The Rotational Spectrum of 2,2-Dimethyloxirane

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The microwave spectrum of 2,2-dimethyloxirane (isobutylene oxide) in the ground and torsionally excited states was assigned and analyzed. The potential barriers hindering the internal rotation described by $V_3 = 11.312(9)$ kJ/mol and $V'_{12} = 1.059(32)$ kJ/mol and the angles between the axes of inertia and the internal rotation axes were determined.

Introduction

In a preceeding publication we reported on a reinvestigation of cis-2,3-dimethyloxirane (CEB) and trans-2,3-dimethyloxirane (TEB) [1–3]. A more precise analysis of the two methyl-top internal rotations and a partial r_s-structure was given. To complete the internal rotation study on the influence of the position of the methyl substitution at an oxirane ring we investigated 2,2-dimethyloxirane (DMO). This molecule has two equivalent methyl tops because of its C_s symmetry, but both tops are bound to the same atom in the oxirane frame. This leads to a stronger steric interaction of the internal rotation of the methyl tops. It was possible to assign the rotational spectrum and to determine rotational and centrifugal distortion constants and the internal rotation parameters.

Experimental

The substance was supplied from Fa. Bayer, Leverkusen, FRG, and used without further purification.

After a quantumchemical calculation [4] of the structure and dipole moment an assignment was possible by using a scanning molecular beam microwave Fourier transform (MB-MWFT) spectrometer [5, 6]. In Fig. 1 we give a drawing based on the calculated structure. As expected, we observed weak μ_a- and strong μ_c-type transitions of the torsional ground state $q = 0$, given in Table 1. No internal rotation splitting could be clearly resolved. So we searched for the two first excited torsional states $q = 1$ and $q = 2$ (or v_1, $v_2 = 0{,}1$ and $1{,}0$) with a Stark spectrometer in the range from 26 to 40 GHz equipped with a synthesizer and a frequency doubler as a source. After an initial assignment the spectrum was more precisely measured with waveguide Fourier transform spectrometers (WG-MWFT) described in [7, 8], the frequencies were refined by evaluating the time domain decay [9]. The measurements are given in Table 2. The pressure was about 0.2–0.5 mTorr (0.03–0.07 Pa), the temperature was about 225 K when using spectrometer [7] and room temperature with [8].

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Table 1. Rotational transitions of 2,2-dimethyloxirane in the torsional ground state $q = 0$. $\delta_v = \nu(\text{obs.}) - \nu(\text{calc.})$, (1): MB-MWFT [5, 6], (2): WG-MWFT [7], (3): WG-MWFT [8].

J'	K'_-	K'_+	–	J	K_-	K_+	ν (obs.)/MHz	δ_v/MHz	
1	0	1	–	0	0	0	9 466.870	−0.002	(1)
1	1	0	–	0	0	0	12 034.945	−0.001	(1)
2	1	1	–	1	1	0	20 543.034	0.023	(2)
2	2	1	–	1	1	1	25 028.549	−0.006	(2)
2	1	1	–	1	0	1	23 111.141	−0.008	(2)
2	2	0	–	1	1	0	24 387.766	−0.005	(2)
2	0	2	–	1	1	0	15 397.043	0.002	(1)
2	2	1	–	2	0	2	8 022.133	0.001	(1)
2	2	0	–	2	1	2	8 672.771	0.005	(1)
3	0	3	–	2	0	2	25 734.258	−0.000	(2)
3	1	2	–	2	1	1	29 864.928	−0.001	(3)
3	1	3	–	2	1	2	25 486.720	−0.000	(2)
3	2	2	–	2	2	1	28 400.478	−0.001	(3)
3	1	2	–	3	1	3	9 206.272	0.007	(1)
3	2	2	–	3	0	3	10 688.346	0.007	(1)
3	3	1	–	3	1	2	10 728.268	−0.001	(1)
3	2	1	–	3	1	3	14 252.740	0.005	(1)
3	3	0	–	3	2	2	9 766.398	0.000	(1)
4	2	2	–	4	2	3	7 832.252	0.005	(1)
4	3	2	–	4	1	3	11 808.803	−0.003	(1)
4	4	0	–	4	3	2	11 631.879	−0.001	(1)
4	4	1	–	4	3	1	9 129.025	0.003	(1)
5	3	3	–	5	1	4	14 468.554	−0.008	(1)
6	3	3	–	6	3	4	11 067.536	−0.002	(1)
6	4	3	–	6	2	4	15 333.986	−0.003	(1)
5	5	0	–	5	4	2	14 090.309	−0.001	(1)
7	3	5	–	7	1	6	21 992.287	−0.003	(2)
7	4	3	–	7	4	4	8 784.679	−0.006	(1)
10	4	6	–10	4	7		24 968.347	−0.028	(2)
12	7	6	–12	5	7		25 379.841	0.018	(2)
15	7	8	–15	7	9		31 186.216	0.026	(3)

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Table 2. Rotational transitions of the first and second excited torsional state. Exact designation of the AA, EE, AE, and EA symmetry species Γ are AA_1, $[E_aE + E_bE]$, AE, and $[E_aA_1 + E_bA_1]$. $\Delta\nu = \nu_{AA} - \nu_\Gamma$, $\delta_{\Delta\nu} = \Delta\nu(\text{obs.}) - \Delta\nu(\text{calc.})$.

J'	K'_-	K'_+	– J	K_-	K_+	Γ	First torsional state $q=1$			Second torsional state $q=2$			
							ν(obs.)	$\Delta\nu$(obs.)	$\delta_{\Delta\nu}$	ν(obs.)	$\Delta\nu$(obs.)	$\delta_{\Delta\nu}$	
2	2	1	– 1	1	1	AA	25 008.198			24 992.848			(3)
						EE	25 008.390	−0.192	0.002	24 993.113	−0.265	0.002	
						AE	25 008.579	−0.380	0.002	24 993.384	−0.535	−0.015	
						EA	25 008.579	−0.380	−0.015	24 993.384	−0.535	0.012	
2	1	1	– 1	0	1	AA	23 096.518			23 101.350			(3)
						EE	23 096.789	−0.271	−0.002	23 101.726	−0.376	−0.003	
						AE	23 097.064	−0.546	−0.008	23 102.098	−0.748	−0.003	
						EA	23 097.064	−0.546	−0.008	23 102.098	−0.748	−0.003	
2	1	1	– 1	1	0	AA	20 531.502			20 541.627			(3)
						EE	20 531.733	−0.231	−0.004	20 541.945	−0.319	−0.005	
						AE	20 531.954	−0.452	0.005	20 542.262	−0.635	−0.004	
						EA	20 531.954	−0.452	0.002	20 542.262	−0.635	−0.011	
2	2	0	– 1	1	0	AA	24 368.679			24 357.042			(3)
						EE	24 368.886	−0.207	0.001	24 357.326	−0.285	0.002	
						AE	24 369.084	−0.404	0.013	24 357.617	−0.576	0.009	
						EA	24 369.084	−0.404	0.001	24 357.617	−0.576	−0.013	
3	0	3	– 2	0	2	AA	25 715.956			25 708.411			(3)
						EE	25 716.012	−0.056	0.000	25 708.488	−0.077	0.001	
						AE	25 716.054	−0.098	0.007	25 708.558	−0.147	−0.009	
						EA	25 716.054	−0.098	0.023	25 708.558	−0.147	0.021	
3	1	3	– 2	1	2	AA	25 469.495			25 466.173			(3)
						EE	25 469.569	−0.074	0.010	25 466.277	−0.105	0.012	
						AE	25 469.648	−0.152	0.022	25 466.383	−0.211	0.038	
						EA	25 469.648	−0.152	0.006	25 466.383	−0.211	0.009	
3	2	1	– 2	2	0	AA	31 050.928			–			(2)
						EE	31 051.332	−0.404	−0.006	–	–	–	
						AE	31 051.741	−0.813	−0.022	–	–	–	
						EA	31 051.741	−0.813	−0.011		–	–	
3	2	1	– 2	1	1	AA	34 888.103			34 889.850			(2)
						EE	34 888.482	−0.380	−0.003	34 890.380	−0.530	−0.008	
						AE	34 888.865	−0.762	−0.011	34 890.904	−1.054	−0.014	
						EA	34 888.865	−0.762	−0.008	34 890.904	−1.054	−0.008	
3	1	2	– 2	0	2	AA	34 989.664			35 001.109			(2)
						EE	34 990.097	−0.434	0.004	35 001.728	−0.619	−0.013	
						AE	34 990.536	−0.872	0.006	35 002.332	−1.223	−0.006	
						EA	34 990.536	−0.872	0.001	35 002.332	−1.223	−0.016	
3	1	2	– 2	1	1	AA	29 845.859			29 849.283			(2)
						EE	29 846.076	−0.217	0.025	29 849.639	−0.356	−0.020	
						AE	29 846.323	−0.463	0.024	29 849.966	−0.683	−0.009	
						EA	29 846.323	−0.463	0.021	29 849.966	−0.683	−0.015	
3	2	2	– 2	2	1	AA	28 383.454			28 391.439			(2)
						EE	28 383.684	−0.230	0.004	28 391.738	−0.299	0.026	
						AE	28 383.903	−0.449	0.025	28 392.043	−0.604	0.060	
						EA	28 383.903	−0.449	0.011	28 392.043	−0.604	0.032	
4	1	4	– 3	1	3	AA	33 415.748			33 408.866			(2)
						EE	33 415.848	−0.099	0.012	33 408.971	−0.105	0.068	
						AE	33 416.102	−0.354	−0.059	33 409.339	−0.472	0.008	
						EA	33 415.939	−0.191	−0.041	33 409.074	−0.208	0.000	
4	0	4	– 3	0	3	AA	–	–	–	33 464.508			(2)
						EE	–	–	–	33 464.508	0.000	0.023	
						AE	–	–	–	33 464.414	0.093	0.006	

Analysis

The rotational and centrifugal distortion constants of the torsional and vibrational ground state were determined with the program ZFAP4 [10] in the representation I^r [11] using Watson's A reduction [12]. For the torsionally excited states the program TTWF2 [13] was used with the internal rotation parameters held fixed. The centrifugal distortion constants were taken from the ground state. Because of the ac-mirror plane of the molecule the calculation was done using the representation II^r. Therefore the

Table 3. Rotational and centrifugal distortion constants of 2,2-dimethyloxirane. Watson's A reduction. σ: single standard deviation of the fit, [...]: parameters held fixed, standard deviation in brackets.

Torsional state		$q=0$	$q=1$	$q=2$	ab initio
Program		ZFAP4	TTWF2	TTWF2	Gaussian
Representation		I'	II'	II'	
A	(MHz)	6496.8320(13)	6491.4926(64)	6484.9018(10)	6599.988
B	(MHz)	5538.1207(13)	5535.3266(31)	5539.1627(55)	5649.839
C	(MHz)	3928.7527(13)	3925.6105(28)	3924.6406(32)	3968.015
Δ_J	(kHz)	1.392(100)	[1.929]	[1.929]	–
Δ_{JK}	(kHz)	−0.290(30)	[−1.903]	[−1.903]	–
Δ_K	(kHz)	2.239(30)	[2.239]	[2.239]	–
δ_J	(kHz)	0.437(4)	[−0.705]	[−0.705]	–
δ_K	(kHz)	0.015(25)	[0.408]	[0.408]	–
σ	(kHz)	6	28	39	–

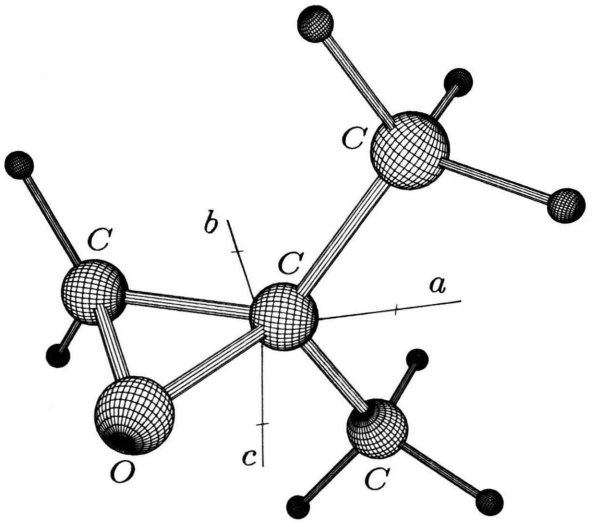

Fig. 1. Perspective drawing of 2,2-dimethyloxirane. The structure is taken from the ab initio calculations.

values of the centrifugal constants are different. Those for $q=1$ and $q=2$ were derived from the constants of $q=0$ [14]. The results are given in Table 3.

For the analysis of the torsional fine structure of the excited states we used a modified principal axis method (PAM) [13]. The invariance group of the Hamiltonian is $C_3^- \otimes C_{3v}^+$ [15].

As both excited states were measured, the potential barrier V_3 and the top-top coupling parameter V_{12}' could be determined. Also the direction cosines $\lambda_g = \cos \sphericalangle (i, g)$ between the internal rotation axis i and the principal inertia axes $g = a, b, c$ were found to be determinable in the form $\lambda_\pm = \lambda_a \pm \lambda_b$.

The sum of the squares of the direction cosines of the three angles is fixed to 1. Because of the high correlation with V_3, the moment of inertia of the methyl tops I_α was fixed to 3.165 uÅ^2 according to the value of CEB and TEB [1].

The internal rotation analysis of both excited states was made simultaneously with one set of fixed rotational constants. They were taken as the average values of the two excited states. Only the frequency splittings $\Delta\nu$ of the torsional multiplets were taken into account.

In Table 4 the results are compared with the values of the two dimethyloxiranes investigated in [1] and propene oxide [16].

Discussion

The barrier hindering the internal rotation V_3 of the trans-2,3-dimethyloxirane is near the value of propane oxide. So one can consider the internal rotations of the two tops in TEB as independent. The higher value of V_3 of DMO can be explained from the steric interaction of the two tops, which is expressed by the magnitude of the parameter V_{12}' (ca. 10% of V_3).

Comparing the values of V_3 of the three dimethyloxiranes, the relatively low barrier of cis-2,3-dimethyloxirane is remarkable. This was pointed out by Emptage [3]. His explanation is, that the minimum energy of the potential function of CEB is raised by the repulsion of the H-atoms in the equilibrium configuration, but the values of maximum energy of the potential function of TEB and CEB are equal. This brings about a smaller difference between minimum and maximum energy and consequently a lower barrier height of CEB.

To give a more detailed explanation of this observation the higher terms of the potential function must be determined.

Molecule		DMO	CEB	TEB	Propene oxide
V_3	(kJ/mol)	11.3120(90)	6.912(22)	10.318(22)	10.72(29)
V_3	(kcal/mol)	2.6896(11)	1.6509(6)	2.4644(2)	2.560(70)
V'_{12}	(kJ/mol)	1.059(32)	[0]	[0]	–
I_a	(amuÅ^2)	[3.165]	3.165(10)	3.165(7)	3.194
$\measuredangle(i,a)$	(deg.)	58.60(39)	56.61(6)	23.20(29)	26.9
$\measuredangle(i,b)$	(deg.)	32.78(38)	42.29(6)	78.88(55)	89.7
$\measuredangle(i,c)$	(deg.)	81.53(19)	67.22(11)	69.91(31)	63.1
F	(GHz)	165.68	165.44(50)	172.15(43)	175.56
s	–	76.05(70)	46.54(30)	66.75(35)	67.93
σ	(kHz)	20	6	6	–

Table 4. Internal rotation parameters of 2,2-dimethyloxirane (DMO), compared with cis-2,3-dimethyloxirane (CEB) [1], trans-2,3-dimethyloxirane (TEB) [1], and propene oxide [16].

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