The Microwave Spectrum of Disilylsulfide

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We report an analysis of the rotational spectrum of $(SiH_3)_2S$, leading to the rotational constants A, B, C and the internal rotation parameters V_3, θ and I_α.

The microwave rotational spectrum of disilylsulfide, $(SiH_3)_2S$, was recorded in the frequency range from 8 to 40 GHz with a conventional microwave spectrometer [1, 2] equipped with an 8 m absorption cell and employing 33 kHz Stark-modulation. The sample pressure was about 15 m Torr at temperatures around $-60\,^\circ C$. $(SiH_3)_2S$ was prepared by two independent ways [3, 4]:

a) $2\,SiH_3I + Hg_2S \rightarrow (SiH_3)_2S + 2\,HgI$,

b) $2\,SiH_3Br + Li_2S \rightarrow (SiH_3)_2S + 2\,LiBr$.

The rotational spectra taken of both samples were identical. Using PAM-theory [5] we have determined the following six parameters (see Table 1): the rotational constants A, B and C, the barrier hight V_3 for the internal rotation of the silylgroups, the angle θ between the principal a-axis and the symmetry axis of the silylgroups and the moment of inertia, I_α, of the internal rotor along its symmetry axis.

Table 1. Internal rotation parameters and rotational constants as determined from a least squares fit applied simultaniously to the absolute frequencies and internal rotation splittings of the observed spectrum of $(SiH_3)_2S$. Errors quoted give one standard deviation. For comparison the rotational constants calculated from the electron diffraction structure [14] within the rigid rotor model, are included in the Table.

V_3	2189.0	± 5.0	J/mol
	(523.1	± 1.2	cal/mol)
θ	39.20°	± 0 06°	
I_α	1.031	± 0.003	10^{-46} kgm^2
	(6.210	± 0.017	amuÅ^2)
A	9533.080	± 0.038	MHZ
B	2851.717	± 0.008	MHz
C	2308.445	± 0.008	MHz
A_{ed}	9366 MHz	calc. from data given in Ref. [14]	
B_{ed}	2894 MHz		
C_{ed}	2317 MHz		

The Hamiltonian we use is [6, 7]

$$
\begin{aligned}
\mathscr{H}_{v_1\sigma_1,\,v_2\sigma_2} &= \mathscr{H}_r + F\sum_{i=1}^{2}\sum_{n=1}^{4} W^{(n)}_{v_i,\,\sigma_i}\mathscr{P}_i{}^n \\
&\quad + \sum_{i=1}^{2} W^{(d)}_{v_i,\,\sigma_i}\mathscr{H}_{i\mathrm{D}}\,, \\
\mathscr{H}_r &= A\mathscr{P}_a{}^2 + B\mathscr{P}_b{}^2 + C\mathscr{P}_c{}^2\,, \\
\mathscr{P}_i &= \frac{\lambda_{bi} I_\alpha}{I_b}\mathscr{P}_b + \frac{\lambda_{ai} I_\alpha}{I_a}\mathscr{P}_a, \\
F &= \frac{h}{8\pi^2 I_\alpha}\frac{r}{r^2 - q^2}\,, \qquad (1) \\
r &= 1 - \frac{\lambda_{b_1}^2 I_\alpha}{I_b} - \frac{\lambda_{a_1}^2 I_\alpha}{I_a} \\
&= 1 - \frac{\lambda_{b_2}^2 I_\alpha}{I_b} - \frac{\lambda_{a_2}^2 I_\alpha}{I_a}\,, \\
q &= -\frac{\lambda_{b_1}\lambda_{b_2} I_\alpha}{I_b} - \frac{\lambda_{a_1}\lambda_{a_2} I_\alpha}{I_a}\,,
\end{aligned}
$$

$$\lambda_{b_1} = \lambda_{b_2} = \sin\theta\,,$$
$$\lambda_{a_1} = -\lambda_{a_2} = \cos\theta\,,$$

I_a, I_b, $I_c \triangleq$ principal moments of inertia,
$I_\alpha =$ moment of inertia of the SiH_3-top about its symmetry axis,

$$
\begin{aligned}
\mathscr{H}_{i\mathrm{D}} &= \tfrac{1}{2}[[\mathscr{P}_i, \mathscr{H}_r], \mathscr{P}_i] \\
&= \mathscr{P}_i\mathscr{H}_r\mathscr{P}_i - \tfrac{1}{2}\mathscr{H}_r\mathscr{P}_i{}^2 - \tfrac{1}{2}\mathscr{P}_i{}^2\mathscr{H}_r\,.
\end{aligned}
$$

$\mathscr{H}_{i\mathrm{D}}$ is Stelman's first denominator correction to the perturbation sums [8]. Values of the perturbation coefficients, $W^{(n)}_{v_i,\sigma_i}$ and $W^{(d)}_{v_i,\sigma_i}$ were obtained from the tables given by Hayashi and Pierce [9].

The interaction of internal- and overall-rotation splits all rotational transitions into clearly resolved quartetts (see Fig. 1) with splittings ranging from 1 to 200 MHz for low values of J. The assignment was aided by the characteristic pattern of spin intensities [10, 11] and checked by MW-MW-double resonance experiments [12].

We note that the barrier to internal rotation, which could not be determined from the IR-spectrum of $(SiH_3)_2S$ [13] or from the electron difraction work [14] is much smaller than in $(CH_3)_2S$, $(2136 \pm 2$ cal/mole) [15].

We further note, that the effective Hamiltonian given above is based on the complete neglect of interactions between the two tops, i.e. only the

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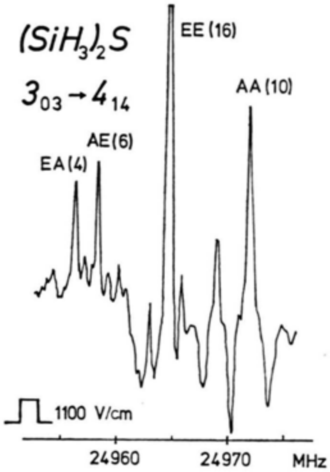

Fig. 1. Low resolution scan of the region of the $3_{03} \rightarrow 4_{14}$ rotational transition. The interaction of internal- and overall-rotation splits the transition into a clearly resolved quartett. Its components are labelled with the symmetry species of the torsional substate: EA (torsional quantum numbers $(v_1, \sigma_1; v_2, \sigma_2) = (0, \pm 1; 0, \mp 1)$); AE $(0, \pm 1; 0, \pm 1)$; EE $(0, \pm 1; 0, 0)$, $(0, 0; 0, \pm 1)$; and AA $(0, 0; 0, 0)$. The symmetric displacement of the AA and the centre of the EA/AE pair around the EE species is characteristic for this type of molecule. The statistical spin weights for a molecule with two equivalent SiH_3-tops are given in parantheses.

first two terms on the right side of Eq. (2) are included:

$$\begin{aligned} V(\alpha_1, \alpha_2) = {} & \frac{V_3}{2}(\cos 3\alpha_1 - 1) + \frac{V_3}{2}(\cos 3\alpha_2 - 1) \\ & + V_{12}(\cos 3\alpha_1 \cos 3\alpha_2 - 1) \\ & + V_{12}' \sin 3\alpha_1 \sin 3\alpha_2 + \cdots . \end{aligned} \tag{2}$$

As a consequence the experimentally determined V_3-value of the ground torsional state will be approximately $V_3 + 2V_{12}$, as can be seen by expanding Eq. (2) into a Taylor series around the equilibrium values of $\alpha_1 = 0 \bmod \frac{2\pi}{3}$ and $\alpha_2 = 0 \bmod \frac{2\pi}{3}$

$$\begin{aligned} V(\alpha_1, \alpha_2) = {} & \frac{V_3}{2}\left(\frac{3\alpha_1}{2}\right)^2 + \frac{V_3}{2}\left(\frac{3\alpha_2}{2}\right)^2 \\ & + V_{12}\left(\frac{3\alpha_1}{2}\right)^2 + V_{12}\left(\frac{3\alpha_2}{2}\right)^2 \\ & + V_{12}' \, 3\alpha_1 \cdot 3\alpha_2 + \cdots . \end{aligned} \tag{3}$$

From this argument it follows, that in general V_3 and V_{12} should show a rather strong correlation, if they were determined from low lying excited torsional states, with torsional levels still well below the barrier.

Measurements of the electric dipolmoment and the exact analysis of 72 observed transitions of $(SiH_3)_2S$ including the effect of centrifugal distortion will be reported shortly. In a subsequent paper on this subject we shall present the rotational spectra of isotopically substituted molecules, which are presently under investigation.

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