# The $^{33}$S Nuclear Quadrupole Hyperfine Structure in the Rotational Spectrum of $^{32}$S, $^{33}$S Dimethyl Disulfide

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*Dedicated to Prof. Dr. D. Sutter on occasion of his 60th birthday*

We investigated the rotational spectrum of $^{32}$S, $^{33}$S dimethyl disulfide in natural abundance by molecular beam Fourier transform microwave spectroscopy. We were able to determine the complete $^{33}$S quadrupole coupling tensor, the rotational and centrifugal distortion constants and the internal rotation parameters of the two methyl tops. The rotational constants were found to be $A = 8113.8847(23)$ MHz, $B = 2800.6203(30)$ MHz and $C = 2557.2245(32)$ MHz. The results are compared with former publications.

## Introduction

In the course of our studies on the $^{33}$S nuclear quadrupole coupling we have become interested in the coupling constants of dimethyl disulfide (DMDS), as sulfur is bonded differently in comparison to the hitherto investigated molecules [1]. The disulfide bridge, –S–S–, is an important structural feature in organic chemistry.

First studies on the microwave spectrum of DMDS were made by Sutter et al. [2]. A partial $r_0$ structure was determined. Kuhler et al. [3] carried out an analysis of the deuterated isotopomer $CH_3SSCD_3$ (DMDS-$d_3$) in order to investigate the interaction between the methyl internal rotation and the torsion along the SS bond. Frankiss [4] presented a detailed IR and Raman study of non-deuterated DMDS. Molecular structures are available from electron diffraction studies [5] and *ab-initio* calculations [6]. General force fields for dialkyl disulfides have been derived from experimental data by Sugeta [7]. An *ab-initio* force field for this type of molecule was published by Zhao and co-workers [8], [9]. Recently Meyer [10] has measured three isotopic species of DMDS in order to determine the heavy-atom geometry and methyl internal rotation parameters. *Ab-initio* calculations have been carried out to determine the complete structure, the cis and trans barriers to torsion along the SS bond, the dipole, and molecular quadrupole moments.

After having finished some investigations on the sulfur containing heterocycles thiophene [11], thiazole [12], and isothiazole [13] we extend our studies to molecules with other sulfur bond types. Among these the –S–S– bridge type is interesting. In DMDS the methyl internal rotation complicates the rotational spectrum, but additional information can be obtained. Using molecular beam (MB) Fourier transform microwave (FTMW) spectroscopy, the high sensitivity of this method allows us to measure $^{33}$S isotopomers of many molecules in natural abundance. No difficult and expensive preparation work is needed.

In this work we will present our studies on $^{32}$S, $^{33}$S DMDS, using our program XIAM which calculates the microwave spectra of molecules with one quadrupole nucleus and two internal $C_{3v}$-rotors.

## Experimental

A sample of DMDS (purity 99%) was obtained from Aldrich-Chemie, Steinheim. The spectra were recorded using a MB-FTMW spectrometer [14] in the frequency range from 8 to 17.5 GHz. In order to increase sensitivity and resolution of the spectrometer, the molecular beam was pulsed through one of the mirrors along the resonator axis [15]. For all measurements we used a mixture of 1% DMDS in argon with a backing pressure of 50 kPa (0.5 bar). The time domain signals were recorded sampling 16 k data points at an interval of 10 ns. The frequencies were calculated using a Fourier transformation. Up to 30 k averaging

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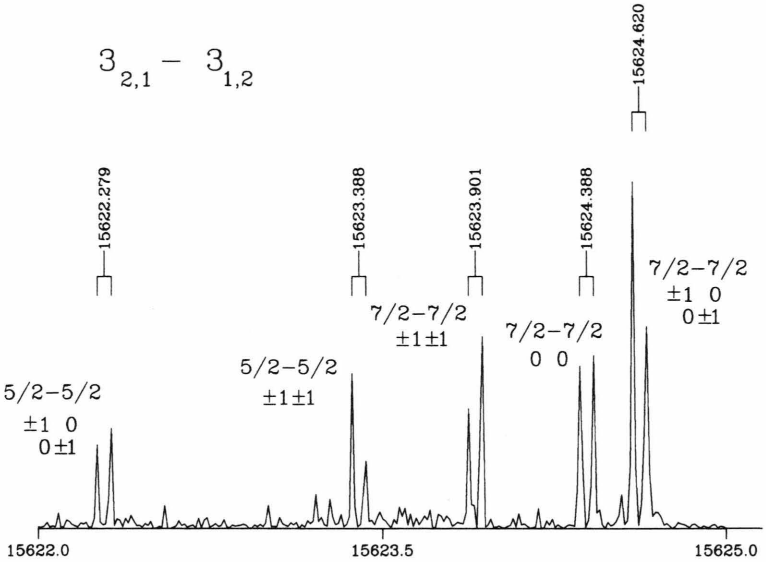

Fig. 1. Part of the $J_{K_-K_+} = 3_{2,1} - 3_{1,2}$ transition of $^{32}$S, $^{33}$S-DMDS measured in natural abundance. The quantum numbers $F = J + I$ and the symmetry species $\sigma_1 \sigma_2$ are given. Experimental conditions: 27 768 averaged experiment cycles, measuring time 30 min, 0.5 µs MW pulse duration, 16 k data points, 10 ns sample interval, polarizing frequency 15 623.50 MHz, 1% dimethyl disulfide in argon, backing pressure 50 kPa.

cycles, taking approximately 30 minutes, were necessary to get a sufficient signal-to-noise ratio for the $^{32}$S, $^{33}$S dimethyl disulfide as displayed in Figure 1. We measured the spectra up to the angular momentum quantum number $J = 4$.

## Spectral Analysis

The spectrum of the $^{32}$S, $^{33}$S isotopomer of DMDS shows two kinds of fine structures for each transition: a wide splitting into hfs components caused by the nuclear quadrupole coupling of the $^{33}$S nucleus and a smaller splitting due to the internal rotation of the two non equivalent methyl groups. The former one is up to 10 MHz, the latter one mostly below 1 MHz. The prediction of the spectrum was done by taking the mean value of the corresponding $^{32}$S, $^{32}$S, and $^{32}$S, $^{34}$S transitions given by [16]. The hyperfine free line centers were found within a few MHz around the mean value of the corresponding $^{32}$S and $^{34}$S frequencies, the internal rotation splittings were similar to the one of $^{32}$S, $^{34}$S DMDS. Due to the low natural abundance of $^{33}$S and the splitting of the rotational lines into various components the spectrum turned out to be rather week. For DMDS the natural abundance of the $^{33}$S isotopomer is 1.52% because of the two equivalent sulfur nuclei. This compensates partially the loss of intensity by the splitting.

We started assigning the $J_{K_-K_+} = 1_{1,1} - 0_{0,0}$ and the $2_{1,2} - 1_{0,1}$ transitions. Using the program HFS [17], [18], which diagonalizes the Hamiltonian matrix containing overall rotation, nuclear quadrupole coupling, and centrifugal distortion, the $^{33}$S quadrupole coupling constants could be extracted from the spectra. With these constants and the internal rotation splittings of the $^{32}$S, $^{34}$S isotopomer we were able to measure and assign all the transitions given in Table 1.

A final analysis of the nuclear quadrupole coupling was done by a least squares fit of all rotational lines of the $\sigma_1 \sigma_2 = 0\,0$ (or AA) torsional sublevel, because these follow a pseudo rigid rotor spectrum. We were able to determine the complete $^{33}$S quadrupole coupling tensor of DMDS and the effective rotational constants of the $\sigma_1 \sigma_2 = 0\,0$ spectrum. The results are given in Table 2, together with the values for the $^{32}$S, $^{32}$S, and $^{32}$S, $^{34}$S isotopomers. Because only seven transitions were measured, the centrifugal distortion constants had to be fixed to the mean value of those resulting from the $^{32}$S and $^{34}$S spectra.

To obtain moments of inertia of the molecule, which reflect the real structure of DMDS, internal rotation components are to be taken into account. To analyze the multiplet pattern we used the internal axis method (IAM) in the formulation of Woods [19] and modified by Vacherand et al. [20]. It uses an internal axis system for each top. These coordinate systems are fixed in the frame of the whole molecule, called ϱ-axis system, therefore this treatment is also called ϱ-axis method

Table 1. Measured transitions of $^{32}$S, $^{33}$S dimethyl disulfide. $\nu_{\text{obs}}$ denotes the observed frequency, $\nu_{\text{calc}}$ the calculated frequency. $\delta$ gives a) the difference between the observed and calculated component of $\sigma_1\sigma_2 = 0\,0$ and b) the difference between the observed $\Delta\nu_{\text{obs}} = (\nu_{00} - \nu_{\Gamma})_{\text{obs}}$ and the calculated internal rotation splitting. $\sigma_{\text{HFS-FIT}} = 2.0$ kHz is the standard deviation of the hfs fit and $\sigma_{\text{INTROT-FIT}} = 4.5$ kHz of the internal rotation fit, respectively.

| $J\,K_-\,K_+$ | $J'\,K'_-\,K'_+$ | $\Gamma$ | $\nu_{\text{obs}}$/MHz | $\delta$/kHz INTROT-FIT | $\nu_{\text{obs}}-\nu_{\text{calc}}$/kHz HFS-FIT |
|---|---|---|---|---|---|
| $F$ | $F'$ | $\sigma_1\,\sigma_2$ | | | |
| 1 1 1 | 0 0 0 | | | | |
| 5/2 | 3/2 | 0 0 | 10670.646 | −3.2 | 2.0 |
| | | ±1 0 | 10670.506 | −2.2 | |
| | | 0 ±1 | 10670.506 | 1.4 | |
| | | ±1 ±1 | 10670.408 | 0.1 | |
| | | ±1 ∓1 | 10670.327 | 0.2 | |
| 1/2 | 3/2 | 0 0 | 10667.938 | −1.3 | 0.1 |
| | | ±1 0 | 10667.798 | −2.2 | |
| | | 0 ±1 | 10667.798 | 1.3 | |
| | | ±1 ±1 | 10667.701 | 1.2 | |
| | | ±1 ∓1 | 10667.618 | 0.4 | |
| 3/2 | 3/2 | 0 0 | 10673.756 | 4.5 | 0.7 |
| | | ±1 0 | 10673.618 | −1.2 | |
| | | 0 ±1 | 10673.618 | 2.3 | |
| | | ±1 ±1 | 10673.519 | −1.0 | |
| | | ±1 ∓1 | 10673.439 | 0.4 | |
| 2 1 2 | 1 0 1 | | | | |
| 7/2 | 5/2 | 0 0 | 15785.559 | −6.7 | 2.2 |
| | | ±1 0 | 15785.416 | −2.7 | |
| | | 0 ±1 | 15785.416 | 1.0 | |
| | | ±1 ±1 | 15785.286 | −3.5 | |
| | | ±1 ∓1 | 15785.260 | −0.4 | |
| 5/2 | 3/2 | 0 0 | 15788.745 | 5.2 | 0.8 |
| | | ±1 0 | 15788.601 | −4.6 | |
| | | 0 ±1 | 15788.601 | −0.9 | |
| | | ±1 ±1 | 15788.476 | −0.4 | |
| | | ±1 ∓1 | 15788.448 | 0.5 | |
| 3/2 | 1/2 | 0 0 | 15778.439 | 2.2 | −1.0 |
| | | ±1 0 | 15778.298 | −1.3 | |
| | | 0 ±1 | 15778.298 | 2.4 | |
| 5/2 | 5/2 | 0 0 | 15781.327 | −1.3 | −1.7 |
| | | ±1 0 | 15781.186 | −1.7 | |
| | | 0 ±1 | 15781.186 | 2.0 | |
| | | ±1 ∓1 | 15781.028 | −2.1 | |
| 3/2 | 3/2 | 0 0 | 15791.778 | 0.6 | −1.7 |
| | | ±1 0 | 15791.637 | −0.5 | |
| | | 0 ±1 | 15791.637 | 3.2 | |
| | | ±1 ±1 | 15791.510 | 1.3 | |
| | | ±1 ∓1 | 15791.483 | 3.1 | |
| 2 2 0 | 2 1 1 | | | | |
| 7/2 | 7/2 | 0 0 | 15945.054 | −8.7 | 0.4 |
| | | 0 ±1 | 15946.750 | −4.3 | |
| | | ±1 0 | 15946.718 | 0.4 | |
| 5/2 | 5/2 | 0 0 | 15955.666 | 0.0 | −0.1 |
| | | 0 ±1 | 15957.360 | 3.0 | |
| | | ±1 0 | 15957.335 | 0.6 | |
| 2 2 1 | 2 1 2 | | | | |
| 7/2 | 7/2 | 0 0 | 16666.621 | 8.9 | 3.8 |
| | | ±1 0 | 16664.389 | −3.8 | |
| | | 0 ±1 | 16664.346 | −1.2 | |
| | | ±1 ±1 | 16666.011 | 2.4 | |
| 5/2 | 5/2 | 0 0 | 16678.262 | 1.7 | 1.1 |
| 3/2 | 3/2 | 0 0 | 16669.923 | −6.6 | −3.0 |
| 3 2 1 | 3 1 2 | | | | |
| 9/2 | 9/2 | 0 0 | 15619.328 | 13.7 | 2.0 |
| | | ±1 0 | 15619.555 | −2.2 | |
| | | 0 ±1 | 15619.555 | −0.6 | |
| | | ±1 ∓1 | 15620.668 | −3.3 | |
| 7/2 | 7/2 | 0 0 | 15624.388 | −16.4 | −0.8 |
| | | ±1 0 | 15624.620 | 2.4 | |
| | | 0 ±1 | 15624.620 | 3.8 | |
| | | ±1 ±1 | 15623.901 | 2.2 | |
| 5/2 | 5/2 | 0 0 | 15622.048 | 12.9 | 0.3 |
| | | ±1 0 | 15622.279 | 1.8 | |
| | | 0 ±1 | 15622.279 | 3.1 | |
| | | ±1 ±1 | 15621.559 | 1.0 | |
| | | ±1 ∓1 | 15623.388 | −2.9 | |
| 3 2 2 | 3 1 3 | | | | |
| 9/2 | 9/2 | 0 0 | 17037.996 | −2.3 | 0.1 |
| | | ±1 0 | 17037.203 | 0.0 | |
| | | 0 ±1 | 17037.184 | 1.3 | |
| | | ±1 ±1 | 17037.337 | −1.8 | |
| 7/2 | 7/2 | 0 0 | 17044.086 | 6.2 | 0.9 |
| | | ±1 0 | 17043.293 | 0.5 | |
| | | 0 ±1 | 17043.275 | −0.5 | |
| | | ±1 ±1 | 17043.427 | −1.0 | |
| 5/2 | 5/2 | 0 0 | 17041.229 | −5.8 | −3.9 |
| | | ±1 0 | 17040.438 | 2.5 | |
| | | 0 ±1 | 17040.417 | −1.6 | |
| 4 2 2 | 4 1 3 | | | | |
| 11/2 | 11/2 | 0 0 | 15225.078 | −3.1 | 0.2 |
| | | ±1 0 | 15225.019 | 2.5 | |
| | | 0 ±1 | 15225.006 | −0.1 | |
| | | ±1 ±1 | 15224.633 | 5.6 | |
| | | ±1 ∓1 | 15225.260 | 0.7 | |
| 9/2 | 9/2 | 0 0 | 15227.992 | 1.3 | 0.6 |
| | | ±1 0 | 15227.931 | 0.0 | |
| | | 0 ±1 | 15227.918 | −3.0 | |
| | | ±1 ±1 | 15227.541 | −1.9 | |
| | | ±1 ∓1 | 15228.174 | −0.8 | |
| 7/2 | 7/2 | 0 0 | 15226.972 | −1.8 | 2.3 |
| | | ±1.0 | 15226.915 | 4.8 | |
| | | 0 ±1 | 15226.896 | −3.8 | |
| | | ±1 ±1 | 15226.517 | −4.9 | |
| 5 2 3 | 5 1 4 | | | | |
| 13/2 | 13/2 | 0 0 | 14797.343 | – | −4.5 |

Table 2. Rotational, van Eijck's centrifugal distortion constants [27] ($I^r$ representation) and $^{33}$S quadrupole coupling constants of the $\sigma = 0\,0$ (AA) species of the sulfur isotopomers of dimethyl disulfide. * denotes derived constants, $\sigma$ the standard deviation of the fit and $^+$ marks the centrifugal distortion constants kept fixed in the fit to the mean value of the $^{32}$S, $^{32}$S and $^{32}$S, $^{34}$S isotopomers. Basis for the data of the $^{32}$S, $^{32}$S and $^{32}$S $^{34}$S isotopomers was the frequency list of [16]. For the sign of $\chi_{gg}$, see text.

| | | $CH_3SSCH_3$ | $CH_3{}^{34}SSCH_3$ | $CH_3{}^{33}SSCH_3$ |
|---|---|---|---|---|
| $A'$ | /MHz | 8163.8928 (31) | 8066.55639 (63) | 8114.03235 (37) |
| $B'$ | /MHz | 2816.5019 (16) | 2785.31400 (34) | 2800.62324 (41) |
| $C'$ | /MHz | 2570.4164 (12) | 2544.49968 (26) | 2557.29712 (33) |
| van Eijck's centrifugal distortion constants: | | | | |
| $D'_J$ | /kHz | 1.588 (26) | 1.5378 (54) | 1.563 $^+$ |
| $D'_{JK}$ | /kHz | −5.055 (68) | −4.624 (10) | −4.840 $^+$ |
| $D'_K$ | /kHz | 27.19 (80) | 25.36 (17) | 26.28 $^+$ |
| $\delta'_J$ | /kHz | 0.4832 (30) | 0.4613 (37) | 0.4723 $^+$ |
| $R'_6$ | /kHz | −0.0872 (33) | −0.0861 (37) | −0.8670 $^+$ |
| $\sigma$ | /kHz | 2 | 1 | 2 |

Quadrupole coupling constants of sulfur $^{33}$S:

| | | | | |
|---|---|---|---|---|
| $\chi_{aa}$ | /MHz | −29.6475 (42) | $\chi_{xx}$/MHz | 48.7 (12) |
| $\chi_{bb} - \chi_{cc}$ | /MHz | −4.0334 (95) | $\chi_{yy}$/MHz | −39.2 (11) |
| $\chi_{ab}$ | /MHz | 20.2 (13) | $\chi_{zz}$/MHz | −9.52 (32) |
| $\chi_{ac}$ | /MHz | 18.3 (12) | | |
| $\chi_{bc}$ | /MHz | 24.43 (17) | | |
| $\chi_{bb}$ | /MHz | 12.807 (31) * | | |
| $\chi_{cc}$ | /MHz | 16.840 (26) * | | |

Table 3. Simplified correlation table of the groups $C_{3v}^- \otimes C_3^+$ and $C_3^1 \otimes C_3^2$. $i, j = 1, 2$.

| $C_{3v}^- \otimes C_3^+$ | $C_3^1 \otimes C_3^2$ | $\sigma_1 \sigma_2$ |
|---|---|---|
| AA | AA | 0 0 |
| EE | $E_i A$<br>$AE_i$ | ±1 0<br>0 ±1 |
| AE | $E_i E_i$ | ±1 ±1 |
| EA | $E_i E_j$ | ±1 ∓1 |

(RAM) in [21]. It should be mentioned that the top-top interaction described by $F'$ and some potential parameters are neglected here as only the torsional ground state is analyzed. Because of the shift and rotation of the principle axes of $^{32}$S, $^{33}$S DMDS compared with the $C_2$ symmetric $^{32}$S, $^{32}$S isotopomer the methyl groups are no longer equivalent. The symmetry group of the Hamiltonian of $^{32}$S, $^{32}$S DMDS is $C_{3v}^- \otimes C_3^+$, for the nonsymmetric isotopomers it is reduced to $C_3^1 \otimes C_3^2$ [22]. This leads to a confusing nomenclature of the torsional sublevels as shown in Table 3. We decided to use the symmetry label $\sigma$ of each top to specify the symmetry of the internal rotation levels.

Table 4. Rotational, centrifugal distortion, nuclear quadrupole coupling and internal rotation constants of $^{32}$S, $^{33}$S dimethyl disulfide fitted to all measured transitions simultaneously. Top 1 is bond to the $^{33}$S and top 2 to the $^{32}$S nucleus, $\varrho$, $\beta$, and $\gamma$ are internal rotation parameters given by [19], $V_3$ is the hindering potential and $F$ the internal rotation constant. $^+$ marks parameters held fixed in the fit and * denotes derived constants.

| | | | Freedom [a] |
|---|---|---|---|
| Rotational constants: | | | |
| $A$ | /MHz | 8113.8847 (23) | 0.20 |
| $B$ | /MHz | 2800.6203 (30) | 0.13 |
| $C$ | /MHz | 2557.2245 (32) | 0.09 |
| Watson's A centrifugal distortion constants: | | | |
| $\Delta_j$ | /kHz | 1.82 (32) | 0.17 |
| $\Delta_{JK}$ | /kHz | −6.17 (11) | 0.25 |
| $\Delta_K$ | /kHz | 27.47 $^+$ | – |
| $\delta_J$ | /kHz | 0.378 (30) | 0.20 |
| $\delta_K$ | /kHz | 15.52 $^+$ | – |
| Quadrupole coupling constants: | | | |
| $\chi_{aa}$ | /MHz | −29.645 (7) | 0.94 |
| $\chi_{bb} - \chi_{cc}$ | /MHz | −4.064 (15) | 0.92 |
| $\chi_{bc}$ | /MHz | −24.803 (41) | 0.59 |
| International rotation parameters of top 1: | | | |
| $V_3$ | /kJ | 6.426 (32) | 0.02 |
| $V_3$ | /cm$^{-1}$ | 537.2 (2.9) * | |
| $\varrho$ | | 0.030877 (108) | 0.03 |
| $\beta$ | /rad | 0.4947 (21) | 0.03 |
| $\gamma$ | /rad | 0.5354 (82) | 0.15 |
| $F$ | /GHz | 162.38 * | |
| Internal rotation parameters of top 2: | | | |
| $V_3$ | /kJ | 6.442 (36) | 0.02 |
| $V_3$ | /cm$^{-1}$ | 538.5 (26) * | |
| $\varrho$ | | 0.031155 (116) | 0.03 |
| $\beta$ | /rad | 2.6563 (18) | 0.03 |
| $\gamma$ | /rad | 0.5500 (69) | 0.17 |
| $F$ | /GHz | 162.66 * | |

[a] Grabow [28].

Finally all transitions given in Table 1 where used to fit rotational, centrifugal distortion, quadrupole coupling, and internal rotation constants simultaneously. The result is given in Table 4. The absolute frequency of each hfs component $F - F'$, $\sigma_1 \sigma_2 = 0\,0$ and the splittings between the $\sigma_1 \sigma_2 = 0\,0$ and the other four torsional states of the same hfs component were used as input data. The determined internal rotation parameters are $\varrho, \beta, \gamma$, and the hindering barrier $V_3$ for each top. $\varrho$ is given by

$$\varrho_g = \frac{I_\alpha}{I_g} \lambda_g, \quad g = a, b, c, \quad \varrho = \left( \sum_{g=a,b,c} \varrho_g^2 \right)^{1/2}$$

were $I_g$ is the moment of inertia of the molecule for rotation about the $g$ axis and $I_\alpha$ is the moment of inertia of the top for rotation about the internal rotation axis. $\beta$ and $\gamma$ are in the $I^r$ representation defined by

$$\beta = \arccos\frac{\varrho_a}{\varrho}, \quad \gamma = \arccos\frac{\varrho_b}{\sqrt{\varrho_b^2 + \varrho_c^2}}.$$

The value of the internal rotation constant $F$, which is needed in the calculation, is derived from $\varrho, \beta, \gamma$ and the rotational constants $A, B, C$ in each iteration. In this fit only one off-diagonal quadrupole coupling parameter $\chi_{bc}$ was determinable because no off-diagonal elements in $J$ are included in this calculation of the nuclear quadrupole Hamiltonian matrix. This leads to a worse residuum and to higher errors in the rotational constants compared with the fit of the $\sigma_1\sigma_2 = 0\,0$ lines only, were the nuclear quadrupole Hamiltonian is treated without any neglections (Table 2). This simplification affects mainly the absolut frequencies of the hfs patterns, the internal rotation splittings are not influenced.

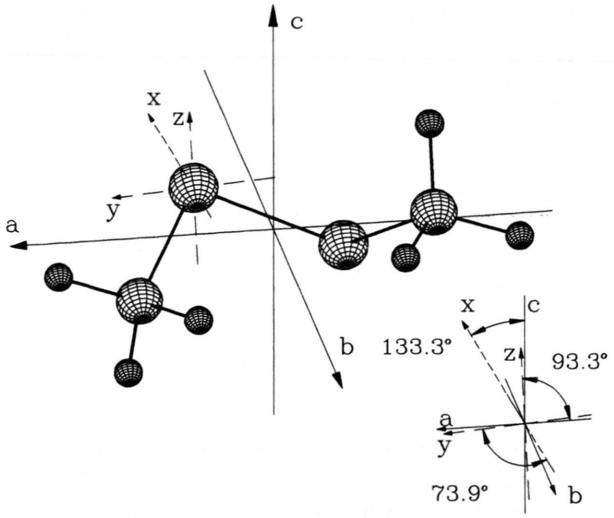

Fig. 2. Position of the principal inertia and principal $^{33}$S quadrupole coupling tensor axes of $^{32}$S, $^{33}$S dimethyl disulfide. The structure was given by Meyer [29]. The position of the hydrogen nuclei results only from quantum chemical calculations. The principal axes of the coupling tensor are drawn with dashed lines. There is no coincidence between a principal coupling axis and the sulfur bonds nor the bisector of the $\sphericalangle(C^{33}S^{32}S)$.

## Discussion

Since we were able to extract the whole quadrupole coupling tensor $\chi$ from our $\sigma_1\sigma_2 = 0\,0$ spectra, we were able to calculate the quadrupole coupling tensor in his own principle axis system by diagonalizing $\chi$. We derived the principal coupling constants of $^{33}$S in $^{32}$S, $^{33}$S DMDS to be

$$\chi_{xx} = \ \ 48.7\ \ (12)\,\text{MHz},$$
$$\chi_{yy} = -39.2\ \ (11)\,\text{MHz},$$
$$\chi_{zz} = -\ \ 9.52\,(39)\,\text{MHz},$$

and the corresponding eigenvectors are

$$\boldsymbol{x} = \begin{pmatrix} 0.327\ \ (15) \\ 0.6502\,(74) \\ 0.6858\,(71) \end{pmatrix}, \quad \boldsymbol{y} = \begin{pmatrix} 0.9424\,(54) \\ -0.277\ \ (39) \\ -0.186\ \ (40) \end{pmatrix},$$

$$\boldsymbol{z} = \begin{pmatrix} -0.069\,(49) \\ -0.707\,(22) \\ 0.704\,(17) \end{pmatrix}.$$

So we can calculate the angles between the principal inertia axes system of $^{32}$S, $^{33}$S DMDS and the principal coupling tensor axes system of the $^{33}$S nucleus. In Fig. 2 we have indicated the following angles:

$$\sphericalangle(\boldsymbol{c}, \boldsymbol{x}) = 46.7\,(56)^\circ, \quad \sphericalangle(\boldsymbol{b}, \boldsymbol{y}) = 106.1\,(24)^\circ,$$
$$\sphericalangle(\boldsymbol{a}, \boldsymbol{z}) = 93.3\,(28)^\circ.$$

An illustration is given in Figure 2. The structure of DMDS given by Meyer was used. No principal axis of the quadrupole tensor coincides exactly with the SC or SS bond nor with the bisector of the angle $\sphericalangle(C^{33}S^{32}S)$.

It should be noted that only the product of the sign of the three off-diagonal elements of the nuclear quadrupole coupling tensor can be obtained from the spectra [23].

These results should be compared with quantum chemical calculations. These calculations are very expensive because of the sophisticated methods and basis sets that have to be applied [24].

The internal rotation analysis gives analogeous results compared with the $^{32}$S, $^{32}$S, and $^{32}$S, $^{34}$S isotopomers in [25]. The value of $V_3$ and $I_\alpha$ are within the errors of the other isotopomers. To compare the direction cosines $\lambda_g = \cos(\sphericalangle\, i, g)$, $i = 1, 2$ (internal rotation axes) $g = a, b, c$ of all isotopomers it is necessary to

Table 5. Comparison of the internal rotation constants of three isotopomers of dimethyl disulfide. The given angles $\sphericalangle (g, i)$, $g = a, b, c$ are between the internal rotation axes $i = 1, 2$ and the principal axes of the $^{32}$S, $^{32}$S isotopomer. Top 1 is bond to the $^{32}$S, $^{34}$S or $^{33}$S and top 2 to the $^{32}$S nucleus. $I_\alpha$ is the moment of inertia and $V_3$ is the hindering barrier of the internal rotating top.

| | $^{32}$S, $^{32}$S* | $^{32}$S, $^{33}$S | | $^{32}$S, $^{34}$S | | $r_s$-Structure* |
|---|---|---|---|---|---|---|
| | | Top 1 | Top 2 | Top 1 | Top 2 | |
| $V_3$/kJ | 6.394 (2) | 6.426 (32) | 6.442 (35) | 6.460 (50) | 6.531 (54) | – |
| $I_\alpha$/uÅ$^2$ | 3.213 (9) | 3.198 (20) | 3.193 (20) | 3.187 (25) | 3.152 (26) | – |
| $\sphericalangle (a, i)/°$ | 57.84 (6) | 57.79 (15) | 57.55 (13) | 57.17 (10) | 57.45 (20) | 60.83 |
| $\sphericalangle (b, i)/°$ | 45.31 (6) | 45.20 (39) | 45.00 (33) | 45.17 (10) | 45.27 (19) | 43.81 |
| $\sphericalangle (c, i)/°$ | 61.89 (8) | 62.06 (44) | 62.57 (37) | 62.29 (17) | 62.35 (24) | 60.56 |

* IAM [29], angles of the SC bond.

take the change of the principal axes system into account. This calculation was based on the $r_0$ structure given by Meyer. After the transformation of the direction cosines of the nonsymmetric DMDS into the principal axes system of the $^{32}$S, $^{32}$S isotopomer the values of the angles $\sphericalangle (g, i)$ are in a good agreement. It must be noted that the transformed direction cosines contain additional errors caused by the uncertainty of the $r_0$ structure. These errors are not considered in Table 5. It should be noted that the angles arccos $(\lambda_g)$ disagree with the angles between the S–C bonds and the principal axes calculated from the structure. The value of this tilt angle (about 3.1°) is beyond the standard error of the calculated angles and also larger than for comparable molecules with methyl groups not bound to the same atom (trans-2,3-dimethyloxiran: 0.4° [26]). One explanation is the influence of other low vibrational modes, particularly the SS torsion. This motion can modify the rotational constants or couple with the internal rotation, but a more precise treatment can not be given presently.

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