Determination of a High Potential Barrier Hindering Internal Rotation from the Ground State Spectrum. The Methylbarrier of Ethylbromide

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For ethylbromide a determination of the parameters of internal rotation is given derived from the rotational spectrum of the torsional and vibrational ground state. The Br-hyperfine structure is reanalysed with higher precision. As high J transitions were measured a centrifugal distortion analysis was necessary.

This paper presents an investigation of the rotational spectrum of ethylbromide, CH_3CH_2Br, in the torsional and vibrational ground state. The barrier hindering internal rotation was previously determined from the rotational transitions of the first excited torsional state [1], because the barrier is too high that the splittings in the ground state could be resolved. The use of microwave Fourier transform (MWFT) spectroscopy with its higher resolution [2, 3] made it possible to resolve the fine structure like in similar cases [4–7].

The sample was purchased from Fa. Merck with a purity of 98%. The spectra were recorded with MWFT-spectroscopy in the range of 8 to 18 GHz at temperatures between −55° and −70 °C and pressures between 0.1 and 0.5 mTorr. In the range of 26–40 GHz Starkspectroscopy [8, 9] was used for some high J transitions. The temperatures were in the same range. The pressure were between 3 and 10 mTorr.

The measured lines are given in Tables 1 and 2 for the isotopic species ^{79}Br and ^{81}Br. In Fig. 1 we give an example of the measurements. The torsional splittings $\Delta\bar{\nu}_{AE}$ were refined by a line shape analysis [10]. They are given under $\Delta\bar{\nu}_{sim}$. The assignment is based on earlier work [11, 12] in which lines up to $J = 7$ were reported.

We extended the range up to $J = 37$ to get enough resolvable lines, because the splitting is very narrow. The assignment was checked by the consistency of the analysis of centrifugal distortion, Br-hyperfine and torsional fine structure. The Stark-measurements had been useful for the evaluation of the first two effects. The three perturbation effects were calculated separately. The modifications of the spectrum were refined by an iterative procedure.

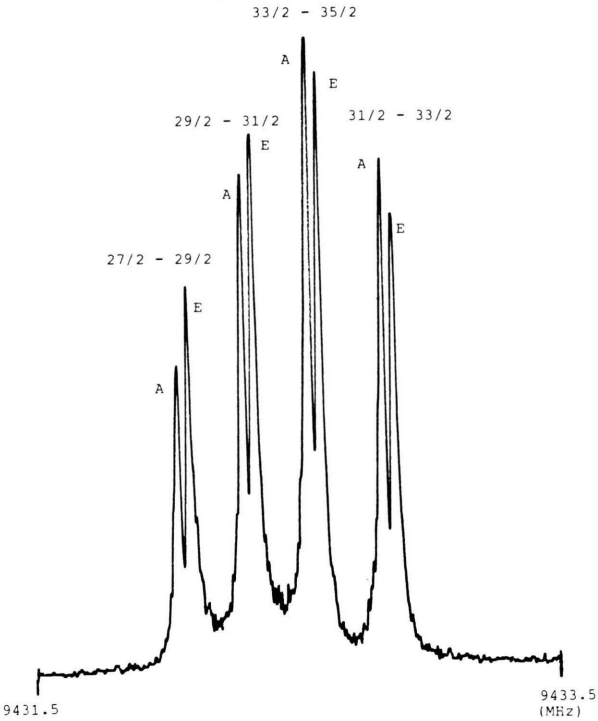

Fig. 1. A rotational transition with Br-hfs and internal rotation splitting of $CH_3CH_2{}^{79}Br$, $J\,K_-\,K_+ - J'\,K'_-\,K'_+ = 15\,3\,13 - 16\,2\,14$, the F quantum numbers and the symmetry species are attached to the components. Power spectrum, sample intervall 100 ns, 128 K averaging cycles in the time domain, 28 averaging cycles in the frequency domain, 1024 data points supplemented by 3072 zeros before Fourier transformation, microwave polarising frequency: $\nu = 9431.5$ MHz, pressure: $p = 0.4$ mTorr, temperature: $T = -70$ °C.

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Table 1. Measured transitions of $CH_3CH_2{}^{79}Br$. Γ: symmetry species, ν_{exp}: experimental frequency, $\bar{\nu}$: arithmetic mean of the frequencies belonging to the same hfs transition and split by internal rotation, $\bar{\nu}_0$: line center (see text), $\bar{\nu}-\bar{\nu}_0$: measured hfs shift, $\Delta\bar{\nu}_{AE}$: experimental torsional splitting (arithmetic mean of all hfs components), $\Delta\bar{\nu}_{sim}$: corrected torsional splitting, nr: not resolved, S: measured by using Stark spectroscopy, *: not used for quadrupole hfs analysis, δ_{c-e} difference between calculated and experimental results; frequencies, splittings and deviations in MHz.

J	K_-	K_+	$2F$	J'	K'_-	K'_+	$2F'$	Γ	ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	δ_{c-e}	$\Delta\bar{\nu}_{AE}$	$\Delta\bar{\nu}_{sim}$	δ_{c-e}	$\bar{\nu}_0$
2	1	1	7	1	1	0	5		14911.463	-23.347	-0.011	nr			14934.810
			5				3		15015.841	81.031	-0.006				
			3				1		14868.034	-66.776	0.014				
2	1	2	7	1	1	1	5		14346.231	-26.437	0.003	nr			14372.668
			5				3		14450.887	78.219	-0.001				
5	0	5	13	4	1	4	11		11671.269	- 2.348	-0.025	nr			11673.617
			11				9		11672.122	- 1.495	-0.023				
8	1	7	19	8	1	8	19		10124.943	13.532	-0.020	nr			10111.411
			17				17		10092.658	-18.753	-0.006				
			15				15		10098.318	-13.093	-0.008				
			13				13		10130.806	19.395	-0.087				
7	2	6		8	1	7		A	15283.814						15281.992
			17				19	E	15283.842	1.836	0.110	-0.028	-0.023	0.000	
								A	15281.547						
			15				17	E	15281.574	- 0.431	0.103				
								A	15279.963						
			13				15	E	15279.988	- 2.016	0.099				
								A	15282.188						
			11				13	E	15282.217	0.211	0.103				
9	1	8	21	9	1	9	21		12648.442	13.782	-0.024	nr			12634.660
			19				19		12616.016	-18.644	-0.003				
			17				17		12621.234	-13.426	-0.020				
			15				15		12653.451	18.791	-0.074				
9	1	8	21	9	0	9	21		33185.268	9.551	-0.044	nr			33175.717
	S		19				19		33162.526	-13.191	-0.033				
			17				17		33166.348	- 9.369	-0.020				
			15				15		33188.478	12.761	-0.074				
10	1	10	23	10	1	9	23		15448.806	13.942	-0.032	nr			15434.864
			21				21		15418.551	-16.313	-0.061				
			19				19		15421.220	-13.644	-0.032				
			17				17		15456.239	21.375	-0.131				
11	1	10		10	2	9		A	10740.542						10738.501
			25				23	E	10740.563	2.051	-0.056	-0.020	-0.018	-0.002	
								A	10734.690						
			23				21	E	10734.709	- 3.802	-0.064				
								A	10735.972						
			21				19	E	10735.991	- 2.517	-0.051				
								A	10743.114						
			19				17	E	10743.136	4.625	-0.067				
15	1	15		14	2	12		A	9594.988						9608.786
			33				31	E	9595.038	-13.776	0.037	-0.044	-0.040	0.004	
								A	9592.820						
			27				25	E	9592.858	-15.947	-0.089				

Table 1 (continued)

J	K_-	K_+	$2F$	J'	K'_-	K'_+	$2F'$	Γ	ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	δ_{c-e}	$\Delta\bar{\nu}_{AE}$	$\Delta\bar{\nu}_{sim}$	δ_{c-e}	$\bar{\nu}_0$
15	3	12		16	2	15		A	16166.477						16161.145
			33				35			5.353	0.105	−0.044	−0.038	0.002	
								E	16166.519						
								A	16155.736						
			31				33			−5.385	0.103				
								E	16155.783						
								A	16156.415						
			29				31			−4.709	0.093				
								E	16156.456						
								A	16166.768						
			27				29			5.646	0.083				
								E	16166.813						
15	3	13		16	2	14		A	9432.539						9432.274
			33				35			0.286	0.081	−0.040	−0.036	0.001	
								E	9432.580						
								A	9432.825						
			31				33			0.570	0.092				
								E	9432.863						
								A	9432.288						
			29				31			0.034	0.084				
								E	9432.329						
								A	9432.041						
			27				29			−0.213	0.072				
								E	9432.080						
17	2	15	37	17	2	16	37		8157.496	5.179	0.026	nr			8152.317
			33				33		8147.192	−5.125	0.007				
			31				31		8156.865	4.548	0.027				
16	3	13		17	2	16		A	9391.652						9384.773
			35				37			6.901	0.121	−0.043	−0.039	−0.001	
								E	9391.693						
								A	9379.741						
			33				35			−5.032	0.063				
								E	9379.779						
								A	9381.842						
			31				33			−2.906	0.094				
								E	9381.889						
								A	9390.339						
			29				31			5.588	0.043				
								E	9390.383						
18	2	16	39	18	2	17	39		10044.137	5.663	0.038	nr			10038.474
			37				37		10033.153	−5.321	0.020				
			35				35		10032.898	−5.576	0.014				
			33				33		10046.488	8.014	0.010				
19	2	17	41	19	2	18	41		12199.278	6.141	0.042	nr			12193.137
			39				39		12185.727	−7.410	0.031				
			37				37		12187.085	−6.052	0.016				
			35				35		12199.908	6.771	0.039				
19	2	17		18	3	16		A	16609.594						16607.320
			41				39			2.292	0.034	−0.035	−0.031	0.001	
								E	16609.630						
								A	16604.919						
			39				37			−2.383	0.024				
								E	16604.954						
								A	16605.976						
			37				35			−1.327	0.013				
								E	16606.009						
								A	16610.083						
			35				33			2.781	0.044				
								E	16610.118						

Table 1 (continued)

J	K_-	K_+	$2F$	J'	K'_-	K'_+	$2F'$	Γ	ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	δ_{c-e}	$\Delta\bar{\nu}_{AE}$	$\Delta\bar{\nu}_{sim}$	δ_{c-e}	$\bar{\nu}_0$
20	2	18	43	20	2	19	43		14633.409	6.575	0.050	nr			14626.834
			41				41		14619.179	− 7.655	0.025				
			39				39		14620.316	− 6.518	0.019				
			37				37		14634.350	7.516	0.028				
20	2	19		19	3	16		A	10198.578						10203.391
			41				39			− 4.792	0.016	−0.041	−0.036	−0.003	
								E	10198.619						
								A	10208.814						
			39				37			5.443	0.025				
								E	10208.853						
								A	10208.241						
			37				35			4.870	0.035				
								E	10208.280						
								A	10198.384						
			33				35			− 4.985	0.036				
								E	10198.427						
21	2	19	45	20	3	18	43		34885.867	2.956	0.012	nr			34882.911
S	*		43				41		34879.449	− 3.462	0.080				
			41				39		34880.198	− 2.713	0.073				
			39				37		34886.687	3.776	0.109				
21	2	20		20	3	17		A	16424.299						16429.220
	*		45				43			− 4.898	0.000	−0.045	−0.040	0.001	
								E	16424.345						
								A	16434.712						
			43				41			5.514	0.046				
								E	16434.755						
								A	16434.165						
			41				39			4.967	0.055				
								E	16434.209						
								A	16424.040						
			39				37			− 5.157	0.055				
								E	16424.087						
22	4	18		23	3	21		A/E							14862.204
	*		47				49		14864.538	2.379	−0.121				
									14864.582						
			41				43		14864.625	2.379	−0.082				
								A	14859.701						
			45				47			− 2.478	−0.029	−0.051	−0.047	0.002	
								E	14859.752						
								A	14859.880						
			43				45			− 2.299	−0.169				
								E	14859.931						
22	4	19		23	3	20		A	12319.438						12318.519
	*		47				49			0.943	−0.130	−0.047	−0.044	0.001	
								E	12319.485						
								A	12317.664						
			45				47			− 0.832	−0.080				
								E	12317.711						
								A	12317.567						
			43				45			− 0.929	−0.137				
								E	12317.613						
								A	12319.278						
			41				43			0.783	−0.125				
								E	12319.325						
24	2	23	51	23	3	20	49		33917.343	− 5.636	0.029	nr			33922.979
S	*		49				47		33929.078	6.099	−0.164				
			47				45		33928.385	5.406	0.070				
			45				43		33917.093	− 5.886	−0.181				

Table 1 (continued)

J	K_-	K_+	$2F$	J'	K'_-	K'_+	$2F'$	Γ	ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	δ_{c-e}	$\Delta\bar{\nu}_{AE}$	$\Delta\bar{\nu}_{sim}$	δ_{c-e}	$\bar{\nu}_0$
26	3	23		25	4	22		A	12119.456						12119.270
	*		55				53			0.209	-0.129	-0.044	-0.040	0.002	
								E	12119.502						
								A	12118.796						
			53				51			- 0.453	-0.110				
								E	12118.839						
								A	12119.116						
			51				49			- 0.132	-0.183				
								E	12119.161						
								A	12119.660						
			47				49			0.410	-0.082				
								E	12119.700						
27	3	25		26	4	22		A	14168.733						14170.720
	*		57				55			- 1.965	-0.031	-0.046	-0.042	0.000	
								E	14168.777						
								A	14172.796						
			55				53			2.100	-0.055				
								E	14172.843						
								A	14172.641						
			53				51			1.946	0.075				
								E	14172.690						
								A	14168.629						
			51				49			- 2.069	0.049				
								E	14168.673						
30	3	27	63	30	3	28	63		10848.773	3.372	0.051	nr			10845.401
	*		61				61		10841.681	- 3.720	0.011				
			59				59		10842.052	- 3.349	-0.009				
			57				57		10849.120	3.719	0.055				
29	5	24		30	4	27		A	14935.436						14933.982
	*		61				63			1.478	-0.141	-0.046	-0.042	-0.002	
								E	14935.483						
								A	14932.570						
			59				61			- 1.390	-0.140				
								E	14932.615						
								A	14932.469						
			57				59			- 1.490	-0.054				
								E	14932.515						
								A	14935.350						
			55				57			1.391	-0.070				
								E	14932.396						
29	5	25		30	4	26		A	14106.708						14105.639
	*		61				63			1.090	-0.111	-0.044	-0.043	-0.002	
								E	14106.750						
								A	14104.581						
			59				61			- 1.037	-0.060				
								E	14104.624						
								A	14104.548						
			57				59			- 1.068	-0.083				
								E	14104.594						
								A	14106.617						
			55				57			1.001	-0.076				
								E	14106.662						
31	3	28	65	31	3	29	65		12915.753	3.715	0.041	nr			12912.038
	*		63				63		12907.954	- 4.084	-0.013				
			61				61		12908.341	- 3.697	-0.025				
			59				59		12916.128	4.090	0.040				

Table 1 (continued)

J	K_-	K_+	$2F$	J'	K'_-	K'_+	$2F'$	Γ	ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	δ_{c-e}	$\Delta\bar{\nu}_{AE}$	$\Delta\bar{\nu}_{sim}$	δ_{c-e}	$\bar{\nu}_0$
32	3	29	67	32	3	30	67		15253.923	4.064	0.023	nr			15249.859
	*		65				65		15245.401	- 4.458	-0.038				
			63				63		15245.815	- 4.044	-0.055				
			61				61		15254.322	4.463	0.021				
32	1	32		31	2	29		A	17091.332						17109.406
	*		67				65	E	17091.431	-18.025	-0.149	-0.103	-0.089	-0.005	
								A	17129.023						
			65				63	E	17129.126	19.669	-0.005				
								A	17127.402						
			63				61	E	17127.512	18.051	-0.004				
								A	17089.570						
			61				59	E	17089.671	-19.786	-0.005				
33	1	33		32	2	30		A	13956.798						13937.171
	*		67				65	E	13956.906	19.681	0.021	-0.109	-0.099	0.000	
								A	13955.228						
			65				63	E	13955.337	18.112	0.018				
33	4	29		32	5	28		A	9357.552						9358.086
	*		69				67	E	9357.597	- 0.512	-0.113	-0.045	-0.042	0.003	
								A	9358.471						
			67				65	E	9358.515	0.407	-0.158				
								A	9358.570						
			65				63	E	9358.613	0.506	-0.164				
								A	9357.670						
			63				61	E	9357.718	- 0.392	-0.140				
34	1	34		33	2	31		A	10421.179						10439.278
	*		71				69	E	10421.298	-18.040	-0.096	-0.111	-0.107	0.004	
								A	10458.818						
			69				67	E	10458.922	19.592	0.066				
								A	10457.304						
			67				65	E	10457.409	18.079	0.051				
								A	10419.499						
			65				63	E	10419.616	-19.721	0.058				
34	4	31		33	5	28		A	15141.516						15142.636
	*		71				69	E	15141.558	- 0.826	0.176	-0.042	-0.038	-0.001	
								A	15143.641						
			69				67	E	15143.682	1.299	0.139				
								A	15143.708						
			67				65	E	15143.749	1.366	0.105				
								A	15141.637						
			65				63	E	15141.682	- 0.704	0.088				

Table 1 (continued)

J	K_-	K_+	$2F$	J'	K'_-	K'_+	$2F'$	Γ	ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	δ_{c-e}	$\Delta\bar{\nu}_{AE}$	$\Delta\bar{\nu}_{sim}$	δ_{c-e}	$\bar{\nu}_0$
36	6	31		37	5	32		A	15364.484						15365.505
	*		75				77			1.002	0.061	-0.043	-0.040	0.001	
								E	15364.529						
								A	15362.558						
			73				75			-0.925	0.093				
								E	15362.602						
								A	15362.493						
			71				73			-0.992	0.132				
								E	15362.534						
								A	15364.401						
			69				71			0.918	0.117				
								E	15364.444						

Table 2. Measured transitions of $CH_3CH_2{}^{81}Br$. Γ: symmetry species, ν_{exp}: experimental frequency, $\bar{\nu}$: arithmetic mean of the frequencies belonging to the same hfs transition and split by internal rotation, $\bar{\nu}_0$: line center (see text), $\bar{\nu}-\bar{\nu}_0$: measured hfs shift, $\Delta\bar{\nu}_{AE}$: experimental torsional splitting (arithmetic mean of all hfs components), $\Delta\bar{\nu}_{sim}$: corrected torsional splitting, nr: not resolved, S: measured by using Stark spectroscopy, *: not used for quadrupole hfs analysis, δ_{c-e}: differences between calculated and experimental results; frequencies, splittings and deviations in MHz.

J	K_-	K_+	$2F$	J'	K'_-	K'_+	$2F'$	Γ	ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	δ_{c-e}	$\Delta\bar{\nu}_{AE}$	$\Delta\bar{\nu}_{sim}$	δ_{c-e}	$\bar{\nu}_0$
2	1	1	7	1	1	0	5		14826.952	-19.621	-0.005	nr			14846.573
			5				3		14914.230	67.657	0.007				
2	1	2	7	1	1	1	5		14268.511	-22.153	0.032	nr			14290.664
			5				3		14356.013	65.349	0.005				
5	0	5	13	4	1	4	11		11431.878	-1.972	-0.028	nr			11433.850
			11				9		11432.568	-1.282	0.001				
			9				7		11438.267	4.417	-0.023				
			7				5		11438.117	4.267	0.006				
8	1	7	19	8	1	8	19		10010.312	11.289	-0.003	nr			9999.023
			17				17		9983.404	-15.619	0.016				
			15				15		9988.143	-10.880	0.001				
			13				13		10015.175	16.152	-0.036				
7	2	6		8	1	7		A	15717.440						15715.925
			17				19			1.527	0.107	-0.026	-0.024	-0.001	15715.925
								E	15717.463						
								A	15715.505						
			15				17			-0.408	0.088				
								E	15715.529						
								A	15714.184						
			13				15			-1.728	0.085				
								E	15714.211						
								A	15716.083						
			11				13			0.173	0.095				
								E	15716.113						
9	1	8	21	9	1	9	21		12505.825	11.487	-0.009	nr			12494.338
			19				19		12478.838	-15.500	0.007				
			17				17		12483.165	-11.173	-0.005				
			15				15		12510.047	15.709	-0.045				
9	1	8	21	9	0	9	21		33113.850	7.959	-0.057	nr			33105.891
S			19				19		33094.971	-10.920	-0.050				
			17				17		33098.131	-7.760	-0.059				
			15				15		33116.580	10.689	-0.076				
10	1	9	23	10	1	10	23		15275.211	11.615	-0.013	nr			15263.596
			21				21		15250.616	-12.980	0.005				
			19				19		15252.258	-11.338	-0.012				
			17				17		15282.511	18.915	-0.061				

Table 2 (continued)

J	K_-	K_+	$2F$	J'	K'_-	K'_+	$2F'$	Γ	ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	δ_{c-e}	$\Delta\bar{\nu}_{AE}$	$\Delta\bar{\nu}_{sim}$	δ_{c-e}	$\bar{\nu}_0$
11	1	10		10	2	9		A	10135.758						10134.021
			25				23			1.748	-0.053	-0.021	-0.018	-0.001	
								E	10135.779						
								A	10130.822						
			23				21			- 3.190	-0.041				
								E	10130.841						
								A	10131.979						
			21				19			- 2.030	-0.045				
								E	10132.003						
								A	10137.824						
			19				17			3.813	-0.049				
								E	10137.844						
15	1	15		14	2	12		A	9206.340						9217.819
			33				31			-11.459	0.001	-0.041	-0.037	0.001	
								E	9206.380						
								A	9231.263						
			31				29			13.465	0.010				
								E	9231.305						
								A	9229.267						
			29				27			11.468	0.027				
								E	9229.307						
								A	9204.507						
			27				25			-13.291	0.058				
								E	9204.549						
15	3	12		16	2	15		A	16866.920						16862.540
			33				35			4.401	0.101	-0.042	-0.038	-0.001	
								E	16866.961						
								A	16858.018						
			31				33			- 4.500	0.097				
								E	16858.061						
								A	16858.541						
			29				31			- 3,978	0.091				
								E	16858.582						
								A	16867.197						
			27				29			4.679	0.073				
								E	16867.241						
15	3	13		16	2	14		A	10280.960						10280.736
			33				35			0.247	0.060	-0.043	-0.039	0.005	
								E	10281.003						
								A	10281.107						
			31				33			0.391	0.073				
								E	10281.150						
								A	10280.676						
			29				31			- 0.042	0.068				
								E	10280.718						
								A	10280.532						
			27				29			- 0.180	0.055				
								E	10280.576						
16	3	13		17	2	16		A	10120.731						10115.889
			35				37			4.863	0.090	-0.042	-0.037	-0.002	
								E	10120.772						
								A	10111.644						
			33				35			- 4.225	0.059				
								E	10111.683						
								A	10112.660						
			31				33			- 3.207	0.076				
								E	10112.702						
								A	10120.456						
			29				31			4.589	0.041				
								E	10120.500						

Table 2 (continued)

J	K_-	K_+	$2F$	J'	K'_-	K'_+	$2F'$	Γ	ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	δ_{c-e}	$\Delta\bar{\nu}_{AE}$	$\delta\bar{\nu}_{sim}$	δ_{c-e}	$\bar{\nu}_0$
18	2	16	39	18	2	17	39		9832.763	4.674	0.050	nr			9828.089
			37				37		9823.377	- 4.712	0.049				
			35				35		9823.482	- 4.607	0.025				
			33				33		9834.405	6.316	0.039				
19	2	17	41	19	2	18	41		11946.242	5.066	0.056	nr			11941.176
			39				39		11935.017	- 6.159	0.042				
			37				37		11936.167	- 5.009	0.031				
			35				35		11946.745	5.569	0.037				
19	2	17		18	3	16		A	15555.090						15553.228
			41				39			1.880	0.054	-0.035	-0.031	0.002	
								E	15555.126						
								A	15551.230						
			39				37			- 1.979	0.044				
								E	15551.268						
								A	15552.147						
			37				35			- 1.064	0.036				
								E	15552.180						
								A	15555.463						
			35				33			2.252	0.057				
								E	15555.496						
20	2	18	43	20	2	19	43		14334.553	5.432	0.066	nr			14329.121
			41				41		14322.794	- 6.327	0.040				
			39				39		14323.735	- 5.386	0.032				
			37				37		14335.344	6.223	0.040				
20	2	19		19	3	16		A	9397.060						9401.056
			43				41			- 3.973	0.004	-0.044	-0.042	0.003	
								E	9397.106						
								A	9405.523						
			41				39			4.489	0.016				
								E	9405.566						
								A	9405.065						
			39				37			4.030	0.025				
								E	9405.107						
								A	9396.876						
			37				35			- 4.157	0.031				
								E	9396.922						
21	2	20		20	3	17		A	15606.423						15610.501
	*		45				43			- 4.056	-0.010	-0.044	-0.039	0.000	
								E	15606.467						
								A	15615.027						
			43				41			4.547	0.029				
								E	15615.069						
								A	15614.591						
			41				39			4.112	0.036				
								E	16614.635						
								A	16606.186						
			39				37			- 4.293	0.045				
								E	16606.231						
22	4	18		23	3	21		A/E	15936.982						15935.027
	*		47				49			1.980	-0.078				
			41				43			1.980	-0.046				
									15937.032						
								A	15932.946						
			45				47			- 2.057	-0.014	-0.049	-0.046	0.001	
								E	15932.995						
								A	15933.080						
			43				45			- 1.923	-0.115				
								E	15933.128						

Table 2 (continued)

J	K_-	K_+	$2F$	J'	K'_-	K'_+	$2F'$	Γ	ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	δ_{c-e}	$\Delta\bar{\nu}_{AE}$	$\Delta\bar{\nu}_{sim}$	δ_{c-e}	$\bar{\nu}_0$
22	4	19		23	3	20		A	13476.692						13475.905
	*		47				49			0.812	-0.094	-0.045	-0.041	-0.001	
								E	13476.741						
								A	13475.166						
			45				47			- 0.718	-0.058				
								E	13475.208						
								A	13475.080						
			43				45			- 0.803	-0.100				
								E	13475.124						
								A	13476.561						
			41				43			0.679	-0.088				
								E	13476.607						
26	3	23		25	4	22		A	10765.681						10765.553
	*		55				53			0.150	-0.083	-0.041	-0.037	0.000	
								E	10765.725						
								A	10765.181						
			53				51			- 0.352	-0.046				
								E	10765.222						
								A	10765.464						
			51				49			- 0.069	-0.126				
								E	10765.504						
								A	10765.830						
			49				47			0.297	-0.026				
								E	10765.870						
27	3	25		26	4	22		A	12949.387						12951.044
	*		57				55			- 1.634	0.010	-0.044	-0.042	0.001	
								E	12949.433						
								A	12952.750						
			55				53			1.728	-0.021				
								E	12952.794						
								A	12952.642						
			53				51			1.621	0.087				
								E	12952.687						
								A	12949.316						
			51				49			- 1.707	0.065				
								E	12949.358						
29	3	26	61	29	3	27	63		8754.246	2.485	0.045	nr			8751.761
	*		59				59		8749.010	- 2.751	0.022				
			57				57		8749.299	- 2.462	0.000				
			55				55		8754.509	2.748	0.050				
30	3	27	63	30	3	28	63		10513.929	2.763	0.036	nr			10511.166
	*		61				61		10508.122	- 3.044	0.004				
			59				59		10508.426	- 2.740	-0.013				
			57				57		10514.215	3.049	0.037				
29	5	24		30	4	27		A/E							16364.570
	*		61				63		16365.699	1.183	-0.078				
									16365.750						
			55				57		16365.809	1.183	-0.091				
								A	16363.361						
			59				63			- 1.187	-0.121	-0.044	-0.042	-0.003	
								E	16363.404						
								A	16363.287						
			57				59			- 1.261	-0.047				
								E	16363.331						

Table 2 (continued)

J	K_-	K_+	$2F$	J'	K'_-	K'_+	$2F'$	Γ	ν_{exp}	$\bar{\nu}-\bar{\nu}_0$	δ_{c-e}	$\Delta\bar{\nu}_{AE}$	$\delta\bar{\nu}_{sim}$	δ_{c-e}	$\bar{\nu}_0$
29	5	25		30	4	26		A/E	15572.131						15573.057
	*		59				61			- 0.893	-0.035				
			57				59			- 0.893	-0.080				
									15572.198						
								A	15573.958						
			61				63			0.925	-0.089	-0.047	-0.044	0.000	
								E	15574.005						
								A	15573.883						
			55				57			0.849	-0.057				
								E	15573.929						
31	3	28	65	31	3	29	65		12522.757	3.042	0.020	nr			12519.715
	*		63				63		12516.368	- 3.347	-0.024				
			61				61		12516.686	- 3.029	-0.036				
			59				59		12523.070	3.355	0.013				
32	3	29	67	32	3	30	67		14797.050	3.471	-0.119	nr			14793.579
	*		65				65		14789.722	- 3.857	0.172				
			63				63		14790.288	- 3.291	-0.069				
			61				61		14797.276	3.697	-0.020				
34	1	34		33	2	31		A	11071.023						11054.726
	*		69				67			16.350	-0.023		-0.106	0.000	
								E	11071.129						
								A	11069.735						
			67				65			15.062	-0.008				
								E	11069.841						
36	6	31		37	5	32		A/E							17152.537
	*		73				75		17151.677	- 0.811	0.117				
									17151.726						
			71				73		17151.772	- 0.811	0.094				
			75				77		17153.294	0.809	0.096				
									17153.350						
			69				71		17153.395	0.809	0.073				

The Br-hyperfine structure was calculated for transitions up to $J = 20$ by diagonalising the Hamiltonian matrix [13]. This procedure was necessary because of the large hfs-splittings induced by the quadrupole coupling of the bromine nucleus. Also the magnitude of the off-diagonal coupling-tensor element $|\chi_{ab}|$ could be determined by using this procedure. Above $J = 20$ first order perturbation theory was applied [14], because the computation time would have been very large. The deviations from the rigid rotor lines were added to the experimental frequencies ν_{exp} of the hfs-components. The hypothetical unsplit line $\bar{\nu}_0$ was then calculated as a mean value. As consequence of the different calculation methods the accuracy is higher for $\bar{\nu}_0$ up to $J = 20$. In cases were the torsional splitting was resolved, the mean value of the A- and E-species components was considered as frequency of the hfs-component. It was assumed, that nuclear quadrupole coupling and internal rotation do not interact. The fourth order Hamiltonian of van Eijck [15, 16] was used for the centrifugal distortion. The results are given in Table 3.

The torsional fine structure $\Delta\bar{\nu}_{sim}$ was analysed by the internal axis method (IAM) by a program written by Woods [17, 18] and modified by others [19]. For the ^{79}Br-species the Fourier coefficient $w_1(s)$, s the reduced barrier, the angle $\measuredangle(a, i)$ between the a intertia and internal rotation axis i and the moment of intertia of the methyl group I_α could be fitted. For the ^{81}Br-species I_α had to be assumed. The results are given in Table 4. The rotational constants of Table 3 were taken for this calculations.

The angles $\measuredangle(a, i)$ of the ^{79}Br- and ^{81}Br-species disagree slightly out off the error limits. From structure calculations we derived a variation of $\measuredangle(a, i)$ from ^{79}Br to ^{81}Br of $+0.05°$ (Program DHS1C.FOR).

Table 3. Rotational [MHz], centrifugal distortion [kHz] and bromine-hfs [MHz] constants of ethylbromide. N: number of lines, N_{spl}: number of splittings, σ: standard deviation of the fit [kHz], $\overline{\Delta\nu_{exp}}$: mean experimental hfs-splittings [MHz]; standard errors in units of the last digit in brackets.

	$CH_3CH_2{}^{79}Br$	Correlation matrix							
A	29 955.614(50)	1.000							
B	3 803.974 (6)	0.988	1.000						
C	3 522.896 (6)	0.989	0.997	1.000					
D_J	1.833(19)	0.572	0.638	0.613	1.000				
D_{JK}	− 14.08(44)	0.518	0.585	0.557	0.996	1.000			
D_K	247.6 (26)	− 0.355	− 0.426	− 0.395	− 0.950	− 0.974	1.000		
d_1	− 0.213 (1)	− 0.524	− 0.596	− 0.558	− 0.987	− 0.987	0.950	1.000	
d_2	− 0.0073(1)	0.027	0.010	0.048	− 0.211	− 0.284	0.323	0.171	1.000
N	37								
σ	79								
χ_+	− 417.634(77)	1.000							
χ_-	129.492(41)	0.097	1.000						
$\lvert\chi_{ab}\rvert$	291.76 (88)	0.097	0.118	1.000					
N	19								
N_{spl}	66								
$\overline{\Delta\nu_{exp}}$	13.877								
σ	30								
χ_{aa}	417.634(77)								
χ_{bb}	− 144.071(59)								
χ_{cc}	− 273.563(59)								
	$CH_3CH_2{}^{81}Br$	Correlation matrix							
A	29 947.338(44)	1.000							
B	3 781.132 (7)	0.985	1.000						
C	3 503.182 (6)	0.991	0.994	1.000					
D_J	1.816(34)	0.565	0.665	0.595	1.000				
D_{JK}	− 13.95 (77)	0.529	0.629	0.557	0.998	1.000			
D_K	247.4 (45)	− 0.429	− 0.533	− 0.455	− 0.976	− 0.988	1.000		
d_1	− 0.210 (1)	− 0.541	− 0.644	− 0.568	− 0.997	− 0.996	0.979	1.000	
d_2	− 0.0071(1)	0.113	0.083	0.144	− 0.235	− 0.280	0.373	0.261	1.000
N	31								
σ	60								
χ_+	− 349.225(67)	1.000							
χ_-	107.878(34)	0.115	1.000						
$\lvert\chi_{ab}\rvert$	246.61 (73)	0.077	0.121	1.000					
N	18								
N_{spl}	66								
$\overline{\Delta\nu_{exp}}$	11.605								
σ	22								
χ_{aa}	349.225(67)								
χ_{bb}	− 120.674(51)								
χ_{cc}	− 228.552(51)								

The values derived from splittings of the first exicted state for both isotopes is $V_3 = 3684$ cal/mol with an $I_\alpha = 3.1819$ amu Å^2 derived from a r_s-structure [12]. This and our value is less than that measured by Raman spectroscopy: $V_3 = 3.72$ kcal/mol and $F = 5.883\ cm^{-1} = 176.5$ GHz [20].

In Table 5 we compare the internal rotation parameters of ethylhalogenids CH_3CH_2X, X = F, Cl, Br. The parameters were determined from the ground state, which is the least vibrationally perturbed state.

It should be noted, that the assumption of $I_\alpha = 3.155$ amu Å^2 for CH_3CH_2Cl is verified by the results for $CH_3CH_2{}^{79}Br$, for which $I_\alpha = 3.151(93)$ amu Å^2 was determined. The barrier V_3 shows a rise by 10% from CH_3CH_2X, X = F to Cl. To CH_3CH_2Br the change is much less.

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Table 4. Internal rotation parameters of ethylbromide. $w_1(s)$: Fourier coefficient, $\measuredangle(a,i)$, $\measuredangle(b,i)$: angle between the inertia axis a resp. b and the internal rotation axis i, I_α: moment of inertia of the methyl group, N: number of lines (torsional splittings), σ: standard deviation of the fit, $\overline{\Delta\nu_{AE}}$: mean experimental torsional splitting, s: reduced barrier height, V_3: barrier to internal rotation, F: reduced rotational constant of the internal rotation, λ_a, λ_b: direction cosines of $\measuredangle(a,i)$ and $\measuredangle(b,i)$; standard errors in units of the last digit in brackets, assumed values in square brackets, derived parameters below the line.

	$CH_3CH_2{}^{79}Br$	Correlation	$CH_3CH_2{}^{81}Br$	Correlation
$w_1(s)$	$-0.4256(96)\cdot10^{-6}$	1.00	$-0.4347(61)\cdot10^{-6}$	1.00
$\measuredangle(a,i)$ [°]	45.71 (38)	−0.70 1.00	46.50 (37)	−0.61 1.00
I_α [amu Å^2]	3.151 (93)	0.88 −0.64 1.00	[3.151 (93)]	– –
N	21		16	
σ [kHz]	2		2	
$\overline{\Delta\nu_{AE}}$ [kHz]	46		41	
s	95.54 (24)		95.32 (15)	
V_3 [cal/mol]	3665. (117)		3647. (114)	
$\measuredangle(b,i)$ [°]	44.29 (38)		43.50 (36)	
λ_a	0.6982(47)		0.6884(46)	
λ_b	0.7158(46)		0.7254(44)	
F [GHz]	178.8 (53)		178.4 (53)	

Table 5. Comparison of internal rotation parameters of ethylhalogenides CH_3CH_2X determined from splittings of rotational lines in the torsional ground state. Assumptions in square brackets, standard errors in brackets. * Errors corrected, ** error reflects only uncertainty of s.

	X: F [4]	^{35}Cl [5]	^{79}Br	^{81}Br
s	80.47 (9)	92.16(24)	95.54 (24)	95.32(15)
$\measuredangle(a,i)$ [°]	33.85 (42)	[42.97]	45.71(38)	46.50(36)
I_α [amu Å^2]	3.155(14)	[3.155]	3.151(93)	[3.151]
V_3 [cal/mol]	3349 (19)*	3602 (10)**	3665 (117)	3647 (114)
F [GHz]	193.98 (90)	182.17	178.8 (53)	178.4 (53)

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