Hyperfine Interaction Induced K-type Doubling in the mmw Spectrum of HS\textsuperscript{33}SH

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Z. Naturforsch. 50 a, 1191–1198 (1995); received November 14, 1995

The rotational spectrum of the disulfane isotopomer HS\textsuperscript{33}SH has been recorded and assigned between 70 and 300 GHz. In the analysis, rotational constants and \textsuperscript{33}S hyperfine parameters are derived, the latter accounting for nuclear electric quadrupole as well as nuclear spin - rotation hyperfine interactions. The quadrupole constants are in qualitative agreement with a published ab-initio calculation. The electric field gradient principal axes are considerably rotated against the principal inertial axes, giving rise to off-diagonal elements in the electric field gradient tensor. In combination with the very small inertial asymmetry of the molecule, this causes the $K$-doubling in the lowest rotational levels to be dominated by the hyperfine structure rather than the inertial asymmetry contributions. By diagonalization of the quadrupole tensor, an estimate for the dihedral angle ($\gamma \approx 94^\circ$) can be obtained, in good agreement with a previous value.

1. Introduction

Disulfane, H\textsubscript{2}S\textsubscript{2}, is unique among asymmetric top molecules in that it is very close to an almost perfectly accidental prolate symmetric top as judged by the principal moments of inertia. Nevertheless, the skew chain geometry of the molecule gives rise to a perpendicular spectrum which a real prolate top cannot exhibit. H\textsubscript{2}S\textsubscript{2} thus displays a rotational and rotation-vibration spectrum of a near symmetric top, but with asymmetric rotor selection rules. Previous experimental work was concerned with the rotational and vibrational spectra of different isotopomers, including D and \textsuperscript{34}S substituted species (cf. \cite{1} - \cite{11}). These studies revealed a plethora of effects and provided the determination of a partial equilibrium structure \cite{10, 11}. Ab initio calculations on the structure have been published by several authors \cite{12} - \cite{17}). Among them, Palmer \cite{17} has not only calculated ab-initio structures using a triple zeta valence + polarization (TZVP) basis of gaussian type orbitals, but also first theoretical values of the nuclear quadrupole hyperfine interaction, and $H_{\text{NSR}}$ the nuclear spin - rotation term. From experiment, however, no data on \textsuperscript{33}S containing disulfane isotopomers have been reported so far.

After the recent reinvestigation of the \textsuperscript{33}S hyperfine structure (hfs) in H\textsubscript{2}\textsuperscript{33}S \cite{18}, we report in this paper the measurement and identification of the HS\textsuperscript{33}SH rotational spectrum between 70 and 300 GHz. In the present analysis, rotational constants and \textsuperscript{33}S hyperfine parameters are determined, the latter accounting for nuclear electric quadrupole as well as nuclear spin - rotation hyperfine interactions. In the discussion section, the relation between the hfs parameters and the molecular geometry will be presented.

2. Hamiltonian

The Hamiltonian used to describe the present rotational spectrum contains three terms as follows:

$$H = H_{\text{Rot}} + H_Q + H_{\text{NSR}},$$

where the $H_{\text{Rot}}$ denotes the rotational part of the Hamiltonian, $H_Q$ the contribution due to nuclear quadrupole hyperfine interaction, and $H_{\text{NSR}}$ the nuclear spin - rotation term.

The rotational part was already described in \cite{9} where it has been employed for the analysis of the HSSH and HS\textsuperscript{34}SH spectra. We use the same matrix elements of the prolate S-reduction here.

The HS\textsuperscript{33}SH ground state rotational constants $A_0, B_0, C_0$ were estimated on the basis of equilibrium rotational constants $A_e, B_e, C_e$ (obtained from...
the partial equilibrium structure [11] where the torsional contribution has been accounted for) by

\[ X_0(S_{33}) = \frac{X_0^{\exp}(S_{32})}{X_e(S_{32})} X_e(S_{33}) + \frac{1}{2} \left[ \frac{X_0^{\exp}(S_{34}) - X_0^{\exp}(S_{32})}{X_e(S_{32})} X_e(S_{34}) \right]. \] (2)

where \( X = A, B, C, S_\alpha = HS^{S_\alpha} SH \), \( \exp \) = determined from experiment. The centrifugal distortion constants have been predicted by averaging the corresponding HSSH and HS\(^{33}\)SH values.

The hyperfine structure in a disulfane isotopomer is considered in this work for the first time. The matrix elements for the nuclear quadrupole hfs of an asymmetric top have been given in tensor notation by Bowater et al. [19]. In a prolate basis, we have

\[ \langle J'K'IF|H_Q|JKIF \rangle = \frac{1}{2} (-1)^{J'J'} F' \left\{ \begin{array}{c} F' J' I \hfill \\
2 I' J \end{array} \right\} \times \sqrt{(I+1)(2I+1)(2J+3)} \sum_{q=-2}^{2} (-1)^{J'-J} \times \sqrt{(2J+1)(2J'+1)} \left\{ \begin{array}{c} J' \hfill \\
2 J \hfill \\
K' \end{array} \right\} eQ(T_q^2(\nabla E)) \] (3)

with the nuclear electric quadrupole coupling (NQC) tensor elements

\[ eQ(T_0^2(\nabla E)) = \frac{\chi_{aa}}{2} \] (4)
\[ eQ(T_{\pm 2}^2(\nabla E)) = (\chi_{bb} - \chi_{cc} \pm 2i\chi_{bc})/\sqrt{24} \] (5)

The \( \chi_{ij} \) are the NQC constants (NQCC); \( \chi_{ab} \) and \( \chi_{ac} \) have been neglected since the inertial axis \( a \) is very close to the NQC principal axis \( c \) as discussed later. The \( \chi_{bc} \) term permits two NQC axes to be rotated against the \( b \) and \( c \) principal axes of the inertial tensor. A nonvanishing \( \chi_{bc} \) will connect states with \( \Delta K = 2 \) and thus cause an hfs contribution to the \( K \)-doubling. However, its effect is usually concealed by much larger inertial asymmetry contribution, so off-diagonal \( \chi_{ij} \) can only be determined by comparing sets of \( \chi_{ij} \) of the same nucleus in different isotopomers [20]. The smaller the inertial asymmetry, however, the more the \( \chi_{bc} \) effect will be noticeable. On the other hand, in slightly asymmetric molecules the principal axes of inertia often coincide with the principal inertial axes, and hence \( \chi_{bc} \) is zero.

In [19] also the matrix elements for the spin-rotation interaction are given. Since \( H_2S_2 \) is not a radical, this interaction is not present; however, these matrix elements are of use here to describe the nuclear spin - rotation interaction after replacing \( N, S, \) and \( J \) by \( J, I, \) and \( F, \) respectively. The result is:

\[ \langle J'K'IF|H_{NSR}|JKIF \rangle = \] \[ \frac{1}{2} \sum_{k=0}^{2} \sqrt{2k+1} (-1)^{J'+F'+1+k} \times \sqrt{(I+1)(2I+1)(2J+1)} \left\{ \begin{array}{c} F' J' I \hfill \\
1 I J \end{array} \right\} \times \left\{ \begin{array}{c} k \hfill \\
1 \hfill \\
J \end{array} \right\} \sqrt{(J+1)(2J+1)} \times \sum_{q=-k}^{k} (-1)^{J'-J} \left\{ \begin{array}{c} J' \hfill \\
2 J \hfill \\
K' \end{array} \right\} eQ(T_q^2(\nabla E))\] (6)

with the nuclear spin - rotation constants \( C_{ij} \):

\[ T_0^0(C) = -(C_{bb} + C_{cc} + C_{aa})/\sqrt{3} \] (7)
\[ T_0^2(C) = (2C_{aa} - C_{bb} - C_{cc})/\sqrt{6} \] (8)
\[ T_{\pm 2}^2(C) = \frac{1}{2} [(C_{bb} - C_{cc}) \pm i(C_{bc} + C_{cb})] \] (9)

The magnitude of the hfs splittings were estimated assuming the dominant nuclear quadrupole hfs to have the same order as in \( H_2^{33}\)S [18].

3. Experiment

The HSSH sample has been produced in the Institute for Anorganische Chemie of the University of Köln. The spectra of \( HS^{33}\)S have been recorded in natural abundance, i.e. about 1.4 percent of the \( H_2S_2 \). For observation of the lines between 70 and 200 GHz, the mm-wave spectrometer was used in the configuration previously described in [11]; the transitions beyond 200 GHz were measured using two phase-locked backward wave oscillators (Carcinotron, Thomson-CSF) as frequency source, one for the 200-250 GHz and one for the 260-300 GHz region. The measurements have been made at room temperature with a sample pressure of 25 - 40 \( \mu \)bar.
Since it was clear from previous measurements on HSSH and HS\textsuperscript{34}SH that the more abundant isotopomers' spectra would overlap the low-J \( ^1Q_0 \) branch of HS\textsuperscript{33}SH, the measurements were started with the \( ^3P_0 \) branch. After the clear detection of two quartets at 71.2 and 84.9 GHz, further transitions belonging to the \( ^3P_1, ^1R_0, ^3P_2 \) and \( ^3P_1 \) branches could be rapidly found. The accuracy of the rotational and centrifugal distortion constants allowed us then to predict and identify the higher-J \( ^1Q_0 \) branch transitions up to \( J = 45 \). Altogether, a total of 133 line positions were recorded, containing 264 partially overlapping transitions. Table 1 shows observed frequencies together with estimates of their experimental uncertainties and calculated relative intensities.

### 4. Data Analysis

The observed frequencies have been fitted in a least squares procedure to the Hamiltonian discussed above. Whereas the hyperfine splittings of higher \( J \) transitions could be fitted easily, the lower \( J \) transitions could not be reproduced at all by fitting the hfs constants \( \chi_{aa}, \chi_{bb}, \) and \( \chi_{cc} \). Introduction of the
Table 2. HS\(^{33}\)SH: Rotational constants/MHz.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experimental (^a)</th>
<th>SCF (^b)</th>
<th>CI (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>146 773.9320 (70)(^a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B)</td>
<td>6 871.81625 (59)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C)</td>
<td>6 869.11235 (65)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(D_J \times 10^3)</td>
<td>5.25250 (83)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(D_{JK} \times 10^3)</td>
<td>83.410 (34)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(D_K)</td>
<td>2.4283 (23)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d_1 \times 10^6)</td>
<td>8.615 (36)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d_2 \times 10^6)</td>
<td>-25.842 (20)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(H_J \times 10^9)</td>
<td>-1.57 (32)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(H_{JK} \times 10^9)</td>
<td>-28 (34)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(H_K \times 10^9)</td>
<td>2.5 (34)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(h_2 \times 10^{12})</td>
<td>207 (323)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(h_3 \times 10^{12})</td>
<td>31.0 (134)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(h_3)</td>
<td>3.53 (146)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) values in brackets: 3\(\sigma\).

Table 3. HS\(^{33}\)SH: Hyperfine constants/MHz due to the \(^{33}\)S nucleus determined in the present work, in comparison to ab-initio values by Palmer [17].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experimental (^a)</th>
<th>SCF (^b)</th>
<th>CI (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\chi_{xx} = \chi_{zz})</td>
<td>-36.28 (28)</td>
<td>-40.28</td>
<td>-38.83</td>
</tr>
<tr>
<td>(\chi_{bb} = \chi_{cc})</td>
<td>-4.156 (79)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\chi_{bc})</td>
<td>28.88° (21)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\chi_{cd})</td>
<td>16.063 (151)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\chi_{ee})</td>
<td>20.219 (139)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\chi_{xe})</td>
<td>-10.82° (25)</td>
<td>-4.87</td>
<td>-4.92</td>
</tr>
<tr>
<td>(\chi_{yy})</td>
<td>47.10° (25)</td>
<td>44.62</td>
<td>43.56</td>
</tr>
<tr>
<td>(\theta_{bc} = \theta_{cy})</td>
<td>42.94°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_{aa} + C_{bb} + C_{cc})</td>
<td>0.059 (55)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2C_{aa} - C_{bb} - C_{cc})</td>
<td>0.082 (83)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_{bb} - C_{cc})</td>
<td>-0.0069 (86)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_{ad})</td>
<td>0.047 (44)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_{ae})</td>
<td>0.0025 (104)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_{ce})</td>
<td>0.0094 (130)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) values in brackets: 3\(\sigma\); \(^b\) From [17]; \(^c\) \(\chi_{xx} < \chi_{yy}\) assumed following [17]; \(^d\) derived value; \(^e\) obtained from diagonalization of NQC tensor.

5. Discussion

The rotational constants are well behaved in the sense that they average fairly well the corresponding HSSH and HS\(^{34}\)SH values. The new and more interesting feature presented here is the hyperfine structure due to the \(^{33}\)S nucleus. And here again, disulfane gives rise to an extraordinary behaviour. Since the molecule comes very close to an accidental prolate top, the asymmetry splitting is very small, especially for the lowest rotational levels. However, the molecular geometry (Fig. 1) is not close at all to a prolate symmetric top. This fact was noticed very early by the selection rules: HS\(^{33}\)SH exhibits \(c\)-type spectra only, whereas a prolate symmetric top can only have \(a\)-type transitions.

To understand our findings concerning the \(^{33}\)S hyperfine structure, one should recall the connection between nuclear quadrupole hyperfine interaction and the chemical bond. From Fig. 1 we see that the SSH bond angle does not differ much from 90°. Therefore, parameter \(\chi_{bc}\) solved the problem immediately, as the o-c values in Table 1 show – we will discuss this finding below in somewhat more detail. Following [21], non-resolved lines have been fitted to the average of the calculated frequencies, weighted by their calculated intensities. This procedure allowed us to take advantage of the full spectrometer precision in the analysis, resulting in a \(\sigma\) of 14 kHz; the observed-minus-calculated (o-c) values are also given in Table 1. Table 2 shows the rotational and centrifugal distortion constants, and the hyperfine constants are given in Table 3, including three parameters due to nuclear spin-rotation interaction. Matrix elements not diagonal in \(J\) did not improve the fit and were subsequently neglected in the analysis.

![Fig. 1. Geometry of HS\(^{33}\)SH. The equilibrium SSH angle is taken from [9]. The orientation of the principal inertial axes \(a, b, c\) and the principal NQC axes \(x, y, z\) show a substantial rotation around the \(a\) axis. The dipole moment vector \(\mu\) is parallel to the \(c\) axis. The \(z\) and \(a\) axes are almost parallel to the SS-bond, while the \(^{33}\)S H bond comes close to the \(x\) axis. Therefore, twice the angle between the \(x\) and \(c\) axis should give a good estimate for the dihedral angle. We find \(\eta \approx 94°\), in good agreement with \(\eta = 90.91°\) obtained in [11] for the ground state of HS\(^{33}\)SH.](image-url)
one may assume two principal axes of the NQHFS to be close to the SS and the SH bond axes. While the SS axis nearly coincides with the \(a\) inertial axis, the SH bond is rotated about 45° versus the \(b\) and \(c\) axes. Thus one may expect \(\chi_{bc}\) to be of considerable magnitude, and \(\chi_{ab}\) and \(\chi_{ac}\) to almost vanish. As discussed in the Hamiltonian section, the matrix element associated with \(\chi_{bc}\) contributes to the asymmetry doubling. However, for most cases, its effect on the energies is not directly observable.

Now the case of HS\(^{33}\)SH special in that a considerably large \(\chi_{bc}\) value appears combined with an extremely small inertial asymmetry. This fact expresses again that the geometry of the bonds cannot belong to a molecule similar to a prolate top, despite of the inertial proximity to the prolate case. The \(K\) doubling is most noticeable in the \(K_a = 1\) levels where the respective matrix elements contribute to the energies in first order, and the effect of the hyperfine structure will be most pronounced in the low \(J\) rotational levels. It is illustrative to regard the \(1_{10}\) and \(1_{11}\) levels. Figure 2 shows their energy contributions due to inertial asymmetry, diagonal, and off-diagonal NQC constants. The first observation is that the hyperfine structure is larger than the asymmetry doubling for this lowest \(K\)-split level. But whereas the diagonal NQC constants mix the two rotational sublevels, the \(\chi_{bc}\) term not only changes the order of the hyperfine sublevels, but it contributes to the \(K\) doubling in a way that separates the \(1_{11}\) and \(1_{10}\) subgroups again. The dominant contribution to the \(K\) doubling of the \(J = 1, K_a = 1\) arises from the non-coincidence between the principal inertial axes and the principal axes of the NQC tensor.

The \(J\)-dependence of the hyperfine splitting with respect to the pure rotational energy levels with \(K_a = 1\) can be seen in Figure 3. The effect of the off-diagonal \(\chi_{bc}\) is visible for the low \(J\) rotational levels only. This explains why initially the higher \(J\) transitions could be well fitted without employing \(\chi_{bc}\). Figure 4 shows the relative frequency splittings in the transition frequencies of the \(P_1\) branch. Incorporated spectra are examples of recorded transitions calling for the need of \(\chi_{bc}\) to explain them.

It should be noted that the sign of \(\chi_{bc}\) cannot be determined from the present measurements. In order to decide the proper choice of sign, additional information is required. In the course of writing this paper we became aware of an ab-initio paper by Palmer [17] who has calculated the \(^{33}\)S NQCC for a series of molecules, including HS\(^{33}\)SH. His NQCC are given in the NQC principal axis system, with the \(z\)-axis almost coinciding with the \(a\) axis and the \(x\) axis close to the SH bond. He found that the latter axis has the smallest NQCC, while \(\chi_{yy}\) is the largest. From our values of \(\chi_{bb}, \chi_{cc}, \chi_{bc}\), the \(\chi_{xx}\) and \(\chi_{yy}\) can be obtained by diagonalization of the NQC tensor:

\[
\begin{pmatrix}
\chi_{xx} & 0 \\
0 & \chi_{yy}
\end{pmatrix} = R_{\theta}^{-1} \begin{pmatrix}
\chi_{bb} & \chi_{bc} \\
\chi_{bc} & \chi_{cc}
\end{pmatrix} R_{\theta},
\]

where

\[
R_{\theta} = \begin{pmatrix}
\cos \theta & -\sin \theta \\
\sin \theta & \cos \theta
\end{pmatrix}.
\]

Besides \(\chi_{xx}\) and \(\chi_{yy}\), this yields also the angle \(\theta\) between the principal axes of inertia and the principal NQC axes. In Table 3, our experimental hyperfine constants can be compared with the ab-initio values from [17]; the NQCC show a good qualitative agreement between experimental and theoretical values. Following Palmer, we assign \(\chi_{xx} < \chi_{yy}\); this choice results in a positive \(\chi_{bc}\) and an angle \(\theta\) of 42.94° between \(b\) and \(x\) axis\(^1\). From Fig. 1, one can easily

\(^1\)The opposite assignment yields an angle of 47.06° between \(b\) and \(x\) axis and the estimate for \(\eta\) would become 86°.
recognize the approximate relationship:

$$\eta \approx 2(90^\circ - \theta).$$

This relation would be exact if the SH axis coincided with the $x$ axis, and the SS bond with the $z$ axis. This condition is not exactly fulfilled, but our estimate of $94^\circ$ for $\eta$ is fairly close to the $90.91^\circ$ obtained by Behrend [11] for the ground state of HSSH, based on the rotational constants of several other isotopomers. This fact underlines the overall consistency of the experimental data on disulfane now available from rotational spectroscopy.

6. Conclusion

Once again, disulfane has given rise to a special spectral feature. The first determination of the HS$^{33}$SH rotational spectra has shown that for low $J$ rotational quantum numbers, the $K$-doubling is dominated by contributions from the $^{33}$S quadrupole hyperfine interaction rather than from the asymmetry of the inertia tensor. The reason is found in the combination of an extremely small inertial asymmetry with a strong rotation of the NQC principal axes against the principal inertial axes. From the NQCC we derive a dihedral angle of $94^\circ$, in good agreement with
a previous value based on the rotational constants of other isotopomers. On the basis of the present experimental data, we had to recur to an ab-initio calculation for the probable assignment of $\chi_{xx}$ and $\chi_{yy}$. As a final remark, we would like to mention that this assignment can be verified on experimental basis by determination of the NQCC in $^{33}$SSD and $^{33}$SD, since for these isotopomers the NQCC and inertial principal axes should almost coincide. Therefore, mm-wave spectra of $^{33}$SSD and $^{33}$SD will be of interest.

**Acknowledgements**

The authors thank Dr. J. Hahn and R. Klünsch of the Institute for Anorganische Chemie for the sample preparation. Valuable discussions with Dr. J. Behrend are thankfully acknowledged. And we appreciate helpful comments on the manuscript by Dr. K. M. T. Yamada. This work was supported in part by the Deutsche Forschungsgemeinschaft via grant SFB 301.