Methyl Internal Rotation Fine Structure in the Ground State Rotational Spectrum of Gauche Butane

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The methyl torsional fine structure in the rotational spectrum of gauche butane in the vibrational ground state was investigated in the frequency range between 10 and 141 GHz. Using the internal axis method (IAM) in the formulation of Woods, all internal rotation parameters were determined with high accuracy. The barrier height of the methyl internal rotation was determined to 11.34 (29) kJ/mol (2.710 (69) kcal/mol).

Key words: gauche-butane, hindered rotation, methyl group, barrier height, rotational spectrum.

Introduction

n-Butane exists in two stable rotational conformers, the non-polar low energetic trans and the high energetic gauche form. The energy difference ΔH, determined with different methods by several authors [1–6], seems to decrease by at least $0.6\ \mathrm{kJ \cdot mol^{-1}}$ when the gas passes through the phase transition into the liquid state. Using the most recent gas-phase result, $\Delta H = 2.94\ \mathrm{kJ \cdot mol^{-1}}$ [6], one calculates relative gauche-butane concentrations of 32% at -30° C and of 24% at -80 °C in a sample cell under microwave spectroscopical low-density conditions. A detailed consideration shows that rovibrational cooling overcomes concentration losses into the trans state down to temperatures as low as -170 °C [7].

The gauche-butane molecule belongs to the point group C_2 where its twofold symmetry axis coincides with the principal inertia *b*-axis. Hence it shows only *b*-type rotational transitions, and the methyl groups are equivalent by symmetry. The rotational spectrum of gauche-butane was first observed in the mm-wave range and assigned by Hüttner, Majer, and Kästle [8]. They determined the electric dipole moment, the rotational constants, all quartic centrifugal distortion constants in Watson *A* reduction [9] and some of the sextic constants. The electric dipole moment of the molecule, μ_b, is 0.0900(15) D.

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Some mm-wave K-doublets were found to be split in three or more components [8]. Though hindered internal rotation of the methyl gropus must be considered as the most important origin of these fine structures, there is also a slight probability that gauche-gauche dihedral tunnelling of the C_2H_5 groups might have some influence. Several experimental [10] and computational [11, 12] attempts have been made to determine the dihedral potential function of the n-butane system which partly resulted in considerable disagreement of the barrier heights. The present contribution aims at the experimental determination of the methyl barrier, but is also thought to ensure whether or not dihedral effects add to the splittings of the ground-state transitions of the molecule.

Experimental

The sample of butane was obtained commercially from Merck, Darmstadt, chemical purity >99.5%.

The fine structure splittings of 45 rotational transitions, listed in Table 1, were investigated, 20 of them are in the frequency region between 10 and 38 GHz, 10 in the range between 57 and 63 GHz and the remaining 15 in the mm region between 113 and 141 GHz.

The spectra of the first group were recorded with the microwave Fourier transform (MWFT) spectrometers at Kiel [13–15]. These transitions were measured at temperatures between -30 and -50 °C and pres-

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Table 1. Transitions of gauche-butane showing internal rotation fine structure. Γ: symmetry species, ν: experimental frequency, $\Delta\nu$: experimental internal rotation splitting, δ: difference between experimental and calculated splitting, ν_0: hypothetical center frequency, u: estimated uncertainty (in kHz) of $\Delta\nu$ used for calculating the weighting factor W_i [1]). $J\ K_-\ K_+$ designates the lower, $J'\ K'_-\ K'_+$ the upper rotational level.

J'	K'_-	K'_+	$-J$	K_-	K_+	Γ	ν [MHz]	$\Delta\nu$ [MHz]	δ [kHz]	ν_0 [MHz]	u [kHz]
7	5	2	6	4	3	AA	140 971.500			140 971.418	(20)
						EE	140 971.920	−0.420	−34		
9	1	8	9	0	9	AA	31 531.308			31 531.225	(5)
						EE	31 531.246	0.062	−2		
						AE	31 531.184	0.124	−3		
						EA	31 531.184	0.124	−3		
10	1	9	10	0	10	AA	37 037.210			37 037.108	(5)
						EE	37 037.133	0.077	2		
						AE	37 037.057	0.153	4		
						EA	37 037.057	0.153	4		
11	2	9	11	1	10	AA	28 059.960			28 059.896	(5)
						EE	28 059.911	0.049	1		
						AE	28 059.865	0.095	−1		
						EA	28 059.865	0.095	−1		
12	5	8	11	6	5	AA	10 074.004			10 074.063	(5)
						AE	10 074.101	−0.097	−9		
						EE	10 073.639	0.365	0		
						EA	10 073.161	0.843	8		
12	2	10	12	1	11	AA	31 614.460			31 614.381	(5)
						EE	31 614.401	0.059	−2		
						AE	31 614.341	0.119	−2		
						EA	31 614.341	0.119	−2		
13	7	6	13	6	7	AA	113 873.979			113 873.903	(20)
						EE	113 874.332	−0.353	−14		
						EE*	113 873.272	0.707	−67		
13	2	11	13	1	12	AA	35 996.343			35 996.244	(5)
						EE	35 996.269	0.074	−1		
						AE	35 996.195	0.148	−2		
						EA	35 996.195	0.148	−2		
13	2	12	13	1	13	AA	59 064.963			59 064.838	(8)
						EE	59 064.867	0.096	5		
						AE	59 064.777	0.186	4		
						EA	59 064.777	0.186	4		
13	7	7	13	6	8	AA	113 875.773			113 875.651	(20)
						EE	113 875.242	0.531	38		
14	6	8	13	7	7	AA	10 244.184			10 244.267	(5)
						AE	10 244.302	−0.118	−16		
						EE	10 244.845	−0.661	−20		
						EE*	10 240.409	3.775	−24		
14	6	9	13	7	6	AA	10 239.814			10 239.881	(5)
						AE	10 239.917	−0.103	−1		
						EE	10 239.271	0.543	4		
						EE*	10 243.716	−3.902	0		
17	8	9	17	7	10	AA	131 105.461			131 105.365	(20)
						EE	131 105.783	−0.322	9		
						EE*	131 104.673	0.788	−26		
						EA	131 105.943	−0.482	6		
						AE	131 105.337	0.124	−34		
17	2	15	17	1	16	AA	59 220.275			59 220.109	(8)
						EE	59 220.146	0.129	4		
						AE	59 220.029	0.246	−4		
						EA	59 220.029	0.246	−4		
17	8	10	17	7	11	AA	131 107.129			131 107.014	(20)
						EE	131 106.621	0.508	19		
18	7	12	17	8	9	AA	28 582.481			28 582.540	(5)
						EE	28 581.904	0.577	11		
18	8	10	18	7	11	AA	130 908.851			130 908.748	(20)
						EE	130 909.211	−0.360	5		
						EE*	130 908.101	0.750	−3		
						AE	130 908.693	0.158	6		
18	8	11	18	7	12	AA	130 912.505			130 912.411	(20)
						EE	130 912.004	0.501	−15		
						EE*	130 913.095	−0.590	11		
						EA	130 911.541	0.964	−5		
						AE	130 912.379	0.126	−26		
19	7	12	18	8	11	AA	37 746.816			37 746.878	(5)
						EE	37 747.399	−0.583	−8		
19	7	13	18	8	10	AA	37 739.212			37 739.268	(5)
						EE	37 738.721	0.491	2		
19	8	11	19	7	12	AA	130 674.034			130 673.957	(20)
						EE	130 674.394	−0.360	−39		
19	8	12	19	7	13	AA	130 681.842			130 681.753	(20)
						EA	130 680.888	0.954	−33		
						EE*	130 682.484	−0.642	4		
						EE	130 681.402	0.440	−26		
						EA*	130 682.984	−1.142	46		
						AE	130 681.736	0.106	−39		
20	9	11	19	10	10	AA	10 735.425			10 735.522	(5)
						EE*	10 735.570	−0.145	−13		
						AE	10 735.570	−0.145	−10		
20	9	12	19	10	9	AA	10 735.425			10 735.519	(5)
						AE	10 735.570	−0.145	−10		
20	8	12	20	7	13	AA	130 395.358			130 395.269	(20)
						EE*	130 394.378	0.980	−19		
						EE	130 395.529	−0.171	45		
						EA*	130 393.798	1.560	−29		
						AE	130 395.233	0.125	−13		

14	7	7–14	6	8	AA	113 729.257			113 729.177	(20)
					EE	113 729.650	−0.393	−22		
					EA	113 729.988	−0.731	−37		
14	1	13–14	0	14	AA	60 378.910			60 378.763	(8)
					EE	60 378.800	0.110	1		
					AE	60 378.690	0.220	2		
					EA	60 378.690	0.220	2		
14	7	8–14	6	9	AA	113 733.557			113 733.441	(20)
					EE*	113 734.077	−0.520	54		
					EE	113 733.030	0.527	6		
					EA	113 732.559	0.998	4		
14	3	12–14	2	13	AA	58 223.965			58 223.864	(8)
					EE	58 223.890	0.075	0		
					AE	58 223.813	0.152	2		
					EA	58 223.813	0.152	2		
14	9	6–15	8	7	AA	16 413.523			16 413.418	(5)
					EE*	16 413.365	0.158	6		
					AE	16 413.365	0.158	6		
14	9	5–15	8	8	AA	16 413.523			16 413.419	(5)
					AE	16 413.365	0.158	6		
15	3	13–15	2	14	AA	61 518.313			61 518.200	(8)
					EE	61 518.230	0.083	0		
					AE	61 518.142	0.171	4		
					EA	61 518.142	0.171	4		
16	3	13–16	2	14	AA	37 226.626			37 226.552	(5)
					EE	37 226.571	0.055	−2		
					AE	37 226.515	0.111	−3		
					EA	37 226.515	0.111	−3		
16	10	7–17	9	8	AA	16 227.722			16 227.608	(5)
					EE*	16 227.554	0.168	12		
					AE	16 227.554	0.168	5		
16	10	6–17	9	9	AA	16 227.722			16 227.611	(5)
					AE	16 227.554	0.168	5		
20	8	13–20	7	14	AA	130 411.130			130 411.037	(20)
					EA	130 410.282	0.848	−19		
					EE	130 410.789	0.341	−13		
					AE	130 410.979	0.151	13		
					EE*	130 411.968	−0.838	23		
21	3	18–21	2	19	AA	61 609.996			61 609.826	(8)
					EE	61 609.874	0.122	−19		
					AE	61 609.741	0.255	−27		
					EA	61 609.741	0.255	−27		
22	10	12–21	11	11	AA	10 904.073			10 904.168	(5)
					EE*	10 904.214	−0.141	−2		
					AE	10 904.214	−0.141	1		
22	10	13–21	11	10	AA	10 904.073			10 904.168	(5)
					AE	10 904.214	−0.141	1		
24	4	20–24	3	21	AA	57 229.944			57 229.784	(8)
					EE	57 229.828	0.116	−6		
					AE	57 229.704	0.240	−4		
					EA	57 229.704	0.240	−4		
25	4	21–25	3	22	AA	62 868.034			62 867.848	(8)
					EE	62 867.894	0.140	−3		
					AE	62 867.756	0.278	−8		
					EA	62 867.756	0.278	−8		
27	5	22–27	4	23	AA	57 098.956			57 098.864	(8)
					EE	57 098.887	0.069	−2		
					AE	57 098.818	0.138	−3		
					EA	57 098.818	0.138	−3		
28	5	23–28	4	24	AA	60 197.082			60 196.947	(8)
					EE	60 196.979	0.103	6		
					AE	60 196.879	0.203	9		
					EA	60 196.879	0.203	9		
36	11	25–35	12	24	AA	121 108.717			121 108.743	(20)
					EE	121 109.077	−0.360	−55		
36	11	26–35	12	23	AA	121 105.624			121 105.611	(20)
					EE	121 105.283	0.341	33		
					EE*	121 108.402	−2.778	1		

[1]) $W_i=(N/\Sigma_i(u_i^{-2}))\ u_i^{-2}$ is the weight of $\Delta\nu_i$, $i=1, 2, \ldots, N(=110)$.

sures between 0.26 and 0.65 Pa (2 and 5 mTorr). All frequencies resulting from these measurements were determined by a least squares fit of the multiplet signals in the time domain to minimize overlapping effects [16, 17]. The remaining transitions were recorded in Ulm with source modulation and time averaging techniques described previously [8]. The cell temperatures were chosen close to $-80\,^{\circ}C$, the gas pressures below 3 mTorr resulting in Doppler-limited line widths. The different degrees of accuracy in the fine structure splitting of the three groups of transitions were accounted for by appropriate weighting, see Table 1.

Results and Discussion of the Internal Rotation Analysis

The transition frequencies of gauche-butane chosen for the fine structure measurements were predicted with the rotational and centrifugal distortion constants given in [8]. First measurements in Kiel were made in the frequency range from 26.5 to 40 GHz. Some of the Q-branch transitions of the molecule showed triplet fine structures, e.g. $9_{18}-9_{09}$. These structures are typical for molecules possessing two equivalent internal rotors; hence it was attempted to analyze the fine structures by IAM, in the formulation of Woods [18, 19]. First the Fourier coefficient $\omega_1(s)$ was fitted using the Q-branch transition splittings, the other internal rotation parameters were fixed to the values of gauche n-propyl fluoride [20]. Further predictions of the fine structure of transitions were made under consideration of the fitted Fourier coefficient. Finally, twenty transitions of several branches showing internal rotation splittings were used to determine the internal rotation parameters. It was possible to fit all of them with the exception of the moment of inertia of the methyl group I_α. By adding the set of data obtained in Ulm in the frequency region above 40 GHz it was possible to fit all parameters. All transitions with observed and calculated splittings are listed in Table 1. The internal rotation parameters were fitted with the program KC3IAM, written by Woods, modified by Kasten and Hübner. H. Hübner incorporated sextic centrifugal distortion constants and a normalized weighting factor in KC3IAM. The results of the fit and the rotational and centrifugal distortion constants used are listed in Table 2 under Fit I. In a second run we have omitted all transitions above 100 GHz. The resulting parameters and their standard deviations (Fit II) are also given in Table 2. They compare well with the results of the first calculation, but the correlation matrix indicates stronger dependencies. We consider, therefore, the parameters obtained with the complete data set (Fit I) as the preferable solution.

Table 2. Results of the internal rotation analysis. $\omega_1(s)$: first Fourier coefficient, I_α: moment of inertia of the methyl group, $\measuredangle(i, g)$: angle between the internal rotation axis i and the inertia axes $g = a, b, c$, s: reduced barrier height, F: reduced internal rotation constant, V_3: barrier height of the internal rotation. Standard deviations are given in parentheses in units of the last significant digits. σ: standard deviation of the fit, $\overline{\Delta\nu}$: mean experimental splitting.

	Fit I*		Fit II**	
$\omega_1(s) \cdot 10^5$	−0.2943	(62)	−0.2965	(47)
I_α [amu · Å^2]	3.191	(70)	3.232	(68)
$\measuredangle(a, i)$ [°]	55.36	(85)	54.85	(53)
$\measuredangle(b, i)$ [°]	40.47	(81)	41.29	(51)
$\measuredangle(c, i)$ [°]	71.7	(17)	71.2	(13)
F [GHz]	166.2	(38)	164.2	(35)
s	76.02	(20)	75.95	(15)
V_3 [kJ · mol^{-1}]	11.34	(29)	11.20	(26)
V_3 [kcal · mol^{-1}]	2.710	(69)	2.675	(63)
σ [MHz]	0.017		0.005	
$\overline{\Delta\nu}$ [MHz]	0.400		0.292	

Correlation coefficients Fit I:

$\omega_1(s)$	1.000			
I_α	−0.825	1.000		
λ_+	−0.192	−0.232	1.000	
λ_-	−0.931	0.864	−0.082	1.000

Fit II

$\omega_1(s)$	1.000			
I_α	−0.954	1.000		
λ_+	0.154	−0.329	1.000	
λ_-	−0.985	0.973	−0.247	1.000

$\lambda_+ = \cos^2 \measuredangle(a, i) + \cos^2 \measuredangle(b, i) = 1 - \cos^2 \measuredangle(c, i)$

$\lambda_- = \cos^2 \measuredangle(a, i) - \cos^2 \measuredangle(b, i)$

Rotational and centrifugal distortion constants used in the analysis:

A	13 211.92105	MHz
B	4 761.72373	MHz
C	4 059.68936	MHz
Δ_J	4.67201	kHz
Δ_{JK}	−20.2086	kHz
Δ_K	62.475	kHz
δ_J	1.46428	kHz
δ_K	12.0467	kHz
Φ_{JK}	0.0191	Hz
Φ_{KJ}	−0.782	Hz
Φ_K	3.140	Hz
φ_J	0.00315	Hz
φ_{JK}	−0.0927	Hz

* includes all data of Table 1.
** excluding mm wave data >100 GHz.

Table 3. Internal rotation parameters of some compounds with the same configuration of the alkyl group as gauche butane. Standard deviation of the parameters in parentheses, assumed values in square brackets.

	$CH_3CH_2CH_2F$ [20]	$CH_3CH_2CH_2CN$ [21]	$CH_3CH_2CH_2CH_3$ [this work]
$\omega_1(s) \cdot 10^5$	−0.2810 (26)	−0.0891 (41)	−0.2943 (62)
I_z [amu · Å^2]	3.168 (35)	[3.139]	3.191 (70)
$\sphericalangle(a, i)$ [°]	55.54 (40)	72.9 (25)	55.36 (85)
$\sphericalangle(b, i)$ [°]	38.74 (38)	25.6 (18)	40.47 (81)
$\sphericalangle(c, i)$ [°]	74.49 (92)	71.6 (32)	71.7 (17)
F [GHz]	168.0 (19)	164.89 (21)	166.2 (38)
s	76.505 (95)	87.85 (57)	76.02 (20)
V_3 [kJ/mol]	11.54 (15)	13.01 (10)	11.34 (29)
V_3 [kcal/mol]	2.758 (35)	3.107 (24)	2.710 (69)

For comparison, the internal rotation parameters of gauche n-propyl fluoride [20] and gauche butyronitrile [21] are listed in Table 3. An ab initio calculation of the potential height V_3 of gauche-butane was accomplished using the procedure discribed by Aljibury, Snyder, and Strauss [22]. First the equilibrium structure and energy were computed. The resulting methyl rotation value, $\alpha = \alpha_0$, was taken as reference for further rotations, the corresponding energy E_0 as zero point for the calculations of energy differences. In the second step one of the methyl groups was rotated by changing the angle α, while the other was fixed to α_0. In the third step every energy $E(\alpha)$ was calculated with 'full structural relaxation', meaning that all bond lenghts and bond angles with the exception of α and α_0 were fitted again. The following results were obtained (ΔE is the energy difference between E_0 and $E(\alpha)$):

α	15°	30°	45°	60°
ΔE [kJ · mol^{-1}]	1.675	5.918	10.331	12.090

The energy variation as a function of α was used to fit V_3 to the expression $\Delta E = 0.5\, V_3(1 - \cos 3\alpha)$ by the method of least squares. The result $V_3 =$ 12.055 (63) kJ · mol^{-1} is gratifyingly close to the experimental potential height of 11.34 (29) kJ · mol^{-1} given in Table 2. All calculations were made with the program GAUSSIAN 86 employing the 4-31 G basis set [23].

These results and the overall agreement between the observed and calculated fine structure splittings in Table 1 convincingly show that the latter are solely caused by internal rotation of the methyl groups. In some cases, the deviation between experimental and calculated splittings increases the tolerable amount compared with the estimated uncertainty. Considering the large range of K_--values involved – up to 12 – it may be possible that this is caused by centrifugal distortion effects in V_3 and I_α.

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