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

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The internal rotation barrier V_3, the moment of inertia I_α of the methyl tops and the angle between the two internal rotation axes were determined from the torsional fine structure of the rotational spectrum in the torsional ground state. A tilt angle of 1.4° of the methyl groups toward each other results.

Propane, $(CH_3)_2CH_2$, one of the fundamental organic molecules, was first investigated with the help of microwave spectroscopy by Lide [1]. He determined the dipole moment and the r_s-structure by measuring a sufficient number of isotopic species. The barrier to internal rotation was determined in a single top approximation by Scharpen and Laurie [2] from the torsional fine structure of the rotational spectra of the first excited states. With a two top approximation it was evaluated by Hirota et al. [3] and Trinkaus et al. [4, 5].

The high resolution and sensitivity of microwave Fourier transform (MWFT) spectroscopy [6–9] made it feasible to investigate the fine structure of the rotational spectrum in the torsional ground state. A more reliable barrier V_3 should result as the influence of the torsion-vibration interactions is at its minimum. A further motivation for our work was the fact, that a CCC-angle of 112.4(2)° results from the r_s-structure given in Table 4 of [1], whereas the internal rotation axes assumed to be perpendicular to the plane defined by the three methyl hydrogens enclose an angle of 110.8°. This means, that the methyl groups are tilted toward each other. It is a second point of this study to determine the position of the internal rotation axes with respect to the inertia axes. As the dipole moment μ is 0.083 D [1] it is difficult to modulate high J transitions by Stark spectroscopy. So only low J transitions were observed hitherto.

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Table 1. Measured transitions of propane, $CH_3–CH_2–CH_3$. Γ: symmetry species, ν_m: measured frequency, $\Delta\nu_m$: measured internal rotation splitting $\nu_{AA}-\nu_\Gamma$, $\Delta\nu_c$: calculated internal rotation splitting, EE* and EA* are forbidden transitions, all frequencies in [MHz].

J	K_-	K_+	J'	K'_-	K'_+	Γ	ν_m	$\Delta\nu_m$	$\Delta\nu_c$
1	1	0	1	0	1	AA	21748.432		
						EE		0.069	0.059
						AE		0.144	0.118
						EA		0.144	0.118
2	0	2	1	1	1	AA	11013.883		
						EE		−0.054	−0.052
						AE		−0.112	−0.103
						EA		−0.122	−0.103
2	1	1	2	0	2	AA	22769.813		
						EE		0.076	0.061
						AE		0.151	0.122
						EA		0.151	0.122
3	1	2	3	0	3	AA	24365.531		
						EE		0.080	0.065
						AE		0.161	0.129
						EA		0.161	0.129
5	1	4	4	2	3	AA	22933.680		
						EE		−0.150	−0.135
						AE		−0.305	−0.271
						EA		−0.305	−0.271
5	3	2	6	2	5	AA	11320.299		
						EE		0.256	0.230
						AE		0.560	0.488
						EA		0.475	0.432
5	3	3	6	2	4	AA	8954.680		
						EE		0.266	0.253
						AE		0.485	0.478
						EA		0.559	0.535
7	2	5	6	3	4	AA	8308.032		
						EE		−0.247	−0.236
						AE		−0.502	−0.462
						EA		−0.502	−0.480
7	4	4	8	3	5	AA	20659.021		
						EE		0.448	0.466
						AE		0.607	0.604
						EA		1.145	1.165
7	4	3	8	3	6	AA	21001.786		
						EE		0.171	0.139
						AE		0.612	0.605
8	2	6	7	3	5	AA	26132.816		
						EE		−0.219	−0.221
						AE		−0.429	−0.442
						EA		−0.429	−0.449

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Table 1 (continued)

J	K_-	K_+	J'	K'_-	K'_+	Γ	ν_m	$\Delta\nu_m$	$\Delta\nu_c$
8	2	7	7	3	4	AA	19250.538		
						EE		-0.228	-0.235
						AE		-0.454	-0.470
10	3	7	9	4	6	AA	12381.595		
						EE		-0.306	-0.306
						AE		-0.570	-0.570
						EA		-0.669	-0.653
10	3	8	9	4	5	AA	11124.522		
						EE		-0.262	-0.266
						EA		-0.485	-0.490
10	5	5	11	4	8	AA	15332.930		
						EE		-0.068	-0.052
						AE		0.618	0.646
						EA		-0.356	-0.327
						EE*		85.278	85.276
						EA*		85.042	85.031
10	5	6	11	4	7	AA	15246.963		
						EE		0.690	0.698
						EA		1.583	1.619
						EE*		-84.636	-84.630
						EA*		-83.743	-83.738
12	6	7	13	5	8	AA	25916.931		
						EE		0.897	0.889
						AE		0.673	0.640
						EE*		-8.641	-8.652
12	6	6	13	5	9	AA	25926.452		
						EE		-0.253	-0.249
						AE		0.648	0.640
						EE*		9.298	9.292
13	4	10	12	5	7	AA	17119.125		
						EE		-0.216	-0.222
						AE		-0.611	-0.604
						EA		-0.311	-0.300
13	4	9	12	5	8	AA	17440.628		
						EE		-0.382	-0.382
						AE		-0.625	-0.603
						EA		-0.893	-0.910
13	6	7	14	5	10	AA	9745.720		
						EE		-0.190	-0.176
						AE		0.575	0.618
						EA		-0.483	-0.456
						EE*		19.738	19.742
13	6	8	14	5	9	AA	9725.680		
						EE		0.796	0.794
						AE		0.595	0.618
						EA		1.717	1.692
						EE*		-19.130	-19.124
15	7	8	16	6	11	AA	20374.951		
						EE		-0.251	-0.255
						AE		0.547	0.555
						EE*		2.087	2.084
15	7	9	16	6	10	AA	20372.790		
						EE		0.800	0.810
						AE		0.528	0.555
						EE*		-1.540	-1.529
16	5	11	15	6	10	AA	22861.950		
						EE		-0.494	-0.500
						AE		-0.578	-0.569
16	5	12	15	6	9	AA	22786.123		
						EE		-0.076	-0.069
						AE		-0.572	-0.569
18	6	13	17	7	10	AA	12061.542		
						EE		0.134	0.120
						AE		-0.461	-0.507
						EA		0.383	0.326
						EE*		-8.704	-8.719
18	6	12	17	7	11	AA	12070.427		
						EE		-0.618	-0.627
						AE		-0.485	-0.507
						EA		-1.315	-1.340
						EE*		8.223	8.212

Table 1 (continued)

J	K_-	K_+	J'	K'_-	K'_+	Γ	ν_m	$\Delta\nu_m$	$\Delta\nu_c$
18	8	10	19	7	13	AA	14825.331		
						AE		0.421	0.429
						EE*		0.589	0.595
18	8	11	19	7	12	AA	14824.870		
						AE		0.419	0.429
						EE*		-0.179	-0.166
21	7	14	20	8	13	AA	17613.194		
						EE		-0.504	-0.469
						EE*		1.518	1.521
21	7	15	20	8	12	AA	17611.284		
						EE		0.103	0.084
21	9	13	22	8	14	AA	9282.238		
						AE		0.298	0.288
21	9	12	22	8	15	AA	9282.328		
						EE*		0.295	0.293

Table 2. Internal rotation parameters of propane $CH_3-CH_2-CH_3$. $w_1(s)$: Fourier coefficient, $\measuredangle(g,i)$: angle between the inertia axis $g=a, b$ and the internal rotation axis i, I_α: moment of inertia of the methyl group, $(\cdots)$: correlation coefficient, σ: standard deviation of the fit, $\overline{\Delta\nu}$: mean experimental splitting, s: reduced barrier height, F: reduced rotational constant of the internal rotation, V_3: barrier to internal rotation. A, B, C rotational constants fitted to the AA-species transitions of Table 1 by a centrifugal distortion analysis, given in square brackets as assumption for this analysis, $\measuredangle(i,i)$: angle between the internal rotation axes. (Standard errors in units of the last digit.)

$w_1(s)$	$-0.1909(29)\ 10^{-5}$
$\measuredangle(a,i)$ [°]	35.17(64)
$\measuredangle(b,i)$ [°]	54.83(64)
I_α [amuÅ^2]	3.198(21)
$(w_1(s), \measuredangle(a,i))$	−0.957
$(w_1(s), I_\alpha)$	−0.931
$(\measuredangle(a,i), I_\alpha)$	0.891
σ [MHz]	0.021
$\overline{\Delta\nu}$ [MHz]	4.797
s	80.22(15)
F [GHz]	183.99(121)
V_3 [kcal/mol]	3.166(27)
A [MHz]	[29207.526]
B [MHz]	[8445.962]
C [MHz]	[7459.001]
$\measuredangle(i,i)$ [°]	109.7(12)

The sample was purchased from Fa. Messer Griesheim, Düsseldorf, with a purity of 99.5% and used without further purification.

The measured transitions in the region from 8 to 26.5 GHz are given in Table 1. The pressure was between 1 and 2 mTorr and the temperature between −30° and −40 °C. The measurements of narrow split multiplets were refined by line shape analysis [10] if necessary.

The assignment of the high J transitions was verified by a centrifugal distortion analysis of the AA-species components. The centrifugal distortion analysis will be published separately with the inclusion of transitions in the millimeter wave region measured in Lille [11]. The consistency of the torsional analysis provides a further check.

The torsional fine structure including "forbidden" transitions was analysed by the internal axis method (IAM) with a program written by Woods [12, 13] and modified by others [14, 15]. The forbidden transitions EE* and EA* connected with the regular μ_b-type transitions AA, EE, EA, and AE belong to selection rules, which are equal to those of μ_c-type transitions (ee-oe, oo-eo). Therefore the forbidden and regular transitions show a different centrifugal distortion effect. Consequently the splittings AA-EE* and AA-EA* were corrected for this difference prior to the torsional analysis. For example for the forbidden transitions EE* and EA* of $10_{55}-11_{48}$ the correction due to centrifugal distortion is 0.279 MHz. So the AA-EE* and AA-EA* splittings of $10_{55}-11_{48}$ were changed from 85.278 and 85.042 MHz to 85.557 and 85.321 MHz. For $10_{56}-11_{47}$ the negative correction has to be applied.

The results are given in Table 2. The reduced barrier s is within the error limits to that from [5] ($s = 80.1(25)$). The value of V_3 is higher than that of [5] as a lower value of $I_\alpha = 3.13$ amuÅ^2 was assumed there. It should further be pointed out that the angle between the internal axes $\sphericalangle(i, i)$ is 109.7(12)°, which is in agreement with the tilt angle resulting from structure considerations.

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