Internal Rotation Fine Structure in the Microwave Spectrum of cis-2-Butene

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The rotational spectrum of cis-2-butene has been measured in the range from 5 to 40 GHz with microwave Fourier transform spectroscopy to determine internal rotation and centrifugal distortion parameters.

Key words: Microwave spectroscopy, Internal rotation, cis-2-Butene.

Introduction

The torsional fine structure in the microwave spectra of molecules with two equivalent internal rotors has attracted the interest of our group since several years. The spectra have been analysed on the basis of the usual principal and internal axis method (PAM and IAM) [1, 2]. Recently we developed a different method [3] for the calculation of the energy levels, transition frequencies and intensities based on a PAM-type hamiltonian [4]. The treatment led to a satisfactory explanation of the spectra of molecules of C_{2v}- or C_s-symmetry possessing a high hindering potential. Cis-2-butene, $(CH_3)_2C_2H_2$, offers the possibility to test the method in the case of a low barrier.

Experimental

The spectra were measured with microwave Fourier transform spectrometers [5] in the frequency region from 5 to 40 GHz at sample pressures of approximately 0.3 Pa (2.3 mTorr) and temperatures between 220 and 250 K. The measured frequencies are listed in Table 1.

Results

For the torsional fine structure analysis the transition frequencies were calculated from the eigenvalues of truncated matrices of the hamiltonian instead of a Van Vleck transformation treatment used in a previous analysis [6]. The stepwise computation of the eigenvalues is described in detail in [3]. Since a simultaneous fit of all spectroscopic parameters converges very slowly, an iterative procedure proposed by Vacherand [7] was used. First we fitted the internal rotation parameters to the splittings relative to the AA-components of the transitions and then the rotational and quartic centrifugal distortion constants of the Watson A-reduction [8] in the representation I^r to the frequencies of the AA-components. A single repetition of this procedure led to the final results in Table 2. The angle between the internal rotation axis of one top and the principal axis of inertia a of 54.74(4)° indicates a tilt of the methyl groups towards each other since the corresponding angle of the bond C_1–C_2 and the axis a from the substitution structure [9] is 53.06(5)°. The barrier height $V_3 = 3.109(5)$ kJ/mol (743.0(12) cal/mol) is in good agreement with a present Raman study [10].

We carried out an ab initio calculation of the barrier height following the method of Aljibury [11]. We assumed that the torsional angle α corresponds to the dihedral angle of the planes $C_1C_2C_3$ and $H_iC_1C_2$. H_i is the in plane hydrogen of the equilibrium structure with $\alpha = 0°$. First we optimised this structure with the program Gaussian 86 [12] employing the 4-31 G basis set. The corresponding energy is E_0. Then we repeated the structure optimizations for different fixed values of α and fitted the barrier height V_3 of the torsional potential function used for the spectroscopic internal rotation analysis to the energy differences $E_\alpha - E_0$. The result $V_3 = 3.18$ kJ/mol is close to the ex-

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Table 1. Observed frequencies and splittings relative to the AA-component with residuals. G: Symmetry species of group $C_{3v}^{-} \times C_{3v}^{+}$ [14]; frequencies in MHz.

J K_- K_+	J' K'_- K'_+	G	ν_{AA}	$\nu_{AA}-\nu_G$	obs.-calc.	obs.-calc.
1 1 1	0 0 0	AA	20 174.087		−0.010	
		EE		52.152		0.475
		EA		159.583		0.930
		AE		39.369		0.484
2 1 1	2 0 2	AA	13 127.475		−0.002	
		EE		10.241		0.167
		EA		4.040		−0.191
		AE		37.197		0.888
2 2 1	2 1 2	AA	35 993.394		−0.009	
2 0 2	1 1 1	AA	7 450.784		0.005	
		EE		−38.620		0.039
		EA		−135.297		0.467
		AE		−9.518		0.253
2 1 2	1 0 1	AA	28 350.008		−0.011	
		EE		30.497		0.612
		EA		83.394		1.136
		AE		38.116		1.101
3 1 2	3 0 3	AA	14 954.175		−0.003	
		EE		21.707		0.251
		EA		40.371		−0.290
		AE		46.279		1.220
3 2 2	3 1 3	AA	37 622.072		0.012	
3 2 1	3 1 2	AA	31 648.006		−0.007	
		EE		−181.161		−0.836
3 0 3	2 1 2	AA	17 450.535		0.003	
		EE		−10.008		0.305
		EA		−46.021		0.964
		AE		6.262		0.356
3 1 3	2 0 2	AA	36 026.374		0.018	
		EE		22.594		0.912
		EA		55.898		−0.668
4 1 3	4 0 4	AA	17 620.094		0.001	
		EE		34.322		0.197
		EA		71.002		−0.553
		AE		65.958		1.212
4 2 2	4 1 3	AA	30 342.243		−0.010	
		EE		−69.364		−0.329
		EA		−278.755		−0.157
		AE		81.099		−0.013
4 0 4	3 1 3	AA	27 602.861		−0.002	
		EE		2.241		0.493
		AE		20.358		0.567
4 1 3	3 2 2	AA	7 600.893		−0.003	
5 1 4	5 0 5	AA	21 270.953		0.003	
		EE		51.144		−0.042
		EA		105.623		−1.000
		AE		98.422		0.620
5 2 3	5 1 4	AA	29 254.163		−0.011	
		EE		−12.145		0.068
		EA		−110.940		0.216
		AE		72.878		0.434
5 0 5	4 1 4	AA	37 721.354		−0.002	
		EE		9.638		0.687
		AE		30.537		0.885
5 1 4	4 2 3	AA	19 177.596		0.013	
		EE		−119.820		0.169
		EA		−387.800		0.546
		AE		−12.223		1.155
6 1 5	6 0 6	AA	26 005.489		−0.001	
		EE		72.679		−0.470
		EA		146.846		−1.657
		AE		143.095		−0.537
6 2 4	6 1 5	AA	28 666.515		0.002	
		EE		12.841		0.292
		EA		−16.026		0.187
		AE		68.520		1.078

Table 2. Spectroscopic parameters of cis-2-butene. A, B, C: rotational constants, Δ_J, Δ_{JK}, Δ_K, δ_J, δ_K: quartic centrifugal distortion constants of the Watson-A reduction, V_3: barrier to internal rotation, $\sphericalangle a, i$: angle between the principal axis of inertia a and the internal rotation axis i, F: internal rotation constant, F': kinetic interaction constant, s: reduced barrier height. Parameters obtained from least squares fits above and derived parameters below the line.

A/MHz	16 061.050 (5)
B/MHz	5 139.706 (3)
C/MHz	4 086.686 (3)
Δ_J/kHz	3.106(33)
Δ_{JK}/kHz	−14.66 (46)
Δ_K/kHz	50.8 (11)
δ_J/kHz	0.949(12)
δ_K/kHz	9.1 (13)
V_3/kJ mol^{-1}	3.109 (5)
I_α/amuÅ^2	3.142 (5)
$\sphericalangle a, i$/°	54.74 (4)
F/GHz	170.19 (27)
F'/GHz	−2.154 (3)
s	20.345(46)

perimental barrier height. Viewing on the differences one should consider that the ab initio and the spectroscopic models are different. For the quantum chemical calculations we use a flexible model of the molecule whereas the analysis of the spectrum is based on a rigid frame and two rigid tops.

Although the spectroscopic parameters are well determined, the differences between observed and calculated splittings exceed the measurement accuracy of approximately 5 kHz. The standard deviation of the fit of the internal rotation parameters is 0.710 MHz compared to a mean experimental splitting of 68.752 MHz. This deficiency has also been observed in the IAM-analysis of the spectrum of acetone [7] with a reduced barrier height of similar magnitude. Our method offers the possibility to include higher order terms of the torsional potential expansion. But these terms are highly correlated with V_3 and do not lead to a reduction of the residuals. An extension of the usual spectroscopic model seems necessary for low barrier molecules. Perhaps a generalisation of the single top hamiltonian with fourth order rotation-torsion interaction derived by Mitra and Gosh [13] to the two-top problem leads to a more accurate reproduction of the measured frequencies.

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