Microwave Spectrum, Quadrupole Coupling Constants and Dipole Moment of Methanesulfenylchloride

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The investigation of the microwave spectrum of Methanesulfenylchloride [1] affords an opportunity to determinate its accurate molecular structure. Moreover additional information about the molecule can be obtained from a determination of its dipole moment, barrier to internal rotation and chlorine quadrupole coupling constants.

The sample of Methanesulfenylchloride was prepared in this laboratory by I. ROSENBAUM, the species of CH_3SCl^{35} and CH_3SCl^{37} were studied in natural abundance.

The microwave spectra were investigated by means of a conventional 100 kHz Stark modulation spectrometer with automatic frequency markers described elsewhere [2, 3].

Frequency measurements are believed to be accurate within ± 0.03 MHz.

The spectrum consists of both a- and b-type transitions, the two $0 \rightarrow 1$ lines were identified on the basis of the quadrupole fine structure and the characteristic Stark lobes at high field conditions, the $1 \rightarrow 2$ lines and the $1_{01} \rightarrow 1_{10}$ lines were identified by their quadrupole fine structure.

The observed and calculated frequencies are listed in Tables 1 and 2.

The lines $5_{14} \rightarrow 5_{15}$, $4_{40} \rightarrow 4_{31}$ of CH_3SCl^{37} and the line $2_{02} \rightarrow 2_{11}$ of CH_3SCl^{35} were also measured but not used for the calculation of the rotational constants which have been derived only from the above mentioned low J transitions in order to minimize the effects due to centrifugal distortion.

$J_{K-1,K_1} \rightarrow J'_{K-1,K_1}$	$F \rightarrow F'$	observed frequencies	calculated frequencies
$0_{00} \rightarrow 1_{01}$	$3/2 \rightarrow 3/2$	8311.24	8311.22
	$3/2 \rightarrow 5/2$	8325.81	8325.77
	$3/2 \rightarrow 1/2$	8337.42	8337.41
$0_{00} \rightarrow 1_{11}$	$3/2 \rightarrow 1/2$	21057.12	21057.12
	$3/2 \rightarrow 5/2$	21060.08	21060.05
	$3/2 \rightarrow 3/2$	21063.76	21063.74
$1_{01} \rightarrow 1_{10}$	$1/2 \rightarrow 3/2$	13616.23	13616.65
	$5/2 \rightarrow 5/2$	13617.37	13617.44
	$3/2 \rightarrow 1/2$	13623.41	13623.30
	$5/2 \rightarrow 3/2$	13628.40	13628.30
	$3/2 \rightarrow 5/2$	13632.01	13631.99
$1_{11} \rightarrow 2_{12}$	$3/2 \rightarrow 5/2$	15750.42	15750.43
	$5/2 \rightarrow 5/2$	15754.13	15754.12
	$3/2 \rightarrow 3/2$	15758.15	15758.19
	$5/2 \rightarrow 7/2$	15764.89	15764.98
	$1/2 \rightarrow 1/2$	15775.77	15775.69
$1_{01} \rightarrow 2_{02}$	$1/2 \rightarrow 3/2$	16586.72	16586.69
	$5/2 \rightarrow 5/2$	16587.71	16587.79
	$5/2 \rightarrow 7/2$	16602.43	16602.55
	$3/2 \rightarrow 3/2$	16612.89	16612.88
$1_{10} \rightarrow 2_{11}$	$3/2 \rightarrow 5/2$	17519.04	17519.00
	$3/2 \rightarrow 3/2$	17521.62	17521.63
	$3/2 \rightarrow 1/2$	17525.30	17525.32
	$5/2 \rightarrow 5/2$	17529.88	17529.86
	$5/2 \rightarrow 7/2$	17533.58	17533.55
	$1/2 \rightarrow 3/2$	17541.22	17541.18
	$1/2 \rightarrow 1/2$	17544.92	17544.87
$2_{02} \rightarrow 2_{11}$	$7/2 \rightarrow 7/2$	14548.61	14548.44
	$3/2 \rightarrow 3/2$	14551.79	14551.60

Table 1. Microwave rotational spectrum of CH_3SCl^{35} (frequencies in MHz).

$J_{K-1,K_1} \rightarrow J'_{K-1,K_1}$	$F \rightarrow F'$	observed frequencies	calculated frequencies
$0_{00} \rightarrow 1_{01}$	$3/2 \rightarrow 3/2$	8105.39	8105.36
	$3/2 \rightarrow 5/2$	8116.96	8116.93
	$1/2 \rightarrow 3/2$	8126.26	8126.19
$0_{00} \rightarrow 1_{11}$	$1/2 \rightarrow 3/2$	20923.71	20923.80
	$3/2 \rightarrow 5/2$	20926.25	20926.23
	$3/2 \rightarrow 3/2$	20929.24	20929.27
$1_{11} \rightarrow 2_{12}$	$3/2 \rightarrow 5/2$	15376.64	15376.63
	$5/2 \rightarrow 7/2$	15388.28	15388.21
	$1/2 \rightarrow 1/2$	15396.66	15396.73
$1_{01} \rightarrow 2_{02}$	$1/2 \rightarrow 3/2$	16177.35	16177.32
	$5/2 \rightarrow 5/2$	16178.11	16178.20
	$5/2 \rightarrow 7/2$	16189.85	16189.93
	$3/2 \rightarrow 3/2$	16198.10	16198.15
$1_{10} \rightarrow 2_{11}$	$3/2 \rightarrow 5/2$	17064.29	17064.31
	$3/2 \rightarrow 3/2$	17066.44	17066.48
	$5/2 \rightarrow 5/2$	17072.96	17072.85
	$5/2 \rightarrow 7/2$	17075.89	17075.88
	$1/2 \rightarrow 3/2$	17081.82	17081.85
	$1/2 \rightarrow 1/2$	17084.96	17084.88
$4_{04} \rightarrow 4_{13}$	$5/2 \rightarrow 5/2$	17939.83	17939.86
	$11/2 \rightarrow 11/2$	17941.63	17941.63
	$7/2 \rightarrow 7/2$	17944.91	17944.91
	$9/2 \rightarrow 9/2$	17946.70	17946.68
$5_{15} \rightarrow 5_{14}$	$13/2 \rightarrow 13/2$	12624.20	12625.31
	$9/2 \rightarrow 9/2$	12628.17	12629.23
	$11/2 \rightarrow 11/2$	12629.73	12630.77

Table 2. Microwave rotational spectrum of CH_3SCl^{37} (frequencies in MHz).

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	CH_3SCl^{35}	CH_3SCl^{37}
A	17341.65 ± 0.03	17291.57 ± 0.03
B	4603.73 ± 0.03	4479.34 ± 0.03
C	3719.14 ± 0.03	3635.27 ± 0.03
$\varkappa$	−0.8701279	−0.8763834
χ_{aa}	−58.31 ± 0.10	−46.29 ± 0.10
χ_{bb}	14.80 ± 0.20	12.15 ± 0.20
μ_a	1.76 ± 0.02	
μ_b	0.95 ± 0.15	
μ	2.00 ± 0.15	

Table 3. Rotational constants, quadrupole coupling constants (in MHz), asymmetry parameter $\varkappa$ and dipole moment (Debye).

Table 3 contains the rotational constants, the quadrupole coupling constants and the asymmetry parameter $\varkappa$.

The dipole moment components, given in Table 3 too, were determined by measuring a) the two Stark lobes at high field approximation in the case of the $0 \rightarrow 1$ lines and b) the $5/2 \rightarrow 5/2$ Stark lobe of the $1_{01} \rightarrow 1_{10}$ line which is independent of the quadrupole energy.

The electric field was calibrated by means of the $0 \rightarrow 1$ transition of OCS using the values of 0.7152 D [4] for the dipole moment.

None of the observed lines showed any relevant effect due to internal rotation, calculations on this subject and measurement are in progress.

The present investigation is not sufficient for a structure determination, an extension is planned.

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BERICHTIGUNG

Zu R. Burger, H. Dittrich und K. M. Koch, Die Änderung der Wärmeleitfähigkeit von ferromagnetischen Nickel-Kupfer-Legierungen im Magnetfeld, Z. Naturforsch. **23 a**, 861 [1968].

Auf S. 862 sollen die Gleichungen richtig lauten:

$$\Delta T = \Delta T_P + \Delta T_E = (W_P + W_E)\ \Phi \qquad \text{für} \quad H = 0\,,$$

$$\Delta T = \Delta T_P' + \Delta T_E' = (W_P + \Delta W_P + W_E)\ \Phi' \qquad \text{für} \quad H \neq 0\,.$$

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