# Partial $r_s$- and $r_0$-Structure, Direction of the Dipole Moment and Quadrupole Coupling Tensor in Methanesulfenyl Chloride ($CH_3SCl$)

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The microwave spectra of three further isotopic species of methanesulfenyl chloride have been investigated. These results together with the results of investigations of isotopic species previously studied enable the calculation of a more accurate $r_0$-structure.

The $r_s$-distance of the S-Cl bond has been determined. Orientation and direction of the dipole moment and the total quadrupole coupling tensor have also been obtained.

## Introduction

In two preceeding papers [1, 2] the investigation of the microwave spectrum of the two isotopic species $CH_3SCl$* and $CH_3S^{37}Cl$ was reported and some structural information was obtained by considering these two species only.

The spectra of the isotopic species $CD_3SCl$, $CD_3S^{37}Cl$, and $CH_3{}^{34}SCl$ have now been investigated for the purpose of obtaining more complete structural data, the direction of the dipole moment, and the quadrupole coupling tensor.

## Experimental

Methanesulfenyl chloride was prepared on a semimicro scale suitable for the synthesis of the isotopic species. The method used was an adaptation of a procedure reported by Brintzinger [3]. The advantage of our method is that small samples (ca. 1 ml) can be prepared completely *in vacuo* without the use of a solvent. The main difficulty is the complete removal of sulfur dioxide produced. The reaction is as follows:

$$CH_3-SS-CH_3+SO_2Cl_2 \xrightarrow{-10°C} 2\,CH_3SCl+SO_2\,.$$

The apparatus consisted of a standard manifold vacuum line, a one-liter ballast flask, and three sample tubes with stopcock and conical joint attachable to the vacuum line. Freshly distilled dimethyldisulfide (5.6 mmole) was pipetted into the first sample tube (reaction vessel) and degassed at $-78\ °C$, $10^{-2}$ torr. A degassed sample of sulfuryl chloride (6.6 mmole) freshly distilled at room temperature was condensed into the reaction vessel. After this the reaction vessel was warmed to approximately $-25\ °C$. Sulfur dioxide was vigorously evolved as the reaction mixture turned red in color with the production of methanesulfenyl chloride. Portions of $SO_2$ were pumped off by repeated brief openings of the stopcock between the pump and the reaction vessel. The mixture was then brought to about $-10\ °C$ where $SO_2$ together with approximately 1/4 of the reaction mixture was removed. The methanesulfenyl chloride was condensed from $-10\ °C$ into a sample tube in liquid air. Larger samples (up to 10 ml) prepared in this way were subjected to a distillation at ca. 30 torr through a short Vigreux column to remove traces of $SO_2$ giving approximately 75% yield for this preparation.

Pure methanesulfenyl chloride is stable at $10\ °C$ for several days in the gas phase under its own vapor pressure but decomposes rapidly in contact with air and ordinary vacuum grease. The stability of methanesulfenyl chloride in the liquid phase is considerably less. Therefore, samples of $CH_3SCl$ and $CD_3SCl$ were stored at $-80\ °C$ in air-tight sample tubes. They could be held several months without decomposition under these conditions.

The experimental apparatus was a conventional Stark-effect spectrometer operating in the range 6 – 40 GHz which has been previously described [4, 5]. The error of the frequency measurement is believed to be less than $\pm 0.03$ MHz. The cell has been calibrated using $\mu_{OCS}=0.71521$ as given in [6].

## Spectrum

The b-type lines of the species $CH_3{}^{34}SCl$, measured in natural abundance, are very weak and thus

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* Atomic symbols with no specified weight refer to the most common isotope.

Table 1. Microwave Spectrum of $CD_3SCl$ Frequencies are in MHz. The transitions marked with an asterisk were not used for the calculation of the rotational constants. The lines marked with two asterisks are disturbed by other absorptions resulting in a measurement error larger than 0.03 MHz. These lines were also disregarded in the calculation of the constants given in Table 4 and in Table 8.

| $J'_{K'_-K'_+}$ | $J_{K_-K_+}$ | $F'$ | $F$ | $\nu$(exp.) | $\bar{\nu}$ | $\bar{\nu}$(calc.) | $\Delta\bar{\nu}$ | $\nu$(calc.) | $\Delta\nu$ (exp. — calc.) |
|---|---|---|---|---|---|---|---|---|---|
| $1_{01}$ | $0_{00}$ | | | | 7,482.829 | 7,482.813 | + 0.016 | | |
| | | 5/2 | 3/2 | 7,485.477 | | | | 7,485.452 | + 0.025 |
| | | 3/2 | 3/2 | 7,472.247 | | | | 7,472.256 | — 0.009 |
| | | 1/2 | 3/2 | 7,496.043 | | | | 7,496.010 | + 0.033 |
| $1_{10}$ | $1_{01}$ | | | | 11,227.248 | 11,227.245 | + 0.005 | | |
| | | 5/2 | 5/2 | 11,222.440 | | | | 11,222.430 | + 0.010 |
| | | 3/2 | 5/2 | 11,233.299 | | | | 11,233.308 | — 0.009 |
| | | 1/2 | 3/2 | 11,226.912 | | | | 11,226.924 | — 0.012 |
| | | 5/2 | 3/2 | 11,235.621 | | | | 11,235.627 | — 0.006 |
| | | 3/2 | 1/2 | 11,222.781 | | | | 11,222.751 | + 0.030 |
| $1_{11}$ | $0_{00}$ | | | | 17,932.684 | 17,932.677 | + 0.003 | | |
| | | 5/2 | 3/2 | 17,932.214 | | | | 17,932.213 | + 0.001 |
| | | 3/2 | 3/2 | 17,934.534 | | | | 17,934,532 | + 0.002 |
| | | 1/2 | 1/2 | 17,930.376 | | | | 17,930.358 | + 0.018 |
| $2_{02}$ | $1_{01}$ | | | | 14,923.873 | 14,923.848 | + 0.022 | | |
| | | 7/2 | 5/2 | 14,925.033 | | | | 14,925.099 | — 0.026 |
| | | 5/2 | 3/2 | 14,924.837 | | | | 14,924.778 | + 0.059 |
| | | 3/2 | 1/2 | 14,910.722 | | | | 14,910.778 | + 0.071 |
| | | 5/2 | 5/2 | 14,911.606 | | | | 14,911.582 | + 0.024 |
| | | 3/2 | 3/2 | 14,934.423 | | | | 14,934.405 | + 0.018 |
| | | 1/2 | 1/2 | 14,924.135 | | | | 14,924.129 | + 0.006 |
| $2_{11}$ | $1_{10}$ | | | | 15,743.088 | 15,743.006 | + 0.084 | | |
| | | 7/2 | 5/2 | 15,745.893 | | | | 15,745.844 | + 0.039 |
| | | 5/2 | 3/2 | 15,732.753 | | | | 15,732.649 | + 0.104 |
| | | 3/2 | 1/2 | 15,753.984 | | | | 15,753.884 | + 0.100 |
| | | 5/2 | 5/2 | 15,743.562 | | | | 15,743.526 | + 0.036 |
| | | 3/2 | 3/2 | 15,734.409 | | | | 15,734.303 | + 0.106 |
| | | 1/2 | 1/2 | 15,756.296 | | | | 15,756.203 | + 0.093 |
| $2_{12}$ | $1_{11}$ | | | | 14,188.237 | 14,188.244 | — 0.004 | | |
| | | 7/2 | 5/2 | 14,191.800 | | | | 14,191.816 | — 0.016 |
| | | 5/2 | 3/2 | 14,178.640 | | | | 14,178.619 | + 0.021 |
| | | 3/2 | 1/2 | 14,190.552 | | | | 14,190.556 | — 0.004 |
| | | 5/2 | 5/2 | 14,180.944 | | | | 14,180.938 | + 0.006 |
| | | 3/2 | 3/2 | 14,186.376 | | | | 14,186.389 | — 0.013 |
| | | 1/2 | 1/2 | 14,201.408 | | | | 14,201.411 | — 0.033 |
| * $3_{12}$ | $2_{11}$ | | | | 23,587.640 | 23,587.659 | — 0.019 | | |
| | | 7/2 | 5/2 | 23,585.550 | | | | 23,585.509 | + 0.041 |
| | | 5/2 | 3/2 | 23,586.549 | | | | 23,586.517 | + 0.032 |
| | | 9/2 | 7/2 | 23,588.871 | | | | 23,588.900 | — 0.029 |
| | | ** 3/2 | 1/2 | 23,589.789 | | | | 23,589.908 | — 0.119 |
| * $3_{13}$ | $2_{12}$ | | | | 21,256.907 | 21,256.922 | — 0.015 | | |
| | | 5/2 | 3/2 | 21,254.008 | | | | 21,254.070 | — 0.062 |
| | | 7/2 | 5/2 | 21,255.175 | | | | 21,255.184 | — 0.009 |
| | | 3/2 | 1/2 | 21,257.306 | | | | 21,257.453 | — 0.147 |
| | | 9/2 | 7/2 | 21,258.525 | | | | 21,258.568 | — 0.043 |
| * $3_{22}$ | $2_{21}$ | | | | 22,448.547 | 22,448.437 | + 0.110 | | |
| | | 7/2 | 5/2 | 22,438.966 | | | | 22,439.011 | — 0.045 |
| | | 5/2 | 5/2 | | | | | | |
| | | 5/2 | 3/2 | 22,448.547 | | | | 22,448.437 | + 0.110 |
| | | 3/2 | 3/2 | | | | | | |
| | | 9/2 | 7/2 | 22,452.395 | | | | 22,452.207 | + 0.188 |
| | | 7/2 | 7/2 | | | | | | |
| * $3_{21}$ | $2_{20}$ | | | | 22,614.654 | 22,614.749 | — 0.095 | | |
| | | 3/2 | 1/2 | 22,627.622 | | | | 22,627.669 | — 0.047 |
| | | 9/2 | 7/2 | 22,618.301 | | | | 22,618.367 | — 0.066 |
| | | ** 5/2 | 3/2 | 22,614.609 | | | | 22,614.888 | — 0.279 |
| | | 7/2 | 5/2 | 22,605.600 | | | | 22,605.587 | + 0.013 |
| * $3_{03}$ | $2_{02}$ | | | | 22,282.137 | 22,282.126 | + 0.011 | | |
| | | ** 5/2 | 3/2 | 22,279.651 | | | | 22,279.347 | + 0,304 |
| | | 7/2 | 5/2 | 22,282.329 | | | | 22,282.409 | — 0.080 |
| | | 9/2 | 7/2 | 22,282.797 | | | | 22,282.907 | — 0.110 |
| * $5_{14}$ | $5_{05}$ | | | | 17,776.33 | 17,776.340 | — 0.01 | | |
| | | 7/2 | 7/2 | 17,771.87 | | | | 17,771.655 | + 0.65 |
| | | 13/2 | 13/2 | 17,773.59 | | | | 17,773.637 | + 0.40 |
| | | 9/2 | 9/2 | 17,778.57 | | | | 17,778.683 | + 0.33 |
| | | 11/2 | 11/2 | 17,780.58 | | | | 17,780.665 | + 0.35 |

Table 2. Microwave spectrum of $CD_3S^{37}Cl$. Frequencies are in MHz (see Table 1 for comments).

| $J'_{K'_-K'_+}$ | $J_{K_-K_+}$ | $F'$ | $F$ | $\nu$(exp.) | $\bar{\nu}$ | $\bar{\nu}$(calc.) | $\Delta\bar{\nu}$ | $\nu$(calc.) | $\Delta\nu$ (exp. — calc.) |
|---|---|---|---|---|---|---|---|---|---|
| $1_{01}$ | $0_{00}$ | | | | 7,299.350 | 7,299.334 | + 0.016 | | |
| | | 5/2 | 3/2 | 7,301.461 | | | | 7,301.440 | + 0.021 |
| | | 3/2 | 3/2 | 7,290.923 | | | | 7,290.911 | + 0.012 |
| $1_{10}$ | $1_{01}$ | | | | 11,253.071 | 11,253.046 | + 0.025 | | |
| | | 5/2 | 5/2 | 11,249.377 | | | | 11,249.226 | + 0.151 |
| | | 3/2 | 5/2 | 11,257.745 | | | | 11,257.797 | — 0.050 |
| | | 5/2 | 3/2 | 11,259.728 | | | | 11,259.755 | — 0.027 |
| $1_{11}$ | $0_{00}$ | | | | 17,809.198 | 17,809.223 | — 0.025 | | |
| | | 5/2 | 3/2 | 17,808.813 | | | | 17,808.881 | — 0.018 |
| | | 3/2 | 3/2 | 17,810.752 | | | | 17,810.790 | — 0.038 |
| | | 1/2 | 3/2 | 17,807.245 | | | | 17,807.264 | — 0,020 |
| $2_{02}$ | $1_{01}$ | | | | 14,560.606 | 14,560.636 | — 0.03 | | |
| | | 7/2 | 5/2 | 14,561.547 | | | | 14,561.598 | — 0.051 |
| | | 5/2 | 3/2 | 14,561.343 | | | | 14,561.391 | — 0.048 |
| | | ** 3/2 | 1/2 | 14,549.771 | | | | 14,550.107 | — 0.336 |
| | | 5/2 | 5/2 | 14,550.837 | | | | 14,550.861 | — 0.024 |
| | | 3/2 | 3/2 | 14,569.031 | | | | 14,569.059 | — 0.028 |
| | | 1/2 | 1/2 | 14,560.850 | | | | 14,560.843 | + 0.007 |
| $2_{11}$ | $1_{10}$ | | | | 15.341.816 | 15,341.826 | — 0.01 | | |
| | | 7/2 | 5/2 | 15,344.084 | | | | 15,344.100 | — 0.016 |
| | | 1/2 | 3/2 | 15,336.924 | | | | 15,336.928 | — 0.004 |
| | | 5/2 | 5/2 | 15,342.131 | | | | 15,342.141 | — 0.01 |
| $2_{12}$ | $1_{11}$ | | | | 13,855.525 | 13,855.510 | + 0.015 | | |
| | | 7/2 | 5/2 | 13,858.368 | | | | 13,858.351 | + 0.017 |
| | | 5/2 | 3/2 | 13,847.840 | | | | 13,847.821 | + 0.019 |
| | | 3/2 | 1/2 | 13,857.480 | | | | 13,857.469 | + 0.011 |
| | | 5/2 | 5/2 | 13,849.797 | | | | 13,849.780 | + 0.017 |
| | | 3/2 | 3/2 | 13,853.952 | | | | 13,853.943 | + 0.011 |
| | | 1/2 | 1/2 | 13,865.992 | | | | 13,866.039 | — 0.047 |
| * $3_{22}$ | $2_{21}$ | | | | 21,898.015 | 21,898.002 | + 0.013 | | |
| | | 5/2 | 3/2 | 21,898.016 | | | | 21,898.016 | — 0.00 |
| | | 9/2 | 7/2 | 21,901.022 | | | | 21,901.010 | + 0.012 |

Table 3. Microwave Spectrum of $CH_3{}^{34}SCl$. Frequencies are in MHz (see Table 1 for comments).

| $J'_{K'_-K'_+}$ | $J_{K_-K_+}$ | $F'$ | $F$ | $\nu$(exp.) | $\bar{\nu}$ | $\bar{\nu}$(calc.) | $\Delta\bar{\nu}$ | $\nu$(calc.) | $\Delta\nu$ (exp. — calc.) |
|---|---|---|---|---|---|---|---|---|---|
| $2_{12}$ | $1_{11}$ | | | | 15,611.75 | 15,611.700 | + 0.050 | | |
| | | 5/2 | 3/2 | 15,600.85 | | | | 15,600.813 | + 0.037 |
| | | 7/2 | 5/2 | 15,615.63 | | | | 15,615.586 | + 0.044 |
| $2_{11}$ | $1_{10}$ | | | | 17,405.09 | 17,405.001 | + 0.089 | | |
| | | 7/2 | 5/2 | 17,408.38 | | | | 17,408.29 | + 0.090 |
| $2_{02}$ | $1_{01}$ | | | | 16,461.13 | 16,461.091 | + 0.039 | | |
| | | 7/2 | 5/2 | 16,462.46 | | | | 16,462.419 | + 0.041 |
| $3_{13}$ | $2_{12}$ | | | | 23,388.75 | 23,388.754 | — 0.004 | | |
| | | 5/2 | 3/2 | 23,385.75 | | | | 23,385.829 | — 0.079 |
| | | 7/2 | 5/2 | 23,386.77 | | | | 23,386.766 | 0.004 |
| | | 9/2 | 7/2 | 23,390.48 | | | | 23,390.524 | — 0.044 |
| $3_{03}$ | $2_{02}$ | | | | 24,574.27 | 24,574.356 | — 0.086 | | |
| | | 7/2 | 5/2 | 24,574.78 | | | | 24,574.855 | — 0.075 |
| | | 9/2 | 7/2 | 24,575.08 | | | | 24,575.177 | — 0.097 |
| $3_{21}$ | $2_{20}$ | | | | 24,950.77 | 24,950.696 | + 0.074 | | |
| | | 7/2 | 5/2 | 24,940.39 | | | | 24,940.348 | + 0.042 |
| | | 9/2 | 7/2 | 24,954.91 | | | | 24,954.799 | + 0.111 |
| $3_{12}$ | $2_{11}$ | | | | 26,077.06 | 26,077.145 | — 0.085 | | |
| | | 7/2 | 5/2 | 26,074.77 | | | | 26,074.822 | — 0.052 |
| | | 5/2 | 3/2 | 26,075.52 | | | | 26,075.611 | — 0.091 |
| | | 9/2 | 7/2 | 26,078.46 | | | | 26,078.586 | — 0.126 |
| $2_{11}$ | $2_{02}$ | | | | 14,139.48 | 14,139.477 | + 0.003 | | |
| | | 7/2 | 7/2 | 14,136.31 | | | | 14,136.311 | — 0.001 |

Table 3 (continuation)

| $J'_{K'_-K'_+}$ | $J_{K_-K_+}$ | F′ | $F$ | $\nu$(exp.) | $\bar{\nu}$ | $\bar{\nu}$(calc.) | $\Delta\bar{\nu}$ | $\nu$(calc.) | $\Delta\nu$ (exp. — calc.) |
|---|---|---|---|---|---|---|---|---|---|
| * $4_{13}$ | $4_{04}$ | | | | 17,801.3 | 17,801.093 | + 0.207 | | |
| | | 11/2 | 11/2 | 17,798.66 | | | | 17,798.741 | — 0.081 |
| | | ** 7/2 | 7/2 | 17,803.53 | | | | 17,802.941 | 0.589 |
| | | 9/2 | 9/2 | 17,805.36 | | | | 17,805.208 | 0.152 |
| * $5_{14}$ | $5_{05}$ | | | | 20,726.70 | 20,727.038 | — 0.338 | | |
| | | 7/2 | 7/2 | 20,722.66 | | | | 20,722.995 | — 0.335 |
| | | 13/2 | 13/2 | 20,724.25 | | | | 20,724.706 | — 0.456 |
| | | 11/2 | 11/2 | 20,730.52 | | | | 20,730.77 | — 0.25 |
| * $6_{15}$ | $6_{06}$ | | | | 24,519.33 | 24,520.557 | — 1.227 | | |
| | | ** 15/2 | 15/2 | 24,517.1 | | | | 24,518.168 | — 1.068 |
| | | 11/2 | 11/2 | 24,521.36 | | | | 24,522.729 | — 1.369 |
| | | 13/2 | 13/2 | 24,522.90 | | | | 24,524.140 | — 1.240 |

Table 4. Rotational constants, asymmetry parameters, moments of inertia and $\Delta$'s for all investigated isotopic molecules. The given errors are standard errors. Centrifugal distortion corrections, given in Ref. (2) for the normal species, are not considered here in order to have consistent data for all five species. The conversion factor used is 505.375 GHz/amu·A². $\Delta = I_a + I_b - I_c$.

| Molecule | $A$ (MHz) | $B$ (MHz) | $C$ (MHz) | $x$ | Bibliography |
|---|---|---|---|---|---|
| $CH_3SCl$ | 17,341.65 ± 0.03 | 4,603.73 ± 0.01 | 3,719.14 ± 0.01 | — 0.870128 | (1) |
| $CH_3S^{37}Cl$ | 17,291.57 ± 0.05 | 4,479.34 ± 0.02 | 3,635.27 ± 0.02 | — 0.876383 | (1) |
| $CD_3SCl$ | 14,580.02 ± 0.04 | 4,130.10 ± 0.01 | 3,352.70 ± 0.01 | — 0.861516 | this paper |
| $CD_3S^{37}Cl$ | 14,531.13 ± 0.04 | 4,021.25 ± 0.02 | 3,278.09 ± 0.02 | — 0.867919 | this paper |
| $CH_3{}^{34}SCl$ | 16,874.33 ± 0.09 | 4,575.41 ± 0.04 | 3,678.76 ± 0.04 | — 0.864098 | this paper |
| | $I_a$ (amu · Å²) | $I_b$ (amu · Å²) | $I_c$ (amu · Å²) | $\Delta$ (amu · Å²) | |
| $CH_3SCl$ | 29.14227 | 109.7751 | 135.8849 | 3.0325 | (1) |
| $CH_3S^{37}Cl$ | 29.22667 | 112.8235 | 139.0199 | 3.0302 | (1) |
| $CD_3SCl$ | 34.66216 | 122.3639 | 150.7367 | 6.2893 | this paper |
| $CD_3S^{37}Cl$ | 34.77878 | 125.6761 | 154.1675 | 6.2874 | this paper |
| $CH_3{}^{34}SCl$ | 29.94934 | 110.4546 | 137.3765 | 3.0275 | this paper |

show larger measurement error than quoted above. Some lines are reported even if their measurement was disturbed by other absorptions but were used only for control purposes and not for calculating the rotational constants. A least squares fitting procedure using only low J lines (see Tables 1 to 3) was performed to obtain the rotational constants. Centrifugal distortion effects were neglected since, as shown in [2], they result in only small corrections to the constants. Tables 1, 2, and 3 give the observed spectra for the three isotopic species $CD_3SCl$, $CD_3S^{37}Cl$, and $CH_3{}^{34}SCl$. In Table 4 the rotational constants, the asymmetry parameter, the moments of inertia, and the inertia defect $\triangle$ are reported.

## Structure

Using three isotopic species $CH_3SCl$, $CH_3S^{37}Cl$, and $CH_3{}^{34}SCl$ and applying the Kraitchman equations, the coordinates of the atoms S and Cl can be

Table 5. Coordinates of S and Cl in the principal axis system calculated by Kraitschman's method and obtained from the $r_0$-structure fitting. The errors of the coordinates and of the $r_s$-distance S—Cl include the effects of the standard errors of the rotational constants whereas the standard error of the $r_0$-distance results directly from the fitting procedure. The conversion factor used is 505.375 GHz amu·A².

| Atom | Coordinates calculated by Kraitchman's Method<br>$a$ | $b$ | $c$* |
|---|---|---|---|
| S | 0.5887 (4) | 0.6474 (4) | 0.0 |
| Cl | — 1.2500 (1) | — 0.2134 (6) | 0.0 |
| $r_s$-distance S—Cl = 2.0302 (7) | | | |
| **Atom** | **Coordinates obtained from $r_0$-structure fitting**<br>**$a$** | **$b$** | **$c$** |
| S | 0.5960 | 0.6464 | 0.0 |
| Cl | — 1.2532 | — 0.2086 | 0.0 |
| $r_0$-distance S—Cl = 2.0372 (21) | | | |

* The $c$ coordinate is assumed to be zero.

obtained, thus allowing the calculation of the $r_s$-distance between S and Cl. Alternatively a least squares fitting procedure of all rotational constants given in Table 4 allows the determination of an $r_0$-structure which is more complete than that given in [2] since the only assumption necessary in the present case is the $C_{3v}$-symmetry of the methyl group. The comparison of the S and Cl coordinates obtained in the two procedures shown in Table 5 gives support for the validity of this $r_0$-structure. The calculated $r_0$-structure parameters are shown in Fig. 1 and listed in Table 6. The rotational constants thus obtained differ from the observed ones by not more than 2 MHz for all species.

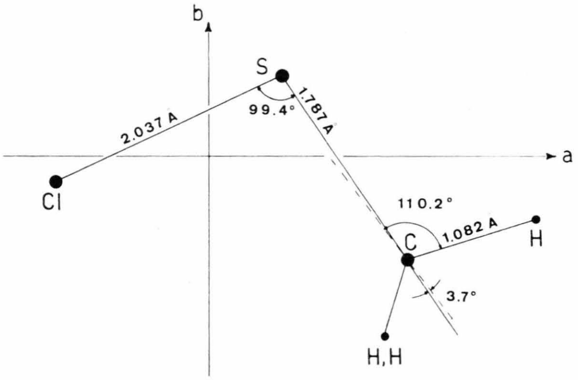

Fig. 1. Structure of methanesulfenyl chloride.

Table 6. $r_0$-Structure calculated by fitting the obtained rotational constants. The errors in parenthesis are given in units of the last figure and are standard errors. Errors on the parameters resulting from consideration of the $r_0$-structure method are not given. The agreement between observed and calculated rotational constants using these structural data is always within 2 MHz.

| C–H (Å) | C–S (Å) | S–Cl (Å) |
|---|---|---|
| 1.0822 (69) | 1.7875 (25) | 2.0372 (23) |
| $H\hat{C}$ SyAx* | $C\hat{S}Cl$ | Tilt angle |
| 110.21° (15) | 99.45° (9) | 3.69° (200) |

* $H\hat{C}$ SyAx is the angle between the CH bond and the methyl group symmetry axis.

As can be seen in Table 6, the tilt angle obtained from the $r_0$-structure has a value of 3.69°. This is in good agreement with the tilt angle of 4.0° obtained from the direction cosines of the $CH_3$-symmetry axis with the principal inertial axes a and b [2] and the direction of the S – C axis given by the $r_0$-structure presented in this work.

## Dipole Moment

The total dipole moment and dipole moment components for the species $CD_3SCl$ have been calculated from the Stark effect pattern. They are given in Table 7 together with the calculated and measured Stark splittings. In order to take into account the quadrupole interactions, calculations have been performed with the entire quadrupole-Stark matrix. The corresponding data for the species $CH_3SCl$ have already been given in [1]. In order to reduce the error of the $\mu_b$ component, additional measurements have been performed for $CH_3SCl$. Combining all these measured values it is possible to determine the orientation of the dipole moment if the assumption is made that the total dipole moment does not change its value appreciably with isotopic substitution.

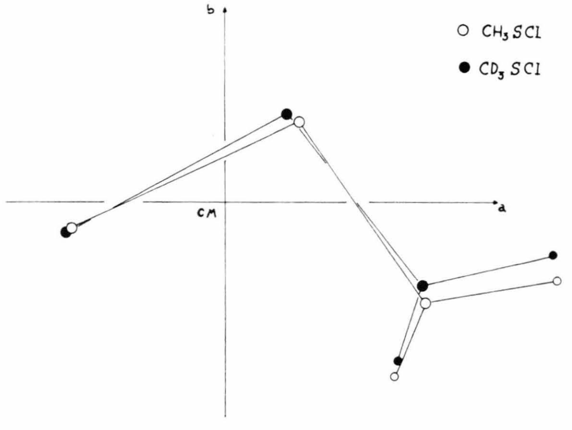

Fig. 2 a. Positions of $CH_3SCl$ and $CD_3SCl$ in the principal axis system. The substitution of hydrogen by deuterium causes a counterclockwise rotation of 3.43 degrees.

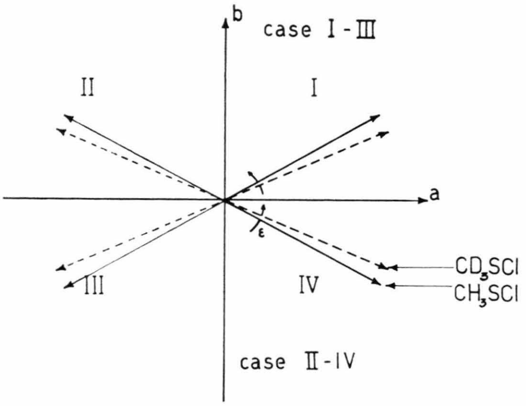

Fig. 2 b. The measured dipole moment components of both molecules are related properly only if the orientation II–IV is assumed for the total dipole moment.

Table 7. Stark effect pattern calculations for the determination of the dipole moment components and of the total dipole moment for the species $CD_3SCl$ and $CH_3SCl$. Measurements for $CH_3SCl$ have been repeated here in an attempt to reduce the measurement errors given in (1). The total quadrupole-Stark energy matrix has been used to fit the Stark splittings for each transition separately. The three values obtained for $\mu_a$ and $\mu_b$ were averaged to give the final values. The errors shown are the largest deviations from the mean values. The calculated $\Delta\nu$ are then obtained with these mean values. (Dipole moment values are in Debye.)

$CD_3SCl$

| Transition | $M_F$ | $E$ (V/cm) | $\Delta\nu$ (exp.) (MHz) | $\Delta\nu$ (calc.) (MHz) | $\Delta\nu$ (exp.) — $\Delta\nu$ (calc.) (MHz) | Comments |
|---|---|---|---|---|---|---|
| $0_{00} \rightarrow 1_{11}$ (Near high field conditions) | ±1/2 | 398.4 | 3.63 | 3.691 | — 0.030 | $\Delta\nu$ is measured with respect to the undisturbed line |
| | | 428.3 | 4.40 | 4.402 | — 0.002 | |
| | | 473.1 | 5.60 | 5.565 | + 0.035 | |
| | ±3/2 | 398.4 | 5.57 | 5.546 | + 0.024 | |
| | | 428.3 | 6.25 | 6.257 | — 0.007 | |
| $0_{00} \rightarrow 1_{01}$ (3/2 — 5/2)* | ±1/2 | 191.7 | 4.30 | 4.368** | — 0.068 | |
| | | 248.0 | 5.50 | 5.493** | + 0.007 | |
| $1_{01} \rightarrow 1_{10}$ (5/2 — 5/2)* | ±5/2 | 100.0 | 2.88 | 2.881 | + 0.001 | $\Delta\nu$ is measured with respect to the 5/2 — 5/2 component |
| | | 152.4 | 6.73 | 6.691 | + 0.039 | |
| | | 157.2 | 7.12 | 7.119 | + 0.001 | |

$\mu_a = 1.85 \pm 0.02$  $\mu_b = 0.80 \pm 0.05$  $\mu_{tot} = 2.01 \pm 0.04$

$CH_3SCl$

| Transition | $M_F$ | $E$ (V/cm) | $\Delta\nu$ (exp.) (MHz) | $\Delta\nu$ (calc.) (MHz) | $\Delta\nu$ (exp.) — $\Delta\nu$ (calc.) (MHz) | Comments |
|---|---|---|---|---|---|---|
| $0_{00} \rightarrow 1_{11}$ (Near high field conditions to high field conditions) | ±1/2 | 452.6 | 3.53 | 3.492 | + 0.038 | $\Delta\nu$ is measured with respect to the undisturbed line |
| | | 585.4 | 6.83 | 6.760 | + 0.070 | |
| | | 633.9 | 8.20 | 8.168 | + 0.032 | |
| | | 677.4 | 9.58 | 9.528 | + 0.052 | |
| | | 716.9 | 10.81 | 10.841 | — 0.031 | |
| | | 886.7 | 17.59 | 17.345 | + 0.245 | |
| | ±3/2 | 452.6 | 6.43 | 6.450 | — 0.020 | |
| | | 585.4 | 9.71 | 9.719 | — 0.009 | |
| | | 633.9 | 10.95 | 11.127 | — 0.177 | |
| | | 677.4 | 12.61 | 12.487 | + 0.123 | |
| | | 716.9 | 13.92 | 13.801 | + 0.120 | |
| | | 886.7 | 20.45 | 20.304 | + 0.150 | |
| $0_{00} \rightarrow 1_{01}$ (3/2 — 1/2)* | ±1/2 | 207.4 | 15.837 | 15.965 | — 0.128 | |
| | | 317.6 | 17.907 | 17.953 | — 0.046 | |
| | | 455.8 | 22.047 | 22.017 | + 0.030 | |
| (3/2 — 5/2)* | ±1/2; ±3/2 | 207.4 | 4.508 | 4.528** | — 0.020 | |
| | | 317.6 | 6.650 | 6.651** | — 0.001 | |
| | | 455.8 | 10.565 | 10.565** | 0.000 | |
| (3/2 — 3/2)* | ±3/2 | 207.4 | — 10.087 | — 9.970 | — 0.117 | |
| | | 317.6 | — 7.79 | — 7.802 | + 0.012 | |
| | | 455.8 | — 4.192 | — 4.117 | — 0.075 | |
| $1_{01} \rightarrow 1_{10}$ (5/2 — 5/2)* | ±5/2 | 170.5 | 6.96 | 6.892 | + 0.068 | $\Delta\nu$ is measured with respect to the 5/2 — 5/2 component |
| | | 191.5 | 8.78 | 8.694 | + 0.009 | |
| | | 226.4 | 12.14 | 12.153 | — 0.013 | |
| | | 293.2 | 20.54 | 20.383 | + 0.157 | |

$\mu_a = 1.78 \pm 0.02$  $\mu_b = 0.95 \pm 0.05$  $\mu_{tot} = 2.01 \pm 0.04$

* $(F - F')$ is the quadrupole component to which the $M_F$ is referred.

** The $\Delta\nu$ (calc) are weighted mean values of both $M_F = 1/2$ and 3/2 Stark components.

As can be seen in Figure 1 a, an isotopic substitution of the hydrogen atoms causes a counterclockwise rotation of the isotopic molecule in the inertial axis system of the normal molecule by an angle $\varepsilon = 3.44$ degrees. The total dipole moment of the isotopic molecule is, therefore, also rotated by the same angle in the same direction. Considering now the measured dipole moment components, the $\mu_a$-component increases from 1.78 D to 1.85 D going from the normal to the isotopic molecule. The $\mu_b$-component, on the contrary, decreases from 0.95 D to 0.80 D. These values are only consistent with a dipole moment having the orientation indicated by case II – IV in Figure 2 b.

The orientation of the total dipole moment is in agreement with the results of an approximate molecular orbital calculation using the $r_0$-structure given in Table 6 with the CNDO/2 Program [7]. As a result of this calculation the sign of the dipole moment can also be given as may be seen in Figure 3.

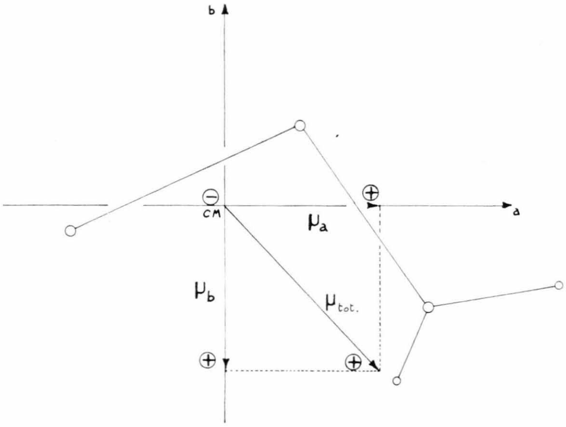

Fig. 3. Dipole moment resulting from a CNDO/2 calculation. The sign of the dipole moment is also given. The obtained values for the components are $\mu_a = 1.25$ D, $\mu_b = -1.30$ D and $\mu_{tot.} = 1.89$ D.

## Quadrupole Coupling Tensor

The quadrupole coupling constants were determined by performing a least squares fitting of all the quadrupole components of the a and b-type lines up to $J = 2$. The values obtained for the different molecular species are given in Table 8. We will now consider the two isotopic species $CD_3SCl$ and $CH_3SCl$. This isotopic substitution gives a possibility to determine the orientation of the principal axis system of the quadrupole coupling tensor, assuming that the electron charge distribution remains unchanged for an isotopic substitution sufficiently far from the nucleus under consideration. The method used is well known, but it is perhaps convenient to repeat it here.

For a molecule with a symmetry plane and having the quadrupole nucleus in this plane, as in our case, the quadrupole coupling tensor has the following form:

$$[\chi_{gg'}] = \begin{bmatrix} \chi_{aa} & \chi_{ab} & 0 \\ \chi_{ba} & \chi_{bb} & 0 \\ 0 & 0 & \chi_{cc} \end{bmatrix}$$

where $a$, $b$, and $c$ are the principal axes of inertia. If $[\chi_{gg'}]$ is the quadrupole coupling tensor for the normal molecule, then there will be a slightly different quadrupole coupling tensor $[\chi'_{gg'}]$ for the isotopic molecule due to the different orientation with respect to the original axes.

Further, let

$$[\chi_Q] = \begin{bmatrix} \chi_{zz} & 0 & 0 \\ 0 & \chi_{xx} & 0 \\ 0 & 0 & \chi_{yy} \end{bmatrix}$$

Table 8. Quadrupole coupling constants in the inertial principal axis system and in the quadrupole coupling principal axis system. $\theta$ is the angle between the S—Cl bond and the $a$-axis in the $r_0$-structure. $\alpha$ is the angle between the reference system of $[\chi_{gg'}]$ and the reference system of $[\chi_Q]$. The errors of the $\chi_{aa}$, $\chi_{bb}$ and $\chi_{cc}$ are standard errors. The errors of the $\chi_{zz}$, $\chi_{xx}$, $\chi_{ab}$, $\alpha$ reflect the inaccuracy of the angle $\varepsilon$.

| | $CH_3SCl$ | $CD_3SCl$ | $CH_3{}^{34}SCl$ | $CH_3S^{37}Cl$ | $CD_3S^{37}Cl$ |
|---|---|---|---|---|---|
| $\chi_{aa}$ | – 58.31 ± 0.05 | – 52.79 ± 0.05 | – 59.09 ± 0.08 | – 46.29 ± 0.05 | – 42.12 ± 0.05 |
| $\chi_{bb}$ | 14.80 ± 0.05 | 9.27 ± 0.05 | 15.63 ± 0.08 | 12.15 ± 0.05 | 7.83 ± 0.05 |
| $\chi_{cc}$ | 43.51 ± 0.05 | 43.52 ± 0.05 | 43.46 ± 0.08 | 34.14 ± 0.05 | 34.29 ± 0.05 |
| $\chi_{ab}$ | 43.94 ± 1.8 | 48.00 ± 2.0 | | 33.59 ± 1.4 | 36.69 ± 1.5 |
| $\chi_{zz}$ | – 78.91 ± 1.4 | – 78.92 ± 1.4 | | – 61.59 ± 1.1 | – 61.53 ± 1.1 |
| $\chi_{xx}$ | 35.40 ± 0.6 | 35.40 ± 0.6 | | 27.45 ± 0.5 | 27.24 ± 0.5 |
| $\chi_{yy}$ | 43.51 ± 0.05 | 43.52 ± 0.05 | | 34.14 ± 0.05 | 34.28 ± 0.05 |
| $\varepsilon$ | | 3.44° ± 0.15° | | | 3.39° ± 0.15° |
| $\alpha$ | $25.12^0$ ± 0.60° | 28.56° ± 0.60° | | 24.49° ± 0.60° | 27.88° ± 0.60° |
| $\theta$ ($r_0$-str.) | $24.82^0$ ± 0.25° | 28.26° ± 0.25° | 24.28° ± 0.25° | 24.46° ± 0.25° | 27.85° ± 0.25° |

be the quadrupole coupling tensor in its own principal axis system $x$, $y$, $z$.

The transformation between $[\chi_{gg'}]$ and $[\chi_Q]$ can be easily performed by an orthogonal similarity transformation where $\alpha$ and $\alpha + \varepsilon$ are respectively the angle between the reference systems of $[\chi_Q]$ and $[\chi_{gg'}]$ and between those of $[\chi_Q]$ and $[\chi'_{gg'}]$. Therefore, using the experimental values of $\chi_{gg}$, $\chi'_{gg}$ and $\varepsilon$, it is possible to calculate $\chi_{zz}$, $\chi_{xx}$ and $\alpha$ which in turn enable the determination of $\chi_{gg'}$ and $\chi'_{gg'}$. All these data are listed in Table 8.

The possibility of obtaining the angle $\alpha$ between the reference system of $[\chi_Q]$ and $[\chi_{gg'}]$ can give an information about the validity of the assumption made in[2] that the $z$ axis of the quadrupole coupling tensor coincides with the S – Cl bond axis. The angle between the S – Cl bond and the $a$-axis given by the structure of Table 6 is 24.82° ± 0.25° and the $\alpha$-angle obtained from the quadrupole coupling tensor is 25.12° ± 0.6°. The two angles have about the same value within the experimental error thus confirming the validity of the assumption on the presence of symmetry in the electronic charge distribution about the S – Cl bond.

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