Determination of a High Potential Barrier Hindering Internal Rotation from the Ground State Spectrum

The Methylbarrier of cis-Propanal

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The barrier hindering internal rotation of the methyl group was determined by analysing the splittings of rotational lines in the ground state. So model errors are minimized. The assignment was checked by double resonances and a centrifugal distortion analysis.

Introduction

The microwave spectrum of propionaldehyde (propanal), CH_3CH_2CHO, has been investigated in its cis and gauche forms by Butcher and Wilson [1]. They determined from the rotational spectrum of the first excited state of the methyl torsion the barrier to internal rotation for the cis conformer. A study of the gauche conformer was given by Pickett et al. [2]. The barrier to methyl internal rotation for this conformer is not yet determined

As the cis conformer shows an interaction of the methyl torsion and C-C torsion [1] influencing the determination of the methyl barrier, we decided independently in both laboratories to study the fine structure of the ground state rotational spectrum. Usually high J transitions show a larger splitting due to internal rotation. Furthermore microwave Fourier transform (MWFT) spectroscopy reaches higher resolution. After noticing that the molecule has been investigated in both laboratories, we decided to publish the results together.

Experimental

The spectra were investigated in Bristol with a Stark spectrometer [3] in the region of 10 to 38 GHz at dry ice temperature and a pressure of about 10 mTorr. The splittings were measured with a precision of about 30 kHz. In Kiel a MWFT-spectrometer [4, 5] in the region from 8 to 18 GHz was used. The accuracy is about 20 kHz. The temperature was $-60\,^{\circ}C$, the pressure down to 0.5 mTorr. Furthermore the assignment of the μ_b-lines was checked by the double resonances in Table 1. The double resonance spectrometer was of the type described in [6]. For pump frequencies the accuracy is estimated to 100 kHz, for signal frequencies 50 kHz.

The samples were purchased from BDH Chemicals Ltd., 95% (Bristol), and from Ega Chemie, 97% (Kiel) and used without further purification.

Centrifugal Distortion Analysis

In a first step a centrifugal distortion analysis was made to guarantee a correct assignment of the high J lines. Table 2 gives the centrifugal distortion analysis of 69 lines measured in both laboratories with different techniques. The Hamilton of van Eijck [7] was used as the correlation of the parameters was better than for other choices. The program ZFAP4 a of Typke [8] was used. The parameters are

Table 1 Investigated double resonances. Frequencies in MHz. Frequencies in brackets ware replaced by those measured with MWFT-spectroscopy.

Pump transition		Signal transition	
$J_{K_-K_+} - J'_{K_-'K_+'}$	ν_p	$J_{K_-K_+} - J'_{K_-K_+'}$	ν_s
$1_{01} - 0_{00}$	(10 492.572)	$2_{12} - 1_{01}$	30 466.560
$2_{02} - 1_{11}$	10 098.842	$3_{13} - 2_{02}$	39 061.035
$6_{24} - 5_{33}$	11 194.740	$6_{24} - 6_{15}$	28 528.510
$7_{25} - 7_{26}$	(11 294.300)	$7_{25} - 7_{16}$	29 488.131
$10_{37} - 10_{38}$	(8 114.500)	$10_{37} - 9_{46}$	33 904.751

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Table 2. Lines of cis-CH_3CH_2CHO used for centrifugal distortion analysis. ν_{calc} with constants of Table 3.

J	K^-	K^+	J'	$K^{-\prime}$	$K^{+\prime}$	Nue (exp.) [GHz]	Nue (calc.) [GHz]	Calc.-exp. [MHz]
1	0	1	0	0	0	10.492466	10.492576	0.110
7	2	5	7	2	6	11.294216	11.294235	0.019
10	3	7	10	3	8	8.114434	8.114301	−0.133
14	4	10	14	4	11	8.521575	8.521414	−0.161
18	5	13	18	5	14	8.332974	8.333011	0.037
23	6	17	23	6	18	12.088283	12.089203	0.920
27	7	20	27	7	21	10.911017	10.912270	1.253
31	8	23	31	8	24	9.603130	9.603638	0.508
35	9	26	35	9	27	8.275799	8.273606	−2.193
2	1	1	2	0	2	13.474899	13.475221	0.322
3	1	2	3	0	3	15.778670	15.778976	0.306
4	1	3	4	1	4	12.903081	12.903314	0.233
8	2	6	8	2	7	17.188725	17.188687	−0.038
11	3	8	11	3	9	12.934768	12.934567	−0.201
15	4	11	15	4	12	13.357279	13.357127	−0.152
19	5	14	19	5	15	12.976415	12.976693	0.278
28	7	21	28	7	22	16.334286	16.336797	2.511
32	8	24	32	8	25	14.446134	14.447854	1.720
36	9	27	36	9	28	12.502805	12.500725	−2.080
2	1	2	1	0	1	30.466560	30.466987	0.427
2	0	2	1	1	1	10.098842	10.098828	−0.014
3	1	3	2	0	2	39.061035	39.061404	0.369
6	2	4	5	3	3	11.194740	11.193849	−0.891
6	2	4	6	1	5	28.528510	28.528241	−0.269
7	2	5	7	1	6	29.488131	29.487543	−0.588
10	3	7	9	4	6	33.904751	33.904325	−0.426
1	1	1	0	0	0	21.268700	21.269003	0.303
1	1	0	1	0	1	12.070810	12.070949	0.139
2	0	2	1	0	1	20.875190	20.875255	0.065
2	1	2	1	1	1	19.690510	19.690561	0.051
2	1	1	1	1	0	22.279260	22.279526	0.266
2	2	0	2	1	1	32.437880	32.438632	0.752
3	0	3	2	0	2	31.043100	31.043323	0.223
3	1	3	2	1	2	29.469520	29.469672	0.152
3	1	2	2	1	1	33.346830	33.347078	0.248
3	2	2	2	2	1	31.477420	31.477373	−0.047
3	2	1	2	2	0	31.911100	31.911181	0.081
3	0	3	2	1	2	21.451620	21.451591	−0.029
3	2	1	3	1	2	31.002200	31.002735	0.535
4	0	4	3	1	3	32.897820	32.897918	0.098
4	1	3	4	0	4	19.182570	19.182673	0.103
4	2	2	4	1	3	29.618950	29.619259	0.309
5	1	4	5	0	5	23.865050	23.865249	0.199
5	2	3	5	1	4	28.672340	28.672447	0.107
6	1	5	6	1	6	26.701360	26.701637	0.277
6	1	5	6	0	6	29.896290	29.896410	0.120
7	1	6	7	1	7	35.069350	35.069488	0.138
7	1	6	7	0	7	37.176680	37.176780	0.100
8	2	7	7	3	4	21.045580	21.045333	−0.247
8	2	6	8	1	7	31.783230	31.782203	−1.027
9	2	8	8	3	5	27.632670	27.632707	0.037
9	2	7	9	2	8	24.389400	24.389190	−0.210
9	2	7	9	1	8	35.582530	35.581251	−1.279
10	2	9	9	3	6	32.538540	32.538654	0.114
10	3	8	9	4	5	25.473020	25.472858	−0.162
10	2	8	10	2	9	32.766680	32.766223	−0.457
11	2	10	10	3	7	35.439570	35.439686	0.116
11	3	9	10	4	6	34.918730	34.918964	0.234
12	2	11	11	3	8	36.123010	36.123062	0.052
12	4	9	11	5	6	26.252890	26.252847	−0.043
12	3	9	12	3	10	19.244530	19.244170	−0.360

Table 2 (continued).

J	K^-	K^+	J'	$K^{-\prime}$	$K^{+\prime}$	Nue (exp.) [GHz]	Nue (calc.) [GHz]	Calc.-exp. [MHz]
13	2	12	12	3	9	34.529220	34.529133	−0.087
13	4	10	12	5	7	37.088880	37.089445	0.565
13	3	10	13	3	11	27.010690	27.010044	−0.646
14	2	13	13	3	10	30.747880	30.747737	−0.143
14	3	11	14	3	12	36.105860	36.104791	−1.069
15	2	14	14	3	11	24.986310	24.986187	−0.123
16	4	12	16	4	13	19.776200	19.775999	−0.201
17	4	13	17	4	14	27.805680	27.805248	−0.432

Table 3. Rotational (MHz) and centrifugal distortion (kHz) constants according to van Eijck.

A	16 670.027 ± 0.095
B	5 893.568 ± 0.035
C	4 599.038 ± 0.028
D_J'	6.00 ± 0.2
D_{JK}'	−8.8 ± 2
D_K'	45.3 ± 4
δ_J	1.676 ± 0.04
R_6'	−0.107 ± 0.02

given in Table 3. The highest correlation is 0.892 for (B, C) and for (D_J', δ_J). The mean square deviation is 702 kHz. For split lines the mean value $\bar{\nu}_{exp} = \frac{1}{3}(\nu_A + 2\nu_E)$ was used, where ν_A and ν_E are the frequencies of the A- and E-species components of the doublets. This procedure was verified by the internal rotation analysis.

A centrifugal distortion analysis with a sixth order theory (program ZFAP6 V. TYPKE) improved the fit to 53 kHz mean square deviation. But the correlation is higher and the errors of the parameters of sixth order are of the magnitude of the parameters. So we do not give the results.

Internal Rotation Analysis

The internal rotation splitting of 28 lines could be resolved, with MWFT also for low J lines.

The analysis was made with the internal axis method (IAM) following the treatment of Woods [8, 9]. The program is a version modified by Meier [10] and by us. It was possible to fit the Fourier coefficient $w(1)$ [11], a function of the reduced barrier, the angle $\sphericalangle(a, i)$ between the internal and the a-inertial axis and the moment of inertia I_α of the methyl top. Numerical values of $w(1)$ are taken from [12].

The rotational constants of Table 3 were used. The lines and splittings are given in Table 4, the parameters in Table 5 and the correlation in Table 6.

Table 4. Experimental splittings $\Delta\nu_{exp} = \nu_A - \nu_E$ (kHz) and calculated splittings $\Delta\nu_{calc}$, calculated with constants of Table 5 and Table 3. ν_A and ν_E may be calculated from $\bar{\nu}_{exp}$ of Table 2 using the relation $\bar{\nu}_{exp} = \frac{1}{3}(\nu_A + 2\,\nu_E)$ and $\Delta\nu_{exp}$.

$J_{K-K+} - J'_{K-'K+'}$	$\Delta\nu_{exp}$	$\Delta\nu_{calc}$
$2_{11} - 2_{02}$	100	90.8
$3_{12} - 3_{03}$	139	128.4
$4_{13} - 4_{14}$	202	192.6
$7_{25} - 7_{26}$	281	240.5
$8_{26} - 8_{27}$	360	348.2
$10_{37} - 10_{38}$	243	234.9
$11_{2,10} - 10_{37}$	− 560	− 606.5
$11_{38} - 11_{39}$	360	352.9
$12_{2,11} - 11_{38}$	− 810	− 794.8
$12_{3,9} - 12_{3,10}$	370	491.1
$13_{2,12} - 12_{3,9}$	− 1020	− 1012.2
$13_{3,10} - 13_{3,11}$	620	642.0
$14_{2,13} - 13_{3,10}$	− 1240	− 1248.3
$14_{3,11} - 14_{3,12}$	800	797.9
$14_{4,10} - 14_{4,11}$	312	298.0
$15_{2,14} - 14_{3,11}$	− 1520	− 1492.5
$15_{4,11} - 15_{4,12}$	451	439.3
$16_{4,12} - 16_{4,13}$	600	605.0
$17_{4,13} - 17_{4,14}$	790	785.0
$18_{5,13} - 18_{5,14}$	349	335.1
$19_{5,14} - 19_{5,15}$	506	492.0
$23_{6,17} - 23_{6,18}$	525	509.7
$27_{7,20} - 27_{7,21}$	500	496.2
$28_{7,21} - 28_{7,22}$	704	697.0
$31_{8,28} - 31_{8,24}$	462	458.3
$32_{8,24} - 32_{8,25}$	649	650.0
$35_{9,26} - 35_{9,27}$	398	404.1
$36_{9,27} - 36_{9,28}$	565	578.1

In contrast to investigations of other molecules the correlation between the barrier V_3, $(w(1))$, and I_α is tolerable. The mean square deviation of the fit is 28 kHz for a mean splitting $\overline{\Delta\nu}$ of 551 kHz.

For comparison the measured splittings of the first excited state of Table VIII of (1) were reanalysed with the same program. From their data the rotational constants were determined to be: $A = 16641.290$ MHz, $B = 5870.508$ MHz, $C = 4592.794$ MHz. I_a and $\sphericalangle$(a, i) were assumed as given by our analysis from the ground state. The results are given in the second column of Table 5. In addition we repeat the values of [1].

Table 5. Internal rotation parameters of cis-propionaldehyde. The first three parameters of column 1 were fitted in our IAM-analysis, the others are derived. In the second column we give a reanalysis of the measurements of (1) with assumed values in brackets. The last column gives the data of (1).

$w(1)$.	$(-0.1725 \pm 0.0036) \cdot 10^{-4}$	$(0.7123 \pm 0.0067) \cdot 10^{-3}$	—
I_α amu Å^2	3.031 ± 0.057	(3.031)	3.11 **
$\sphericalangle$ (a, i)	56.41 ± 0.39	(56.41)	—
S	59.94 ± 0.18	62.00 ± 0.09	—
V_3 cal/mol	2270 ± 7	2347 ± 3	2254 ± 46
V_3 cm^{-1}	793.7 ± 2.5	820.6 ± 1	788 ± 16 *
F GHz	176.54	(176.54)	—
λ_a	0.5532	(0.5532)	0.5850 **
MSD kHz	28	223	—
$\overline{\Delta\nu}$ kHz	551	3708	—

* A mean value of 797 cm^{-1} for three isotopes is given in (1).

** The source of these parameters is not given in (1).

Table 6. Correlation of the internal rotation parameters.

$w(1)$	1.000		
$I\alpha$	0.846	1.000	
$\sphericalangle$(a, i)	0.745	0.350	1.000

Apparently the value of the barrier V_3 is higher than that determined from the first excited state.

This is in agreement with the coupling of methyl torsion and C-C-torsion described in Fig. 4 of [1]. As the ground state is less influenced by interactions, we believe that the model error is less for barrier determinations from the ground state [13].

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