Determination of a High Barrier Hindering Internal Rotation from the Ground State Spectrum. The Methylbarrier of 1-Butyne

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With 1-butyne a series of barrier determinations from rotational spectra in the torsional ground state of ethyl compounds was continued. The barrier is different to the value from an analysis of the rotational spectrum of the first torsional state.

The microwave spectrum of 1-butyne (ethylacetylene), $HC{\equiv}C{-}CH_2{-}CH_3$, was first investigated by Job et al. [1]. Recently a centrifugal distortion analysis and a determination of the barrier to internal rotation of the methyl group from the first excited torsional state was reported by Demaison et al. [2] and Landsberg and Suenram [3]. In [2] and [3] a Coriolis type interaction between the first torsional and the lowest bending state was noticed. The determination of the barrier from an excited state may be perturbed by this interaction [4 – 6].

We decided to investigate the ground state spectrum as this should be the least influenced one. The higher resolution combined with the high sensitivity of microwave Fourier transform spectroscopy [7 – 10] makes this investigation feasible.

The sample was kindly provided by Dr. Landsberg [3] and measured in the pressure and temperature range from 0.8 to 1.5 mTorr and from $-30\,°$ to $-48\,°$C. The measured lines and the internal rotation splittings are given in Table 1. The narrow splitted lines were analysed by a line shape simulation [11]. In the region from 21 to 26 GHz we reproduced the measurements of [3] with higher accuracy. We performed a sixth order centrifugal distortion analysis [12] of 77 A-species or unsplit transitions with J up to 38 with a standard deviation of 5 kHz. The Hamiltonian was the same as used in [2] (Equation (1)). The results are given in Table 2. They differ partly (A, D'_K) from those of [2] possibly because a very different set of lines was measured and different sextic constants were constrained to zero. Our rotational constant A is closer to that of [3].

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Table 1. Measured transitions of ethylacetylene, $CH_3{-}CH_2{-}C{\equiv}CH$. Γ: symmetry species, ν_m: measured frequency, deviation from calculated frequency in brackets in units of the last digit, $\Delta\nu_m$: measured internal rotation splitting $\nu_A - \nu_E$, $\Delta\nu_c$: calculated internal rotation splitting, all frequencies in [MHz]. (*****: not resolved, $: not used for internal rotation analysis).

J	K_-	K_+	J'	K'_-	K'_+	Γ	ν_m	$\Delta\nu_m$	$\Delta\nu_c$
1	0	1	0	0	0	A	8633.419 (4)	*****	0.001
						E			
1	1	0	1	0	1	A	23060.399 (-1)	0.024	0.025
						E			
2	1	1	2	0	2	A	23527.111 (-6)	0.025	0.026
						E			
3	2	1	2	2	0	A	25928.839 (2)	*****	0.010
						E			
3	0	3	2	0	2	A	25872.270 (-1)	*****	0.003
						E			
3	1	3	2	1	2	A	25206.638 (-1)	*****	0.001
						E			
3	2	2	2	2	1	A	25901.108 (-3)	*****	-0.006
						E			
3	1	2	3	0	3	A	24240.086 (6)	0.023	0.027
						E			
4	1	3	4	0	4	A	25214.689 (20)	0.025	0.029
						E			
5	1	4	5	0	5	A	26471.062 (2)	*****	0.031
						E			
5	0	5	4	1	4	A	22407.987 (-5)	*****	-0.017
						E			
4	2	3	5	1	4	A	21918.628 (-1)	0.063	0.062
						E			
6	1	5	6	1	6	A	9644.014 (12)	*****	0.018
						E			
5	2	3	6	1	6	A	21837.266 (-5)	0.085	0.077
						E			
5	2	4	6	1	5	A	11951.100 (-5)	0.063	0.058
						E			
7	2	5	8	1	8	A	8778.182 (1)	0.084	0.082
						E			
8	1	7	7	2	6	A	8597.043 (-1)	-0.050	-0.050
						E			
9	1	8	8	2	7	A	19161.649 (1)	-0.050	-0.046
						E			
9	1	8	9	1	9	A	20611.955 (-2)	0.033	0.037
						E			

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Table 1 (continued)

J	K_-	K_+	J'	K'_-	K'_+	Γ	ν_m	$\Delta\nu_m$	$\Delta\nu_c$
9	3	7	10	2	8	A E	25287.144 (-2)	0.106	0.099
10	1	9	10	1	10	A E	25151.704 (-4)	*****	0.045
10	3	7	11	2	10	A E	20460.211 (-4)	0.108	0.106
12	1	12	11	2	9	A E	11656.016 (7)	-0.106	-0.104
11	3	8	12	2	11	A E	12392.918 (2)	0.101	0.105
13	2	11	13	2	12	A E	8704.778 (-2)	0.021	0.020
14	1	14	13	2	11	A E	18277.470 (1)	-0.117	-0.122
14	2	12	14	2	13	A E	11334.851 (5)	0.022	0.026
15	2	13	14	3	12	A E	25863.003 (-2)	-0.073	-0.071
15	2	14	14	3	11	A E	10647.743 (-1)	-0.109	-0.105
15	1	15	14	2	12	A E	20559.226 (3)	-0.136	-0.133
15	4	12	16	3	13	A E	19203.541 (2)	0.119	0.121
15	4	11	16	3	14	A E	20941.763 (-2)	0.121	0.126
16	1	16	15	2	13	A E	22127.227 (3)	-0.153	-0.145
16	2	14	16	2	15	A E	17993.903 (-3)	0.046	0.040
16	2	15	15	3	12	A E	17814.934 (0)	-0.104	-0.107
16	4	13	17	3	14	A E	9815.726 (2)	0.119	0.116
16	4	12	17	3	15	A E	12280.560 (0)	0.123	0.123
17	1	17	16	2	14	A E	22972.558(-17)	-0.151	-0.158
17	2	16	16	3	13	A E	24652.929 (-4)	-0.105	-0.108
17	2	15	17	2	16	A E	22043.862 (-1)	0.053	0.048
18	1	18	17	2	15	A E	23095.302 (-5)	-0.174	-0.172
19	1	19	18	2	16	A E	22503.813 (4)	-0.176	-0.188
19	3	16	18	4	15	A E	9545.926 (-4)	-0.104	-0.104
20	3	17	19	4	16	A E	19580.715 (-1)	-0.099	-0.097
20	1	20	19	2	17	A E	21213.563 (17)	-0.209	-0.203
21	3	19	20	4	16	A E	21752.955 (1)	-0.115	-0.112
21	1	21	20	2	18	A E	19246.242 (-9)	-0.204$	-0.221
20	5	15	21	4	18	A	22428.752 (-2)	0.122	0.122

Table 1 (continued)

J	K_-	K_+	J'	K'_-	K'_+	Γ	ν_m	$\Delta\nu_m$	$\Delta\nu_c$
20	5	16	21	4	17	A E	21890.059 (2)	0.136	0.145
22	3	19	22	3	20	A E	9980.337 (0)	0.026	0.027
25	3	22	25	3	23	A E	19274.638 (0)	0.052	0.049
25	6	19	26	5	22	A E	24316.490 (-5)	0.097	0.093
26	3	23	26	3	24	A E	23357.798 (2)	0.063	0.057
26	4	23	25	5	20	A E	21991.115 (3)	-0.114$	-0.110
26	4	22	25	5	21	A E	24786.453 (2)	-0.108	-0.102
25	6	20	26	5	21	A E	24162.365 (3)	0.148$	0.167
30	5	25	29	6	24	A E	12179.704 (2)	-0.107	-0.109
30	5	26	29	6	23	A E	11559.633 (2)	-0.102	-0.101
30	7	23	31	6	26	A E	26351.178 (10)	*****	0.025
30	7	24	31	6	25	A E	26309.321 (-4)	0.192	0.199
31	5	26	30	6	25	A E	21441.066 (2)	-0.105	-0.097
31	5	27	30	6	24	A E	20590.394 (-3)	-0.097	-0.099
31	4	27	31	4	28	A E	9732.298 (1)	0.030	0.028
32	4	28	32	4	29	A E	12148.545 (1)	0.033	0.035
32	7	26	33	6	27	A E	8378.862 (0)	0.122	0.131
32	7	25	33	6	28	A E	8466.081 (-3)	0.070	0.069
34	4	30	34	4	31	A E	18322.080 (-1)	0.057	0.050
35	4	31	35	4	32	A E	22149.084 (-1)	0.064	0.060
35	6	29	34	7	28	A E	9707.115 (0)	-0.094	-0.097
35	6	30	34	7	27	A E	9533.726 (-4)	-0.075	-0.076
36	4	32	36	4	33	A E	26505.775 (1)	0.081	0.085
36	6	31	35	7	28	A E	18578.509 (0)	-0.078	-0.073
36	6	30	35	7	29	A E	18819.114 (0)	-0.082$	-0.086
36	8	28	37	7	31	A E	19541.712 (-1)	*****	0.006
36	8	29	37	7	30	A E	19525.765 (-4)	0.170	0.166
37	8	30	38	7	31	A E	10585.209 (-4)	0.134	0.127
37	8	29	38	7	32	A E	10608.173 (7)	*****	0.019

Table 2. Rotational and centrifugal distortion constants of ethylacetylene, $CH_3-CH_2-C\equiv CH$. σ: standard deviation of the fit, standard errors in units of the last digit in brackets.

A = 27147.80348(171) MHz	D_J' = 2.6754 (29) kHz	H_J' = 0.01114(50) Hz
B = 4546.51991 (32) MHz	D_{JK}' = −45.441 (50) kHz	H_{JK}' = 0.000 fixed
C = 4086.91328 (29) MHz	D_K' = 579.792 (145) kHz	H_{KJ}' = −2.065 (277) Hz
	δ_J' = 0.63067(20) kHz	H_K' = 39.19 (266) Hz
	R_6' = −0.03249 (4) kHz	H_5' = 0.00340(13) Hz
		H_6' = 0.00262(41) Hz
	σ = 5 kHz	H_{10}' = 0.00043(14) Hz

Correlation coefficients

1.00													
0.95	1.00												
0.96	0.98	1.00											
0.45	0.64	0.55	1.00										
0.40	0.59	0.50	0.99	1.00									
−0.25	−0.46	−0.35	−0.95	−0.98	1.00								
0.29	0.50	0.34	0.88	0.90	−0.89	1.00							
−0.04	0.07	−0.07	0.32	0.34	−0.36	0.68	1.00						
0.36	0.49	0.47	0.68	0.65	−0.61	0.46	−0.02	1.00					
0.28	0.43	0.38	0.72	0.71	−0.71	0.58	0.15	0.97	1.00				
−0.22	−0.39	−0.32	−0.72	−0.72	0.74	−0.60	−0.19	−0.94	−0.99	1.00			
0.03	0.18	0.02	0.46	0.48	−0.50	0.80	0.93	0.13	0.30	−0.34	1.00		
0.07	−0.04	0.10	−0.25	−0.28	0.32	−0.62	−0.95	−0.03	−0.21	0.26	−0.90	1.00	
−0.21	−0.19	−0.27	−0.19	−0.16	0.11	0.16	0.61	−0.13	0.01	−0.05	0.46	−0.78	1.00

Table 3. Internal rotation parameters of ethylacetylene, $CH_3-CH_2-C\equiv CH$. $w_1(s)$: Fourier coefficient, $\measuredangle(a, i)$: angle between the inertia axis a 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, N: number of splittings, standard errors in units of the last digit in brackets, assumption in square brackets.

$w_1(s)$	$-0.1469(12)\cdot 10^{-5}$	$-0.1471(12)\cdot 10^{-5}$
$\measuredangle(a, i)$ [°]	47.55(19)	47.68(18)
I_α [amuÅ^2]	3.180(12)	[3.155]
$(w_1(s), (a, i))$	−0.688	−0.709
$(w_1(s), I_\alpha)$	0.090	*****
$(\measuredangle(a, i), I_\alpha)$	−0.329	*****
σ [MHz]	0.005	0.005
$\overline{\Delta\nu}$ [MHz]	0.092	0.092
s	82.81(8)	82.79(8)
F [GHz]	175.30(66)	176.66(66)
V_3 [kcal/mol]	3.114(15)	3.138(15)
N	61	61

The internal rotation splittings were analysed by the internal axis method (IAM) with a program written by Woods [13, 14] and modified by [15, 16]. Using the rotational constants from Table 2 we were successful to fit three internal rotation parameters $w_1(s)$, the first Fourier coefficient, $\measuredangle(a, i)$, the angle between the inertia axis a and the internal rotation axis i and I_α, the moment of inertia of the methyl group. They are given together with derived parameters in Table 3. It should be mentioned that the reduced barrier s differs outside the error limits from that given in Table 5 of [2]. This may reflect the neglection of the mentioned interaction in the analysis of the rotational spectrum of the torsional excited state. Consequently the values of V_3 differ also. They are influenced in addition by the different values of I_α. For comparison we give in Table 3 barrier parameters calculated with I_α = 3.155 amu Å^2, a value taken from ethylfluoride [17]. A final answer to this question should be possible if the rotation-torsion-vibration interaction is investigated.

In comparison to CH_3CH_2X, X = F [17], Cl [18], Br [19], and J [20] 1-butyne has the lowest barrier.

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