A Reinvestigation of the Rotational Spectrum of 2-Chloropropene

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The microwave spectrum of 2-chloropropene was reinvestigated using microwave Fourier transform spectroscopy. For the two isotopic species $CH_3C^{35}Cl{=}CH_2$ and $CH_3C^{37}Cl{=}CH_2$ the chlorine quadrupole coupling was determined with higher accuracy. The barrier to internal rotation was determined from the ground state. For comparison the first excited torsional state of $CH_3C^{35}Cl{=}CH_2$ was remeasured and reanalysed.

Introduction

The microwave spectra of halopropenes are of interest for a comparison of the different methyl internal rotation barriers [1]. We found that former analyses were based on data originating from measurements of the rotational spectra of the ground or first excited state of the methyl internal rotation (torsion).

As there may be an interaction of the methyl internal rotation with other vibrations, we analysed the vibrational and torsional ground state rotational spectra of 2-chloro- and 2-bromopropene. This was possible by the increased resolution of microwave Fourier transform (MWFT) spectroscopy [2–4].

In this paper we present our investigation of 2-chloropropene (^{35}Cl and ^{37}Cl) $CH_3CCl{=}CH_2$. This molecule was investigated by Unland et al. [5] and by Good et al. [6]. They could not resolve the ground state torsional splittings.

Experimental

The sample was purchased from the Columbia Organic Company, Inc., and used after vacuum distillation. The MWFT-spectrometers described in [2, 3] were used. The temperature was about $-65\,^{\circ}C$, the pressure down to 0.12 mtorr.

The measured lines for $CH_3C^{35}Cl{=}CH_2$ and $CH_3C^{37}Cl{=}CH_2$ are given in Tables 1 and 2 for the torsional ground state, and in Table 3 for the first excited state of the methyl torsion of $CH_3C^{35}Cl{=}CH_2$. We decided to reanalyse this spectrum, because we found some minor misassignment in [5] and preferred to compare values determined with the same spectroscopic method and theoretical treatment. The accuracy of the lines is about 10–20 kHz. Examples are given in Figs. 1 and 2.

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Analysis

As the spectra had already been assigned and the published constants gave a good prediction, the measurements could easily be extended to higher J-values. The assignment of the high J-lines was checked by a centrifugal distortion analysis and the consistency of the quadrupole hfs and the internal rotation analysis.

The three perturbations, which modify the rigid rotor spectrum of this molecule: centrifugal distor-

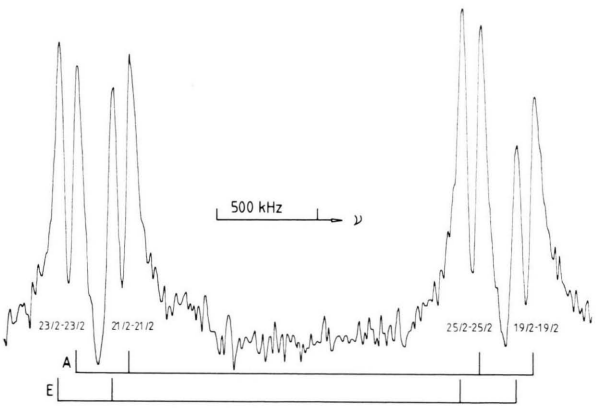

Fig. 1. A range of 2.9 MHz out of a 10 MHz scan of the rotational spectrum of $CH_3C^{37}Cl{=}CH_2$ in natural abundance. $JK_-K_+ - J'K'_-K'_+ = 11\,4\,7 - 11\,4\,8$; amplitude spectrum, sample interval: 50 ns, 512 K cycles, 1024 data points supplemented by 1024 zeros, microwave signal frequency: $\nu_{MW} = 17837$ MHz; pressure: $p = 0.12$ mtorr, temperature: $T = -58\,^{\circ}C$.

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Tables 1–3. Measured transitions of $CH_3CCl{=}CH_2$. Γ: symmetry species, ν_{exp}: experimental frequency, $\bar{\nu}$, $\bar{\nu}_0$, $\Delta\nu_{AE}$: see text, *F*: measured by Unland et al. [5], *: not used for quadrupole hfs analysis, **: not used for torsional analysis, o: overlayed, nr: not resolved; frequencies, splittings and deviations in MHz.

Table 1. Measured transitions of $CH_3C^{35}Cl{=}CH_2$.

J K- K+	J' K-'K+'	F	F'	Γ	ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	$\delta_{calc-exp}$	$\Delta\nu_{AE}$	$\delta_{calc-exp}$	$\bar{\nu}_0$
1 0 1	0 0 0	5/2	3/2	F	8291.697	3.460	-0.056			8288.237
		3/2	3/2		8274.568	-13.669	0.055			
		1/2	3/2		8305.254	17.017	0.001			
2 1 1	2 1 2	7/2	7/2	F	5038.698	0.430	0.007			5038.268
		5/2	5/2		5037.182	-1.086	-0.007			
2 0 2	1 0 1	7/2	5/2	F	16173.072	1.236	-0.031			16171.836
		5/2	3/2		16173.848	2.012	0.080			
		3/2	1/2		16154.850	-16.986	-0.032			
		5/2	5/2		16156.963	-14.873	-0.053			
		3/2	3/2		16185.546	13.710	-0.096			
		1/2	1/2		16170.896	-0.940	0.053			
		3/2	5/2		16168.357	-3.479	0.075			
2 1 2	1 1 1	7/2	5/2	F	14901.239	4.043	0.024			14897.196
		5/2	3/2		14884.266	-12.930	-0.021			
		3/2	1/2		14906.412	9.216	0.058			
		5/2	5/2		14893.510	-3.686	0.010			
		3/2	3/2		14889.857	-7.339	-0.080			
		1/2	1/2		14914.206	17.010	0.008			
3 1 2	3 1 3	9/2	9/2	F	10013.899	0.475	-0.009			10013.424
		7/2	7/2		10012.487	-0.937	0.005			
		5/2	5/2		10013.135	-0.289	0.009			
		3/2	3/2		10014.547	1.123	-0.005			
4 1 3	4 1 4	11/2	11/2	F	16368.390	0.392	-0.024			16367.998
		9/2	9/2		16367.324	-0.674	0.031			
		7/2	7/2		16367.686	-0.312	0.023			
		5/2	5/2		16368.751	0.753	-0.031			
4 2 2	4 2 3	11/2	11/2		5009.060	0.889	0.006			5008.171
		9/2	9/2		5006.630	-1.541	-0.025			
		7/2	7/2		5007.476	-0.695	-0.008			
		5/2	5/2		5009.900	1.729	0.029			
5 2 3	5 2 4	13/2	13/2	A	9911.807	1.012	-0.006	0.035	-0.003	9910.778
				E	9911.773					
		11/2	11/2	A	9909.181	-1.614	0.005			
				E	9909.146					
		9/2	9/2	A	9909.921	-0.875	0.003			
				E	9909.885					
		7/2	7/2	A	9912.541	1.745	-0.002			
				E	9912.505					
6 2 4	6 2 5	15/2	15/2	A	16417.743	0.962	0.006	0.055	-0.006	16416.755
				E	16417.690					
		13/2	13/2	A	16415.331	-1.455	0.003			
				E	16415.269					
		11/2	11/2	A	16415.894	-0.887	0.007			
				E	16415.842					
		9/2	9/2	A	16418.335	1.554	-0.014			
				E	16418.283					
7 3 4	7 3 5	17/2	17/2	A	8640.601	1.035	-0.005	0.044	-0.005	8639.542
				E	8640.553					
		15/2	15/2	A	8638.092	-1.472	0.001			
				E	8638.048					
		13/2	13/2	A	8638.600	-0.963	0.001			
				E	8638.558					
		11/2	11/2	A	8641.100	1.537	0.002			
				E	8641.057					
8 3 5	8 3 6	19/2	19/2	A	14993.179	1.111	0.022	0.064	-0.004	14992.037
				E	14993.116					
		17/2	17/2	A	14990.528	-1.544	-0.014			
				E	14990.457					
		15/2	15/2	A	14990.967	-1.101	0.025			
				E	14990.905					
		13/2	13/2	A	14993.713	1.647	-0.032			
				E	14993.654					
10 4 6	10 4 7	23/2	23/2	A	12617.739	1.085	-0.005	0.067	-0.001	12616.621
				E	12617.673					
		21/2	21/2	A	12615.244	-1.410	0.006			
				E	12615.178					
		19/2	19/2	A	12615.610	-1.045	-0.001			
				E	12615.541					
		17/2	17/2	A	12618.092	1.438	0.000			
				E	12618.025					
12 5 7	12 5 8	27/2	27/2	A	9850.238	0.908	-0.003	0.067	-0.001	9849.297
				E	9850.172					
		25/2	25/2	A	9848.194	-1.135	0.003			
				E	9848.129					
		23/2	23/2	A	9848.446	-0.885	-0.001			
				E	9848.377					
		21/2	21/2	A	9850.480	1.150	0.002			
				E	9850.414					

J K- K+	J' K-'K+'	F	F'	Γ	ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	$\delta_{calc-exp}$	$\Delta\nu_{AE}$	$\delta_{calc-exp}$	$\bar{\nu}_0$
13 5 8	13 5 9	29/2	29/2	A	16949.844	1.103	-0.001	0.098	0.001	16948.692
				E	16949.746					
		27/2	27/2	A	16947.378	-1.361	0.005			
				E	16947.284					
		25/2	25/2	A	16947.659	-1.083	0.002			
				E	16947.558					
		23/2	23/2	A	16950.123	1.381	-0.005			
				E	16950.022					
15 6 9	15 6 10	33/2	33/2	A	13232.134	0.943	-0.004	0.095	0.002	13231.143
				E	13232.038					
		31/2	31/2	A	13230.025	-1.126	-0.001			
				E	13229.970					
		29/2	29/2	A	13230.262	-0.928	0.002			
				E	13230.167					
		27/2	27/2	A	13232.329	1.138	0.002			
				E	13232.233					
17 7 10	17 7 11	37/2	37/2	A	9717.675	0.728	0.001	0.085	0.002	9716.905
				E	9717.591					
		35/2	35/2	A	9716.088	-0.859	0.001			
				E	9716.004					
		33/2	33/2	A	9716.225	-0.723	0.001			
				E	9716.139					
		31/2	31/2	A	9717.818	0.870	-0.004			
				E	9717.732					
18 7 11	18 7 12	39/2	39/2	A	16976.986	0.967	-0.002	0.128	0.003	16975.955
				E	16976.858					
		37/2	37/2	A	16974.888	-1.131	0.005			
				E	16974.760					
		35/2	35/2	A	16975.063	-0.955	-0.001			
				E	16974.936					
		33/2	33/2	A	16977.160	1.136	-0.001			
				E	16977.027					
20 8 12	20 8 13	43/2	43/2	A	12580.749	0.772	-0.003	0.116	0.001	12579.919
				E	12580.632					
		41/2	41/2	A	12579.095	-0.882	-0.002			
				E	12578.979					
		39/2	39/2	A	12579.213	-0.765	0.002			
				E	12579.095					
		37/2	37/2	A	12580.862	0.887	0.003			
				E	12580.749					
22 9 13	22 9 14	47/2	47/2	A	8849.990	0.562	0.003	0.093	0.003	8849.385
				E	8849.903					
		45/2	45/2	A	8848.784	-0.646	0.004			
				E	8848.694					
		43/2	43/2	A	8848.874	-0.556	-0.005			
				E	8848.784					
		41/2	41/2	A	8850.078	0.649	-0.003			
				E	8849.990					
23 9 14	23 9 15	49/2	49/2	A	15785.532	0.805	-0.001	0.155	-0.004	15784.651
				E	15785.379					
		47/2	47/2	A	15782.821	-0.907	-0.001			
				E	15782.667					
		45/2	45/2	A	15782.932	-0.796	-0.003			
				E	15782.778					
		43/2	43/2	A	15785.638	0.909	0.004			
				E	15785.481					
25 10 15	25 10 16	53/2	53/2	A	11232.533	0.607	-0.001	0.126	-0.001	11231.864
				E	11232.408					
		51/2	51/2	A	11231.248	-0.678	-0.001			
				E	11231.122					
		49/2	49/2	A	11231.324	-0.603	0.000			
				E	11231.198					
		47/2	47/2	A	11232.606	0.679	0.003			
				E	11232.480					
28 11 17	28 11 18	59/2	59/2	A	13922.668	0.643	0.002	0.156	-0.001	13921.947
				E	13922.512					
		57/2	57/2	A	13921.314	-0.712	-0.002			
				E	13921.156					
		55/2	55/2	A	13921.386	-0.639	-0.003			
				E	13921.230					
		53/2	53/2	A	13922.737	0.713	0.003			
				E	13922.582					

J K- K+	J' K-'K+'	F	F'		ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	$\delta_{calc-exp}$	$\Delta\nu_{AE}$	$\delta_{calc-exp}$	$\bar{\nu}_0$
30 12 18	30 12 19	63/2	63/2	A	9590.372	0.463	0.001	0.120	0.000	9589.849
				E	9590.252					
		61/2	61/2	A	9589.398	-0.510	-0.001			
				E	9589.279					
		59/2	59/2	A	9589.449	-0.460	-0.003			
				E	9589.328					
		57/2	57/2	A	9590.418	0.509	0.003			
				E	9590.298					
31 12 19	31 12 20	65/2	65/2	A	16930.072	0.678	0.003	0.188	-0.001	16929.302
				E	16929.887					
		63/2	63/2	A	16928.654	-0.745	-0.002			
				E	16928.459					
		61/2	61/2	A	16928.721	-0.673	-0.006			
				E	16928.536					
		59/2	59/2	A	16930.139	0.744	0.005			
				E	16929.952					
33 13 20	33 13 21	69/2	69/2	A	11798.644	0.498	0.004	0.145	0.001	11798.074
				E	11798.499					
		67/2	67/2	A	11797.602	-0.545	-0.002			
				E	11797.455					
		65/2	65/2	A	11797.651	-0.495	-0.005			
				E	11797.506					
		63/2	63/2	A	11798.689	0.544	0.005			
				E	11798.547					
36 14 22 *	36 14 23	75/2	75/2	A	14286.343	0.535	0.003	0.172	0.000	14285.722
				E	14286.171					
		73/2	73/2	A	14285.228	-0.580	-0.003			
				E	14285.056					
		71/2	71/2	A	14285.276	-0.531	-0.006			
				E	14285.105					
		69/2	69/2	A	14286.386	0.578	0.006			
				E	14286.213					
39 15 24 *	39 15 25	81/2	81/2	A	17065.278	0.582	-0.008	0.196	0.003	17064.614
				E	17065.082					
		79/2	79/2	A	17064.096	-0.617	-0.001			
				E	17063.897					
		77/2	77/2	A	17064.142	-0.571	-0.002			
				E	17063.944					
		75/2	75/2	A	17065.317	0.607	0.012			
				E	17065.125					

Table 2. Measured transitions of $CH_3C^{37}Cl{=}CH_2$.

J K- K+	J' K-'K+'	F	F'		ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	$\delta_{calc-exp}$	$\Delta\nu_{AE}$	$\delta_{calc-exp}$	$\bar{\nu}_0$
1 0 1 F	0 0 0	5/2	3/2		8098.244	2.676	0.002			8095.568
		3/2	3/2		8084.814	-10.754	0.044			
		1/2	3/2		8109.022	13.454	-0.066			
2 1 2 F	1 1 1	7/2	5/2		14589.142	3.194	0.005			14585.948
		5/2	3/2		14575.758	-10.190	0.106			
		3/2	1/2		14593.384	7.436	-0.128			
		5/2	5/2		14582.046	-2.902	0.021			
		3/2	3/2		14579.982	-5.966	0.120			
		1/2	1/2		14599.361	13.413	-0.025			
3 1 2	3 1 3	9/2	9/2		9579.142	0.381	-0.001			9578.761
		7/2	7/2		9578.002	-0.759	-0.001			
		5/2	5/2		9578.536	-0.225	-0.003			
		3/2	3/2		9579.673	0.912	0.000			
5 1 5	5 2 4	13/2	13/2		9160.229	0.764	0.009			9159.465
		11/2	11/2		9158.231	-1.234	-0.003			
		9/2	9/2		9158.809	-0.656	-0.014			
		7/2	7/2		9160.796	1.331	0.009			
6 2 4 F	6 2 5	15/2	15/2		15313.803	0.772	-0.007			15313.031
		13/2	13/2		15311.886	-1.145	-0.003			
		11/2	11/2		15312.326	-0.705	0.009			
		9/2	9/2		15314.246	1.215	0.003			
8 3 5	8 3 6	19/2	19/2	A	13468.476	0.857	0.003	0.055	0.000	13467.592
				E	13468.421					
		17/2	17/2	A	13466.444	-1.176	-0.007			
				E	13466.388					
		15/2	15/2	A	13466.805	-0.815	-0.002			
				E	13466.748					
		13/2	13/2	A	13468.837	1.220	0.006			
				E	13468.786					
10 4 6	10 4 7	23/2	23/2	A	10793.413	0.781	0.001	0.061	-0.002	10792.600
				E	10793.348					
		21/2	21/2	A	10791.617	-1.013	-0.003			
				E	10791.556					
		19/2	19/2	A	10791.875	-0.752	-0.005			
				E	10791.821					
		17/2	17/2	A	10793.666	1.034	0.007			
				E	10793.602					

J K- K+	J' K-'K+'	F	F'		ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	$\delta_{calc-exp}$	$\Delta\nu_{AE}$	$\delta_{calc-exp}$	$\bar{\nu}_0$
11 4 7	11 4 8	25/2	25/2	A	17835.854	0.877	0.005	0.088	-0.002	17834.933
				E	17835.765					
		23/2	23/2	A	17833.859	-1.119	-0.003			
				E	17833.768					
		21/2	21/2	A	17834.121	-0.854	-0.005			
				E	17834.037					
		19/2	19/2	A	17836.116	1.140	0.005			
				E	17836.030					
13 5 8	13 5 9	29/2	29/2	A	14099.912	0.787	0.003	0.086	0.001	14099.083
				E	14099.828					
		27/2	27/2	A	14098.157	-0.970	-0.002			
				E	14098.068					
		25/2	25/2	A	14098.353	-0.773	-0.002			
				E	14098.267					
		23/2	23/2	A	14100.109	0.984	0.003			
				E	14100.024					
15 6 9	15 6 10	33/2	33/2	A	10344.226	0.630	0.000	0.078	0.002	10343.558
				E	10344.149					
		31/2	31/2	A	10342.840	-0.757	0.001			
				E	10342.762					
		29/2	29/2	A	10342.981	-0.616	-0.005			
				E	10342.902					
		27/2	27/2	A	10344.357	0.760	0.004			
				E	10344.278					
16 6 10	16 6 11	35/2	35/2	A	17551.689	0.787	0.005	0.120	-0.002	17550.844
				E	17551.573					
		33/2	33/2	A	17549.963	-0.941	0.001			
				E	17549.842					
		31/2	31/2	A	17550.132	-0.774	-0.008			
				E	17550.008					
		29/2	29/2	A	17551.851	0.948	0.002			
				E	17551.732					
18 7 11	18 7 12	39/2	39/2	A	12902.166	0.636	0.004	0.113	-0.005	12901.472
				E	12902.050					
		37/2	37/2	A	12900.786	-0.744	-0.003			
				E	12900.669					
		35/2	35/2	A	12900.895	-0.631	-0.003			
				E	12900.786					
		33/2	33/2	A	12902.277	0.750	0.003			
				E	12902.166					
20 8 12	20 8 13	43/2	43/2	A	8895.809	0.458	0.010	0.085	0.004	8895.309
				E	8895.724					
		41/2	41/2	A	8894.814	-0.540	0.002			
				E	8894.724					
		39/2	39/2	A	8894.892	-0.456	-0.009			
				E	8894.814					
		37/2	37/2	A	8895.894	0.543	-0.001			
				E	8895.809					
21 8 13	21 8 14	45/2	45/2	A	15614.380	0.646	0.002	0.137	0.001	15613.666
				E	15614.244					
		43/2	43/2	A	15612.997	-0.738	-0.003			
				E	15612.859					
		41/2	41/2	A	15613.094	-0.642	-0.002			
				E	15612.954					
		39/2	39/2	A	15614.473	0.740	0.005			
				E	15614.338					
23 9 14	23 9 15	49/2	49/2	A	10840.881	0.481	0.002	0.114	-0.001	10840.343
				E	10840.766					
		47/2	47/2	A	10839.858	-0.542	-0.004			
				E	10839.743					
		45/2	45/2	A	10839.922	-0.478	-0.002			
				E	10839.808					
		43/2	43/2	A	10840.942	0.544	0.005			
				E	10840.832					
26 10 16	26 10 17	55/2	55/2	A	12925.609	0.492	0.005	0.141	-0.002	12925.047
				E	12925.469					
		53/2	53/2	A	12924.567	-0.551	-0.003			
				E	12924.425					
		51/2	51/2	A	12924.629	-0.489	-0.005			
				E	12924.487					
		49/2	49/2	A	12925.667	0.551	0.005			
				E	12925.529					
28 11 17	28 11 18	59/2	59/2	A	8577.888	0.341	0.005	0.105	-0.001	8577.496
				E	8577.785					
		57/2	57/2	A	o	-0.380	-0.003			
				E	8577.063					
		55/2	55/2	A	o	-0.338	-0.007			
				E	8577.105					
		53/2	53/2	A	8577.930	0.381	0.004			
				E	8577.823					

J K- K+	J' K-' K+'	F	F'	Γ	ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	$\delta_{calc-exp}$	$\Delta\nu_{AE}$	$\delta_{calc-exp}$	$\bar{\nu}_0$
29 11 18	29 11 19	61/2	61/2	A	15149.248	0.504	0.005	0.165	-0.001	15148.659
				E	15149.078					
		59/2	59/2	A	15148.179	-0.560	-0.002			
				E	15148.018					
		57/2	57/2	A	15148.240	-0.501	-0.006			
				E	15148.076					
		55/2	55/2	A	15149.302	0.560	0.004			
				E	15149.136					
31 12 19	31 12 20	65/2	65/2	A	10136.349	0.357	0.004	0.122	0.002	10135.931
				E	10136.226					
		63/2	63/2	A	10135.596	-0.394	-0.002			
				E	10135.477					
		61/2	61/2	A	10135.638	-0.355	-0.005			
				E	10135.513					
		59/2	59/2	A	10136.384	0.391	0.003			
				E	10136.265					
32 12 20	32 12 21	67/2	67/2	A	17511.055	0.511	0.010	0.184	0.006	17510.452
				E	17510.870					
		65/2	65/2	A	17509.974	-0.571	0.001			
				E	17509.788					
		63/2	63/2	A	17510.036	-0.508	-0.011			
				E	17509.851					
		61/2	61/2	A	17511.112	0.570	0.001			
				E	17510.931					
34 13 21	34 13 22	71/2	71/2	A	11811.449	0.370	0.005	0.140	0.001	11811.007
				E	11811.305					
		69/2	69/2	A	11810.677	-0.404	-0.004			
				E	11810.533					
		67/2	67/2	A	11810.712	-0.367	-0.007			
				E	11810.568					
		65/2	65/2	A	11811.481	0.402	[illegible]			
				E	11811.338					
37 14 23 *,**	37 14 24	77/2	77/2	A	13603.614	0.380	0.009	0.163	0.001	13603.152
				E	13603.450					
		75/2	75/2	A	13602.820	-0.413	-0.007			
				E	13602.657					
		73/2	73/2	A	13602.856	-0.376	-0.012			
				E	13602.693					
		71/2	71/2	A	13603.645	0.412	0.009			
				E	[illegible]					
39 15 24 *,**	39 15 25	81/2, 75/2	81/2, 75/2	A	8855.820					8855.[illegible]
		81/2, 75/2	81/2, 75/2	E	8855.696					
		79/2, 77/2	79/2, 77/2	A	8855.287					
		79/2, 77/2	79/2, 77/2	E	8855.141					
40 15 25 *	40 15 26	83/2	83/2	A	15513.138	0.396	0.006	0.182	-0.002	15512.652
				E	15512.958					
		81/2	81/2	A	15512.314	-0.428	-0.004			
				E	15512.133					
		79/2	79/2	A	15512.349	-0.395	-0.006			
				E	15512.165					
		77/2	77/2	A	15513.172	0.429	0.004			
				E	15512.989					

Table 3. Measured transitions of $CH_3C^{35}Cl=CH_2$ in the first excited torsional state.

J K- K+	J' K-' K+'	F	F'	Γ	ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	$\delta_{calc-exp}$	$\Delta\nu_{AE}$	$\delta_{calc-exp}$	$\bar{\nu}_0$
1 0 1	0 0 0	5/2	3/2	A	8279.148	3.412	-0.010	-0.218	-0.002	8275.845
				E	8279.365					
		3/2	3/2	A	8262.117	-13.618	0.010			
				E	8262.336					
2 0 2 *,**	1 0 1	7/2	5/2	A	16148.539	1.215	-0.010	-0.329	-0.020	16147.488
				E	16148.866					
		5/2	3/2	A	16149.420	2.093	-0.003			
				E	16149.742					
		1/2	1/2	A	16146.420	-0.899	0.014			
				E	16146.758					
2 1 2	1 1 1	7/2	5/2	A	14882.560	4.053	0.011	-0.221	-0.008	14878.621
				E	14882.787					
		5/2	3/2	A	14865.578	-12.936	-0.009			
				E	14865.792					

J K- K+	J' K-' K+'	F	F'	Γ	ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	$\delta_{calc-exp}$	$\Delta\nu_{AE}$	$\delta_{calc-exp}$	$\bar{\nu}_0$
3 1 2 *,**	3 1 3	9/2	9/2	A	9975.795	0.489	-0.011	-1.253	-0.043	9975.928
				E	9977.039					
		7/2	7/2	A	9974.341	-0.962	0.006			
				E	9975.591					
		5/2	5/2	A	9975.004	-0.303	0.016			
				E	9976.245					
		3/2	3/2	A	9976.449	1.160	-0.013			
				E	9977.727					
4 1 3	4 1 4	11/2	11/2	A	16309.099	0.389	-0.007	-1.996	-0.060	16309.714
				E	16311.107					
		9/2	9/2	A	16308.050	-0.676	0.007			
				E	16310.025					
		7/2	7/2	A	16308.410	-0.302	0.002			
				E	16310.414					
6 2 4	6 2 5	15/2	15/2	A	16324.514	0.967	0.009	-2.670	-0.047	16324.881
				E	16327.181					
		13/2	13/2	A	16322.091	-1.455	-0.009			
				E	16324.760					
		11/2	11/2	A	16322.646	-0.900	0.012			
				E	16325.315					
		9/2	9/2	A	16325.108	1.564	-0.011			
				E	16327.782					
7 3 4	7 3 5	17/2	17/2	A	8555.665	1.028	0.001	-2.141	-0.008	8555.704
				E	8557.799					
		15/2	15/2	A	8553.166	-1.472	0.001			
				E	8555.298					
		13/2	13/2	A	8553.674	-0.956	-0.006			
				E	8555.822					
		11/2	11/2	A	8556.165	1.536	0.002			
				E	8558.314					
8 3 5	8 3 6	19/2	19/2	A	14866.183	1.163	-0.027	-3.248	-0.028	14866.640
				E	14869.423					
		17/2	17/2	A	14863.447	-1.569	0.007			
				E	14866.694					
		15/2	15/2	A	14863.958	-1.058	-0.021			
				E	14867.205					
		13/2	13/2	A	14866.590	1.579	0.040			
				E	14869.848					
10 4 6	10 4 7	23/2	23/2	A	12465.351	1.083	-0.005	-3.597	-0.015	12466.067
				E	12468.949					
		21/2	21/2	A	12462.866	-1.403	0.002			
				E	12466.461					
		19/2	19/2	A	12463.226	-1.043	-0.001			
				E	12466.822					
		17/2	17/2	A	12465.698	1.430	0.005			
				E	12469.295					
12 5 7	12 5 8	27/2	27/2	A	9688.303	0.904	-0.005	-3.618	-0.006	9689.208
				E	o					
		25/2	25/2	A	9686.269	-1.128	0.004			
				E	9689.890					
		23/2	23/2	A	9686.522	-0.879	-0.001			
				E	9690.136					
		21/2	21/2	A	9688.540	1.141	0.003			
				E	o					
13 5 8	13 5 9	29/2	29/2	A	16712.017	1.102	-0.003	-5.342	-0.012	16713.586
				E	16717.358					
		27/2	27/2	A	16709.560	-1.354	0.001			
				E	16714.904					
		25/2	25/2	A	16709.835	-1.079	0.000			
				E	16715.178					
		23/2	23/2	A	16712.287	1.371	0.002			
				E	16717.626					
15 6 9	15 6 10	33/2	33/2	A	12986.350	0.930	0.002	-5.232	-0.005	12988.038
				E	12991.586					
		31/2	31/2	A	12984.299	-1.122	0.003			
				E	12989.532					
		29/2	29/2	A	12984.507	-0.918	-0.001			
				E	12989.732					
		27/2	27/2	A	12986.555	1.135	-0.004			
				E	12991.790					
17 7 10	17 7 11	37/2	37/2	A	9487.779	0.714	0.005	-4.702	-0.005	9489.417
				E	9492.482					
		35/2	35/2	A	9486.216	-0.848	0.002			
				E	9490.921					
		33/2	33/2	A	9486.356	-0.711	-0.001			
				E	9491.055					
		31/2	31/2	A	9487.925	0.859	-0.005			
				E	9492.626					
18 7 11	18 7 12	39/2	39/2	A	16629.532	0.959	-0.002	-7.080	0.006	16632.117
				E	16636.612					
		37/2	37/2	A	16627.453	-1.121	0.004			
				E	16634.531					

J K- K+	J' K-' K+'	F	F'	Γ	ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	$\delta_{calc-exp}$	$\Delta\nu_{AE}$	$\delta_{calc-exp}$	$\bar{\nu}_0$
		35/2	35/2	A	16627.629	-0.945	-0.003			
				E	16634.707					
		33/2	33/2	A	16629.696	1.125	0.001			
				E	16636.779					
20 8 12	20 8 13	43/2	43/2	A	12256.714	0.754	0.004	-6.322	0.011	12259.121
				E	12263.035					
		41/2	41/2	A	12255.087	-0.871	0.000			
				E	12261.412					
		39/2	39/2	A	12255.215	-0.746	-0.006			
				E	12261.535					
		37/2	37/2	A	12256.834	0.875	0.002			
				E	12263.157					
22 9 13	22 9 14	47/2	47/2	A	8573.109	0.552	0.001	-5.205	-0.009	8575.160
				E	8578.314					
		45/2	45/2	A	8571.923	-0.635	0.007			
				E	o					
		43/2	43/2	A	8572.015	-0.543	-0.006			
				E	o					
		41/2	41/2	A	8573.192	0.634	-0.002			
				E	8578.396					
23 9 14	23 9 15	49/2	49/2	A	15349.318	0.787	0.005	-8.097	-0.004	15352.577
				E	15357.409					
		47/2	47/2	A	15347.626	-0.900	0.005			
				E	15355.728					
		45/2	45/2	A	15347.751	-0.778	-0.009			
				E	15355.846					
		43/2	43/2	A	15349.428	0.902	-0.003			
				E	15357.529					
25 10 15	25 10 16	53/2	53/2	A	10857.312	0.590	0.003	-6.689	0.007	10860.066
				E	10864.000					
		51/2	51/2	A	10856.056	-0.666	0.002			
				E	10862.743					
		49/2	49/2	A	10856.135	-0.585	-0.005			
				E	10862.826					
		47/2	47/2	A	10857.389	0.668	-0.001			
				E	10864.078					
28 11 17	28 11 18	59/2	59/2	A	13430.939	0.643	0.020	-8.313	0.020	13434.437
*,**		53/2	53/2	E	13439.220					
		57/2	57/2	A	13429.621	-0.643	-0.019			
		55/2	55/2	E	13437.966					
30 12 18	30 12 19	63/2	63/2	A	9194.310	0.445	0.005	-6.386	-0.005	9197.058
				E	9200.696					
		61/2	61/2	A	9193.370	-0.494	-0.001			
				E	9199.757					
		59/2	59/2	A	9193.420	-0.444	-0.005			
				E	9199.808					
		57/2	57/2	A	9194.363	0.497	0.000			
				E	9200.747					
31 12 19	31 12 20	65/2	65/2	A	16302.988	0.661	0.004	-10.036	0.034	16307.346
				E	16313.025					
		63/2	63/2	A	16301.596	-0.732	0.002			
				E	16311.631					
		61/2	61/2	A	16301.670	-0.659	-0.004			
				E	16311.704					
		59/2	59/2	A	16302.061	0.733	-0.001			
				E	16313.097					
33 13 20	33 13 21	69/2	69/2	A	11287.965	0.479	0.007	-7.751	0.004	11291.362
				E	11295.716					
		67/2	67/2	A	11286.956	-0.530	0.000			
				E	11294.707					
		65/2	65/2	A	11287.009	-0.478	-0.007			
				E	11294.758					
		63/2	63/2	A	11288.016	0.530	0.002			
				E	11295.768					
36 14 22	36 14 23	75/2	75/2	A	13642.231	0.540	0.001	-9.155	-0.014	13646.273
*		69/2	69/2	E	13651.395					
		73/2	73/2	A	13641.160	-0.540	-0.001			
		71/2	71/2	E	13650.309					
38 15 23	38 15 24	79/2	79/2	A	9199.114	0.361	0.004	-6.675	-0.009	9202.002
*				E	9201.702					
		77/2	77/2	A	9194.269	-0.393	0.000			
				E	9200.948					
		75/2	75/2	A	9194.310	-0.357	-0.007			
				E	9200.979					
		73/2	73/2	A	9195.056	0.392	0.002			
				E	9201.731					
39 15 24	39 15 25	81/2	81/2	A	16267.982	0.575	0.000	-10.618	0.018	16272.719
*		75/2	75/2	E	16278.605					
		79/2	79/2	A	16266.837	-0.576	0.001			
		77/2	77/2	E	16277.449					

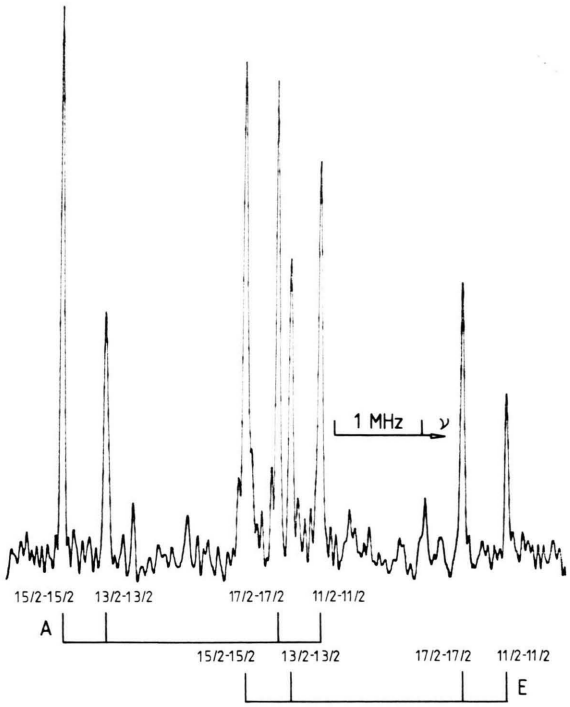

Fig. 2. A range of 6.5 MHz out of a 25 MHz scan of the rotational spectrum of $CH_3C^{35}Cl{=}CH_2$ in natural abundance in the first excited torsional state. $J\,K_-K_+ - J'\,K'_-K'_+ = 7\,3\,4 - 7\,3\,5$; power spectrum, sample interval: 20 ns, 1280 K cycles, 1024 data points supplemented by 3072 zeros, microwave signal frequency: $\nu_{MW} = 8554$ MHz; pressure: $p = 0.3-0.9$ mtorr, temperature: $T = -35\,°C$.

tion, chlorine hfs, and methyl internal rotation, are treated independently. Thus we do not assume any interaction between these three disturbances.

For the quadrupole hfs analysis the mean $\bar{\nu}$ of the A−E torsional doublet was taken for each hfs component. In the case of $CH_3C^{35}Cl{=}CH_2$ in the ground and in the first excited torsional state we proved for lines up to $J = 16$ and $J = 20$ respectively by direct diagonalisation of the hfs Hamiltonian matrix [7] that first order perturbation theory is sufficient. Unfortunately no line in the range of our spectrometer is sensitive to the offdiagonal coupling tensor element χ_{ab}. The difficulties in determining χ_{ab} may also be due to the fact that with an angle $\sphericalangle(\overline{C_2Cl}, a) = 5.5°$ [6] the C−Cl-bond lies close by the main inertial axis a.

For the centrifugal distortion analysis the constants of Table 4 were fitted to the lines of Tables 1 to 3 respectively, which contain our mea-

Table 4. Rotational [MHz], centrifugal distortion [kHz] and chlorine-hfs [MHz] constants of 2-chloropropene. N: number of lines, $|(a, b)|$: highest correlation, σ: standard deviation [kHz], $\overline{\Delta\nu_{exp}}$: mean experimental hfs splitting [MHz]; standard errors in units of the last digit in brackets, results of a direct diagonalisation hfs analysis in square brackets.

	$CH_3C^{35}Cl=CH_2$				$CH_3C^{37}Cl=CH_2$
	$v=0$		$v=1$		$v=0$
A	9271.706 (79)		9270.62 (67)		9270.942 (47)
B	4983.816 (45)		4974.52 (35)		4850.430 (26)
C	3304.414 (45)		3301.59 (35)		3245.114 (26)
D_J'	−0.97 (593)		67 (45)		−5.5 (36)
D_{JK}'	2.2 (18)		−9.7 (157)		2.8 (10)
D_K'	17.7 (70)		63 (60)		16.0 (41)
δ_J'	0.17 (17)		−0.93 (145)		0.238 (88)
R_6'	−0.407 (90)		−0.98 (77)		−0.340 (46)
N	27		25		24
$\lvert(\delta_J', D_K')\rvert$	0.997		0.998		0.998
σ	67		510		39
χ_+	68.072 (51)	[68.081 (64)]	68.036 (38)	[68.069 (23)]	53.763 (41)
χ_-	6.122 (47)	[6.134 (66)]	6.264 (36)	[6.267 (22)]	4.976 (37)
N	25	[13]	18	[12]	21
$\lvert(\chi_+, \chi_-)\rvert$	0.113	[0.093]	0.292	[0.265]	0.193
σ	33	[42]	14	[8]	21
$\overline{\Delta\nu_{exp}}$	3.007	[4.173]	1.855	[2.432]	1.862
χ_{aa}	−68.072	[−68.081]	−68.036	[−68.069]	−53.763
χ_{bb}	37.097	[37.108]	37.150	[37.168]	29.370
χ_{cc}	30.975	[30.974]	30.886	[30.901]	24.394

surements supplemented by lines of [5] Table 3* not measured by us, using the Hamiltonian of Van Eijck and Typke up to fourth order [8, 9]. The unsplit line $\bar{\nu}_0$ was determined as the arithmetic mean of the $\bar{\nu}$ corrected with the hfs-shifts calculated with the quadrupole coupling constants of Table 4. The rotational, centrifugal distortion, and quadrupole coupling constants of Table 4 are the result of some iterative fitting calculations of the quadrupole hfs and the centrifugal distortion. As the errors of the centrifugal constants and their correlation are high, we take the centrifugal distortion analysis as a kind of interpolation only.

Finally we took for the methyl torsion analysis a fictitious A−E doublet $\Delta\nu_{AE}$, calculated by adding the hfs shifts to the hfs components, equivalent to averaging the A−E splittings of the hfs components. As the torsional splitting is nearly independent of the hfs component of one rotational transition, we believe that this procedure is sufficiently accurate. These doublets were analysed by the internal axis method (IAM) with a version** of Wood's program [10−14].

In a first step we tried to fit the Fourier coefficient $w_1(s)$ [14], a function of the reduced barrier s, the moment of inertia of the methyl group I_α and the angle $\sphericalangle(a, i)$ between the internal rotation axis i and the a principal inertia axis to the A−E splittings given in Tables 1 to 3. The rotational constants of Table 4 were used. The fit converged for the isotopic species $CH_3C^{35}Cl=CH_2$ and $CH_3C^{37}Cl=CH_2$ in the ground state to $I_\alpha \geqq 3.36$ amuÅ^2 with $|(w_1(s), \sphericalangle(a, i))| \geqq 0.986$ being the highest correlation. These values of I_α are rather unreasonable in comparison with other cases and values derived from molecular structures [15]. For $CH_3C^{35}Cl=CH_2$ in the first torsionally excited state on the other hand a more reasonable value of I_α was obtained. The results of the corresponding fit are contained in Table 5 (column 3).

In a second internal rotation fitting calculation we therefore used a fixed moment of inertia of the methyl group $I_\alpha = 3.167$ amuÅ^2, determined from a complete r_s-structure of the three H-atoms given in [6] assuming that the internal axis is perpendicular to the plane of the three H-atoms intersecting it in

* The following transitions seem to be assigned in the wrong way by Unland et al.: a) $CH_3C^{35}Cl=CH_2$ $v=0$: 212−111 1/2−3/2 and 3/2−5/2; b) $CH_3C^{35}Cl=CH_2$ $v=1$: 734−735 A: 17/2−17/2, 11/2−11/2 and E: 15/2−15/2, 13/2−13/2.

* Programs DDIRFI, FIDIC, F05MOD.

Table 5. Internal rotation parameters of 2-chloropropene. N: number of lines, $|(a, b)|$: correlation between a and b, σ: standard deviation, $\overline{\Delta\nu_{AE}}$: mean experimental torsional splitting; standard errors in units of the last digit in brackets, fixed values in square brackets, derived parameters below the line.

	$CH_3C^{35}Cl=CH_2$				$CH_3C^{37}Cl=CH_2$
	$v=0$	$v=1$	$v=1$	$v=1$ [5]	$v=0$
$w_1(s)$	$-0.443\,(14)\cdot10^{-5}$	$2.5185\,(98)\cdot10^{-4}$	$2.478\,(11)\cdot10^{-4}$		$-0.421\,(16)\cdot10^{-5}$
$\measuredangle(a, i)$ [°]	59.78 (84)	58.801 (97)	59.36 (14)	[64.67]	61.28 (108)
I_α [amuÅ^2]	[3.167]	[3.167]	3.1286 (80)	[3.110]	[3.167]
N	20	21	21	5	17
$\lvert(w_1(s), \measuredangle(a, i))\rvert$	0.987	0.988	0.987		0.989
σ [kHz]	3	17	12		3
$\overline{\Delta\nu_{AE}}$ [kHz]	110	5476	5476	3128	116
s	72.15 (29)	72.246 (40)	72.410 (45)		72.63 (35)
V_3 [cal/mol]	2568 (10)	2572.3 (14)	2607.9 (16)	2671	2582 (12)
F [GHz]	165.91	165.97	167.89	[168.5]	165.69
$\measuredangle(b, i)$ [°]	30.22 (84)	31.199 (97)	30.64 (14)	[25.33]	28.72 (108)
λ_a	0.5033 (127)	0.5180 (15)	0.5096 (21)	[0.428410]	0.4805 (166)
λ_b	0.8641 (75)	0.85537 (88)	0.8604 (12)	[0.903580]	0.8770 (89)

their centre of mass. We used this value of I_α for both isotopic species and the ground and excited torsional state. The results are given in Table 5 (columns 1, 2 and 5). In investigation [5] $I_\alpha = 3.110$ amuÅ^2 derived from the inertial defect of propylene [16] was taken. One may notice that the values for both isotopic species agree within the error limits. The angle $\measuredangle(a, i) = 59.78°$ for $CH_3C^{35}Cl=CH_2$ in the ground state differs slightly from the angle $\measuredangle(a, i) = 60.69°$ determined from the r_s-structure. The angle $\measuredangle(a, i) = 61.28°$ for $CH_3C^{37}Cl=CH_2$ in the ground state reflects the effect of ^{37}Cl-substitution. By an r_0-calculation we estimated an angle increment of 0.29°.

We think that we have reached a better consistence of all data. A comparison with other molecules is postponed, until the rotational ground state spectra have been analysed or reanalysed.

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