i = 0; \ i = 1, 2) \ W^{(1)}_{v_i, \sigma_i} \) and \( W^{(3)}_{v_i, \sigma_i} \) are zero and within the approximation of Eq. (1) the spectrum may be reproduced by a rigid rotor Hamiltonian plus corrections which are all of fourth order in the angular momentum operators:

\[ \mathcal{H}_{\text{AA}} = \left( A + 2a^2 W^{(3)}_{0,0} \right) \mathcal{P}^2 + \left( B + 2b^2 W^{(3)}_{0,0} \right) \mathcal{P}^2 + C \mathcal{P}_s^2 + \left( \mathcal{P}^4 + \mathcal{P}_e^4 \right) + W^4_{0,0} (\mathcal{H}_{1D} + \mathcal{H}_{2D}) + \mathcal{H}_{\text{CD}} \]

Table 2. Effective rotational constants, centrifugal distortion constants, and correlation matrix for the AA-torsional substate of \((\text{SiH}_3)_2\text{S}\). The quoted uncertainties (in brackets) give one standard deviation as obtained in a least square fit.

| \( A_{\text{AA}} \) [MHz] | 9543.346 (9) | 1.000 |
| \( B_{\text{AA}} \) [MHz] | 2832.534 (2) | 0.030 | 1.000 |
| \( C_{\text{AA}} \) [MHz] | 2908.506 (2) | 0.013 | 0.636 | 1.000 |
| \( D_j \) [kHz] | 2.116 (25) | -0.077 | 0.864 | 0.781 | 1.000 |
| \( D_{jk} \) [kHz] | -13.39 (24) | 0.597 | -0.227 | -0.154 | -0.375 | 1.000 |
| \( D_k \) [kHz] | 60.7 (17) | 0.829 | 0.086 | -0.010 | 0.011 | 0.177 | 1.000 |
| \( \delta_j \) [kHz] | 0.651 (8) | -0.167 | 0.563 | -0.154 | 0.386 | -0.059 | 0.025 | 1.000 |
| \( R_6 \) [kHz] | 0.012 (9) | 0.459 | -0.090 | -0.032 | -0.230 | 0.696 | 0.263 | -0.486 | 1.000 |

Fig. 1. Flowchart showing the fitting procedure followed in the analysis of observed frequencies and torsional splittings in the microwave spectrum of Disilyl sulfide.

\[ a^2 = \frac{\lambda^2_{\alpha i}}{I_{a^2}}, \quad b^2 = \frac{\lambda^2_{\beta i}}{I_{b^2}} (i = 1, 2). \]

With the approximate values for the rotational constants and internal rotation parameters, the fourth order corrections to the frequencies which arise from internal rotation i.e. from

\[ \mathcal{F} \sum_{i=1}^{2} W^{(3)}_{0,0} \mathcal{P}_i^4 + \sum_{i=1}^{2} W^{(3)}_{0,0} \mathcal{H}_{4D} \]

were calculated and subtracted from the observed frequencies. The so corrected frequencies were then...
subjected to a standard centrifugal distortion treatment. The result is given in Table 2.

In the final step the centrifugal distortion contributions obtained for the AA-species were also used for EA, EE and AE species. Since the rotational Eigenfunctions of Eq. (1) are essentially the Eigenfunctions of $H_2$ with some species dependent mixing of the K-doublet functions due to terms linear in $\mathcal{P}_a$ (if present) and since the asymmetric top expectation values for $\mathcal{P}_a^2$ and $\mathcal{P}_a^3$ are essentially the same for the K-doublets, this simplified treatment is justified for Disilylsulfide, where the centrifugal distortion contributions due to $\delta_f$ and $R_6'$ are sufficiently small.

After subtraction of the centrifugal distortion corrections (column 2 in Table 4) from the frequencies given in Table 4, the rotational transitions ($v_{\AA} - v$) are measured relative to the AA-species. A not included in the fit.

Table 4. Microwave spectrum of (SiH₃)₂S in the torsional ground state (all frequencies in MHz). $\Delta v^{(cd)}$ gives the contribution of the centrifugal distortion term [Eq. (1b)] to the transition frequencies. The torsional splittings of the rotational transitions ($v_{\AA} - v$) are measured relative to the AA-species. A not included in the fit.

<table>
<thead>
<tr>
<th>$v_{\AA}$</th>
<th>$\Delta v^{(cd)}$</th>
<th>obs. calc.</th>
<th>$v_{\AA} - v$</th>
<th>obs. calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>000–101</td>
<td>AA 11832.030</td>
<td>-0.040</td>
<td>0.111</td>
<td></td>
</tr>
<tr>
<td>010–201</td>
<td>AA 16470.740</td>
<td>-0.025</td>
<td>0.029</td>
<td></td>
</tr>
<tr>
<td>110–210</td>
<td>AA 30183.107</td>
<td>-0.081</td>
<td>0.040</td>
<td></td>
</tr>
<tr>
<td>210–320</td>
<td>AA 9171.022</td>
<td>-0.026</td>
<td>0.041</td>
<td></td>
</tr>
<tr>
<td>000–111</td>
<td>EE 11840.166</td>
<td>-0.301</td>
<td>12.135</td>
<td>0.412</td>
</tr>
<tr>
<td>101–212</td>
<td>AA 16461.610</td>
<td>-0.102</td>
<td>9.130</td>
<td>0.131</td>
</tr>
<tr>
<td>111–220</td>
<td>AA 31563.477</td>
<td>-0.087</td>
<td>0.041</td>
<td></td>
</tr>
<tr>
<td>210–330</td>
<td>AA 9184.959</td>
<td>-0.129</td>
<td>-6.937</td>
<td>-0.170</td>
</tr>
<tr>
<td>200–321</td>
<td>AA 20830.215</td>
<td>-0.035</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>000–111</td>
<td>EE 20822.143</td>
<td>-0.029</td>
<td>8.062</td>
<td>0.022</td>
</tr>
<tr>
<td>101–212</td>
<td>AA 20815.810</td>
<td>0.009</td>
<td>14.625</td>
<td>-0.016</td>
</tr>
<tr>
<td>111–220</td>
<td>AA 20812.525</td>
<td>-0.163</td>
<td>17.680</td>
<td>0.156</td>
</tr>
<tr>
<td>200–321</td>
<td>AA 20827.561</td>
<td>-0.029</td>
<td>8.062</td>
<td>0.022</td>
</tr>
<tr>
<td>300–331</td>
<td>AA 22353.682</td>
<td>-0.052</td>
<td>0.032</td>
<td></td>
</tr>
<tr>
<td>000–111</td>
<td>EE 22465.684</td>
<td>-0.008</td>
<td>67.998</td>
<td>0.040</td>
</tr>
<tr>
<td>101–212</td>
<td>AA 22486.852</td>
<td>-0.033</td>
<td>46.830</td>
<td>0.065</td>
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<tr>
<td>111–220</td>
<td>AA 22361.197</td>
<td>-0.075</td>
<td>172.485</td>
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<tr>
<td>200–321</td>
<td>AA 24971.855</td>
<td>-0.079</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>000–111</td>
<td>EE 24964.578</td>
<td>0.009</td>
<td>7.277</td>
<td>-0.002</td>
</tr>
</tbody>
</table>

Table 3. Rotational constants and internal rotation parameters as used in Eq. (1); correlation matrix for the torsional groundstate of (SiH₃)₂S (conversion factor 605391 MHz amu Å²).

| $A$ [MHz] | 9533.058 (9) | 1.000 |
| $B$ [MHz] | 2851.927 (2) | -0.151 |
| $C$ [MHz] | 2308.507 (2) | 0.257 |
| $V_3$ [cal/mol] | 522.6 (4) | 0.258 |
| $\Theta$ [°] | 39.176 (28) | 0.160 |
| $I_\alpha$ [amu Å²] | 6.219 (6) | -0.302 |

Derived constants: $F$ [MHz] 89106 (82); $s$ 27.339 (7).
(For comparison the corresponding values for (CH₃)₂S are also given in Table 6.) This may indicate deficiencies of the theoretical model but it certainly also reflects the fact that the observed rotational constants are vibrational expectation values rather than rigid rotor values. The underlying problem becomes also apparent if one tries to calculate the moment of inertia of the silyl tops from the observed rotational constants. If the Si—S—Si frame and the silyl tops could be treated as rigid bodies $I_\alpha$ would be given by the following relation:

$$I_\alpha = \frac{1}{2} (I_{aa} + I_{bb} - I_{cc})$$

$$= \frac{\hbar}{8\pi^2} \left( \frac{1}{A} + \frac{1}{B} - \frac{1}{C} \right).$$

(2)

If one uses the rotational constants of Table 3 to calculate $I_\alpha$ according to Eq. (2) one obtains $I_\alpha = 5.64973(2)$ amu Å², as compared to the directly determined value of $I_\alpha = 6.219(6)$ amu Å². In the light of this result, some older investigations which in their analysis of the torsional splittings relied on the validity of Eq. (2) should be reviewed critically. Although the deviations between observed and calculated rotational constants are apparently big, it has been found for (CH₃)₂S, that the differences between $r_0$- and $r_s$-bond distances are smaller than 0.01 Å. We think that this holds for (SiH₃)₂S as well.

Discussion

At the end of this work we contentedly noted that the Hamiltonian of Eq. (1) gave a really good fit to the observed spectrum (see Table 4), although the barrier to internal rotation is very low ($V_3 = 522.6$ cal/mol). The limitation for the PAM Hamiltonian we use seems to lie at s-values below 10 [16].

The bond angle at the central sulfur atom observed here (\(\angle\)Si—S—Si = 98.35°) is found to be nearly equal to the one observed for (CH₃)₂S (\(\angle\)C—S—C = 98.9°) [2]. Contrary to Disilyl-ether/Dimethylether, where the corresponding bond angles differ considerably (\(\angle\)Si—O—Si = 145°) [5], (\(\angle\)C—O—C = 124°) [1], no such effect is observed here. This has been interpreted [15] in terms of a partial double bond character (pπ-dπ bonding) being present in the Si—O bond of (SiH₃)₂O but not in the Si—S bond of (SiH₃)₂S.

If, on the other hand, the electric dipole moments of (CH₃)₂S ($\mu_b = 1.551$ D [2]) and (SiH₃)₂S ($\mu_b = 0.896$ D) are compared, it is realized that, although the difference in the electronegativities of silicon and sulfur is bigger than the one of carbon and sulfur and although the bond distance $r$(Si—S) is bigger than $r$(C—S), the observed dipole moment is smaller for (SiH₃)₂S. This effect is observed in all comparisons between silyl- and their homologous methylecompounds (as e.g. $\mu$(SiH₃Br) = 1.318 D [17], $\mu$(CH₃Br) = 1.797 D [18]) and is generally explained by assuming pπ-dπ bonding to be present in Silylcompounds. In the following we shall discuss the barrier to internal rotation. Since the barrier to internal rotation was not known for a Si—S bond so far, it is difficult to make any comparisons. In a group of related molecules the relatively low value of the barrier observed here is noticeable.

![Fig. 3. Energy level scheme for the torsional vibration of (SiH₃)₂S as determined from torsional splittings of ground state rotational transitions in the microwave spectrum. The levels are characterized by the vibrational quantum numbers ($v_1$, $v_2$) of the two internal rotors and the symmetry species of the torsional wavefunction. For greater perspicuity the EA and AE levels are not included in this diagram. The torsional transition (0, 0) → (0, 1) of (SiH₃)₂S, which has not been observed so far, should be found near 63 cm⁻¹ in the IR-spectrum.](image)
Using the experimental data given in Table 3 it becomes possible to construct the energy level diagram for the torsional vibration of (SiH₃)₂S (see Figure 3).

We are now able to predict the first torsional transitions to lie around 63 cm⁻¹ ((0, 0) → (0, 1)) and 112 cm⁻¹ ((0, 0) → (0, 2)) in the IR- and Raman spectrum.


Die Rechnungen wurden auf dem PDP-10-Computer des Rechenzentrums der Universität Kiel durchgeführt.