High Resolution Microwave Spectroscopy of Ethyl Vinyl Ether: Accurate Determination of the Methyl Top Internal Rotation Barrier

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We have performed an investigation of the internal rotation of the methyl group in *trans-cis* ethyl vinyl ether by using molecular beam-Fourier transform Microwave (MB-FTMW) spectroscopy. Rotational spectra (up to $J = 20$) were recorded in the frequency region 4 - 19 GHz. Due to the internal rotation of the methyl group, some rotational transitions were split and the torsional barrier could be determined to $V_3(CH_3) = 1074.4(4)\ cm^{-1}$.

Key words: Molecular Beam; Microwave Spectroscopy; Internal Rotation.

Introduction

During efforts to observe the vinoxy radical, CH_2=CHO, by molecular beam-Fourier transform microwave spectroscopy (MB-FTMW) [1], we noticed that rotational transitions with low angular momentum quantum number J of the precursor ethyl vinyl ether, CH_3CH_2-O-CH=CH_2, showed narrow splittings.

The rotational spectrum was first investigated by Owen and Sørensen [2] with Stark spectroscopy initiated by a work on the IR-spectrum and rotational isomerism by Owen and Sheppard [3]. Owen and Sørensen determined the barrier to methyl internal rotation V_3 from two excited vibrational states and from high J and K transitions of the ground state. They mentioned an interaction of the two excited states perturbing the evaluation of the barrier, which has been observed also in other cases [4].

In 1981 Durig and Gerson [5] published data on the methyl internal rotation derived from the far infrared spectrum.

Finally, Hayashi and Inada [6] published in 1994 the investigation of nine deuterated isotopomers in addition to the parent isotopomer. The information was used to determine a structure of the molecule by a method proposed by Nössberger, Bauder, and Günthard [7].

They confirmed that the *trans-cis* isomer (*trans* with respect to the CH_2-O bond and *cis* with respect to the O-CH bond) has been observed by Owen and Sørensen. In Fig. 1 we reproduce this isomer. In [6] no splittings of the lines have been reported.

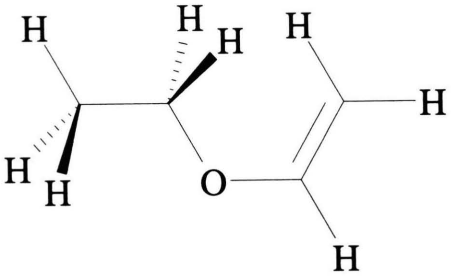

Fig. 1. Conformation of ethyl vinyl ether, CH_3CH_2-O-CH=CH_2.

The mentioned observation of line splittings initiated our reanalysis of the rotational spectrum by MB FTMW spectroscopy, which is superior in resolution, precision and sensitivity to older techniques.

Experimental

We used in an initial state of the work a MB-FTMW spectrometer equipped for laser photolysis in the range from 8 to 26 GHz [8]. Most measurements have been made by an improved MB-FTMW spectrometer in the range from 4 to 19 GHz with a novel layout of the microwave system [9]. More detailed information on the measuring process has been given in [10, 11].

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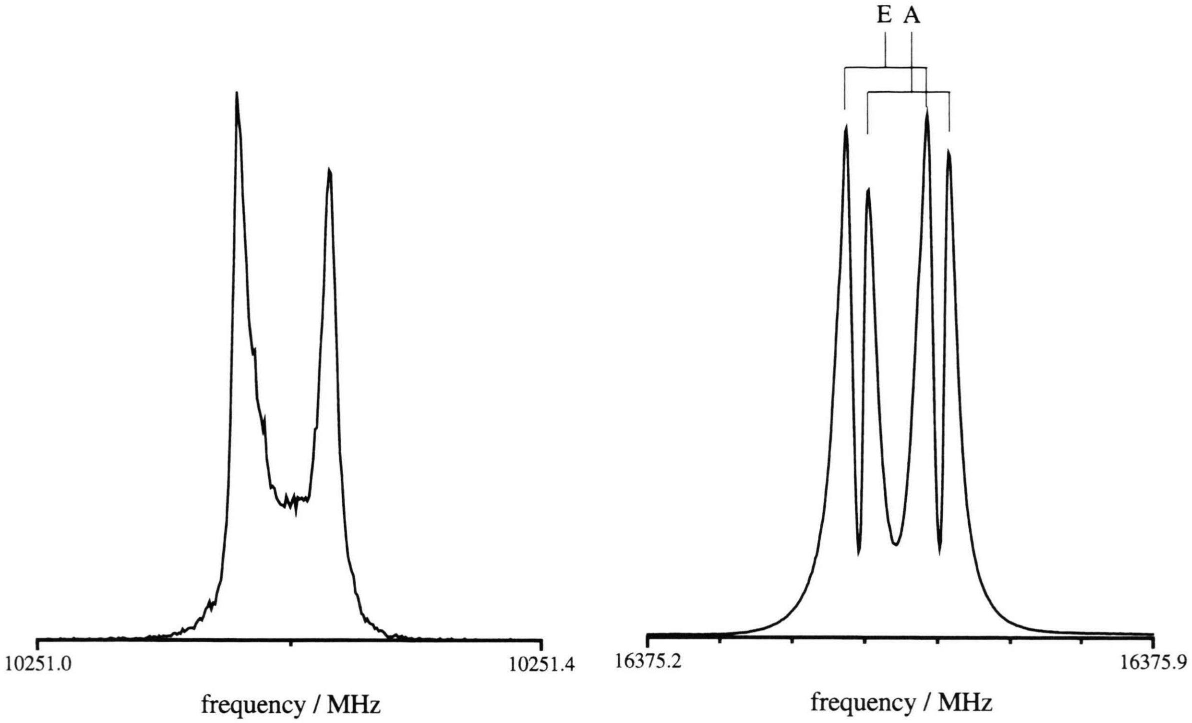

Fig. 2. *Left:* A 400 kHz section of the amplitude spectrum of the $J_{K-,K+} = 2_{1,2} - 1_{1,1}$ transition showing a Doppler splitting of 73.4 kHz. 40 ns sample intervall, 16 k data points, 1 averaging cycle, He as carrier gas at 1.4 bar, sample container in dry ice. *Right:* A 700 kHz section of the amplitude spectrum of the $J_{K-,K+} = 5_{1,4} - 5_{0,5}$ transition showing a Doppler splitting of 111 kHz and an internal rotation splitting of 21.0 kHz. 40 ns sample interval, 16 k data points, 2 k averaging cycles, He as carrier gas at 1.66 bar, sample container in dry ice.

The substance was used as received from Fa. Aldrich, Steinheim, and exposed to a stream of the rare gas in a vessel of stainless steel 10 cm upstream the beam nozzle. Helium, neon, and argon were used as carrier gas with backing pressures from 1.4 to 1.7 bar.

As the internal rotation splittings are less or roughly in the order of the splittings of the Doppler doublets of the lines, the rare gas was selected in a way that an overlapping is minimized.

Most measurements were made with 40 ns sample interval and 16 k data points in the time domain or 100 ns sample interval and 8 k data points, resulting in a point distance of 1.5 kHz or 1.2 kHz respectively in the frequency domain. The number of averaging cycles varied between 1 and 4096 cycles. The polymerization of the substance interferes with a proper performance of the nozzle. Cooling the sample container by ice or dry ice reduced this effect. In dealing with such narrow splittings we fitted the rotational frequencies directly to the time domain MB-FTMW data instead of using the values derived from the amplitude spectrum. In this way, distortions observed in the spectrum when treating such multiplets could be avoided [12 - 15]. The differences between the frequencies from the time domain fit and those resulting from the power or amplitude spectrum were of the same order of magnitude as the estimated experimental uncertainties. The fitted time domain data were used throughout this analysis to derive the transition frequencies.

In Fig. 2a and 2b we present two recordings of the $J_{K-,K+} = 2_{1,2} - 1_{1,1}$ and $5_{1,4} - 5_{0,5}$ transitions.

The measured and refined frequencies of μ_a and μ_b-type are given in Table 1. They agree reasonably with the measurements of Owen and Sørensen supplied by Sørensen [16] and those of Table 1 of [6], if one considers the different accuracy of MB-FTMW and Stark spectroscopy.

Table 1. Measured rotational transitions with internal rotation splittings of *trans-cis* ethyl vinyl ether, CH_3CH_2-O-CH=CH_2. Γ characterizes the torsional state. $\Delta\nu$ gives the difference of the observed and calculated frequencies.

J	K_-	K_+	J'	K'_-	K'_+	Γ	ν_{obs}/MHz	$\Delta\nu$/kHz
1	0	1	0	0	0	A	5295.0240	0.6
						E	5295.0240	0.7
2	0	2	1	0	1	A	10583.7325	0.7
						E	10583.7325	0.8
2	1	1	1	1	0	A	10928.8935	–0.2
						E	10928.8935	–0.2
2	1	2	1	1	1	A	10251.1960	0.5
						E	10251.1960	0.5
3	0	3	2	0	2	A	15859.8255	0.1
						E	15859.8255	0.3
3	1	2	2	1	1	A	16389.3305	0.1
						E	16389.3305	0.1
3	1	3	2	1	2	A	15372.8661	–0.2
						E	15372.8661	0.0
3	2	2	2	2	1	A	15885.0820	1.9
						E	15885.0861	–0.5
6	1	5	6	1	6	A	7109.4488	1.4
						E	7109.4488	0.7
1	1	1	0	0	0	A	18785.1231	0.0
						E	18785.1002	–1.8
1	1	0	1	0	1	A	13828.9490	–1.8
						E	13828.9297	–0.2
2	1	1	2	0	2	A	14174.1102	–2.5
						E	14174.0933	1.5
3	1	2	3	0	3	A	14703.6186	0.8
						E	14703.5961	–0.9
3	2	2	4	1	3	A	18120.7803	–0.4
						E	18120.7169	–0.2
4	0	4	3	1	3	A	8446.4744	0.7
						E	8446.4958	1.4
4	1	3	4	0	4	A	15431.3920	0.2
						E	15431.3716	0.5
4	2	3	5	1	4	A	12002.2219	–0.3
						E	12002.2850	0.3
5	0	5	4	1	4	A	14306.0302	0.5
						E	14306.0509	0.6
5	1	4	5	0	5	A	16375.5566	0.4
						E	16375.5356	–0.2
5	2	4	6	1	5	A	5729.4443	0.0
						E	5729.5067	0.3
6	1	5	6	0	6	A	17557.7952	–0.2
						E	17557.7753	–0.1
7	1	6	7	0	7	A	19002.2930	0.6
						E	19002.2722	–0.7
8	1	7	7	2	6	A	7255.4284	0.2
						E	7255.4895	–0.6
8	3	6	9	2	7	A	19100.1387	0.6
						E	19100.0324	–0.1
9	1	8	8	2	7	A	13952.2631	–0.7
						E	13952.3242	–1.3
9	3	7	10	2	8	A	13092.4616	0.1
						E	13092.3561	–0.5
10	3	8	11	2	9	A	6886.8704	–0.4
						E	6886.7652	–0.3
14	2	12	13	3	11	A	13046.0308	0.5
						E	13046.1379	–1.1
14	4	11	15	3	12	A	14362.6788	0.8
						E	14362.5348	0.0
19	3	16	18	4	15	A	10310.6345	0.2
						E	10310.7796	–0.6
19	5	15	20	4	16	A	15218.5511	0.8
						E	15218.3644	–1.2
20	3	17	19	4	16	A	16996.8644	1.3
						E	16997.0109	–0.6

Table 2. Rotational constants, centrifugal distortion (Watson S reduction) and internal rotation parameters fitted and derived from the fitted values $B_J = (B + C)/2$, $B_K = A - (B + C)/2$, and $B = (B - C)/2$. n number of internal rotation doublet components, σ standard deviation, F internal rotation constant, V_3 barrier height, for ρ, and γ see [10]. In brackets errors in units of the last digit. In square brackets assumed or derived values from assumed parameters.

	This work	[2][a]	[5]	[6]
rotational constants:				
A / MHz	16307.0564(2)	16307.085(7)		16307.044(5)
B / MHz	2817.02598(5)	2816.9430(13)		2816.925(1)
C / MHz	2477.99924(6)	2478.0885(12)		2478.082(1)
centrifugal distortion constants (Watson S reduction):				
D_J / kHz	0.469(1)	0.479(3)		
D_{JK}/kHz	–2.29(1)	–2.208(52)		
D_K / kHz	37.08(2)	37.03(14)		
d_1 / kHz	0.0821(2)	0.08218(38)		
d_2 / kHz	–0.00178(8)	0.515(76)		
hindering potential for the internal rotation of the methyl group:				
V_3 / cm^{-1}	1074.4(4)	1074(9)	1199.7	
V_6 / cm^{-1}			–120.6	
s	81.683			
F / GHz	[175.253]		179.2	
I_α / uÅ^2	[3.193]	[3.193]		
$\angle(a, i)$ /°	[15.4]	[15.4]		
$\angle(b, i)$ /°	90	[90]		
fit properties:				
n	64	106		17
σ / kHz	0.9	87		14

[a] Owen and Sørensen set up the Hamiltonian using Watson's A reduction.

Analysis

The analysis has been performed on the basis of the rigid top-rigid frame model for the internal and overall rotation of an asymmetric top supplemented by fourth order centrifugal distortion in the form of Watson's S reduction [17]. The general internal rotation theory is described in detail in [18 - 22]. The program XIAM of Hartwig [23] has been used. The method of evaluation has been described in more detail in [24]. In principle the Hamiltonian matrix is set up in the principal axes and ρ axis systems and diagonalized.

The frequencies of the components of Table 1 have been fitted with an RMS deviation of less than 1 kHz. The measurements of [6] and [16] have not been included, as the precision of the data differs.

The fitted and derived parameters are given in Table 2 and compared with data from the literature. Unfortunately the moment of inertia I_α of the methyl top and the angle between the internal rotation axis i and the a principal inertia axis $\angle(i, a)$ could not be determined from the spectra. The same situation occurs for not obvious reasons for other molecules [25]. In accordance with [2] it was assumed that

$$I_\alpha = 3.193 \text{ u}\mathring{\text{A}}^2 \text{ and } \angle(i, a) = 15.4°.$$

It should be mentioned that the internal rotation analysis is consistent with the statement in [2] and [6] that the heavy atoms are in plane, which is indicated by the value $\gamma = 0°$. And what is more, we fitted the experimental data with an initial value of $\gamma \neq 0°$ but γ converged to zero. This confirms the assumption, that the heavy atoms are in plane, and therefore γ was fixed to zero in the final fit.

From Table 2 it can be seen, that the values V_3 of [2] and the present work agree rather well. The values of [5] differ presumably as $V_6 = -120.6$ cm^{-1} was included in the analysis of the IR-data. The values obtained by MB-FTMW spectroscopy are more precise, indicating in addition that the molecular model works sufficiently well for rotational spectra in the vibrational ground state.

In Table 3 we compare parameters of methyl internal rotation of related molecules of the type CH_3CH_2O-X. The barrier values agree in a range of 250 cal/mol, which indicates that the influence of the substituent X is small. It should also be mentioned that the data of Table 3 result from different methods.

Table 3. Comparison of the methyl top internal rotation parameters of molecules of type CH_3CH_2-O-X. 1 cm^{-1} ≡ 2.859 cal/mol.

	s	V_3 / cm^{-1}	F / GHz
trans CH_3CH_2OH [26]		1158	
trans $CH_3CH_2OCD_3$ [27]	79.74(270)	1153(35)	192.486
$CH_3CH_2OCH_2F$ [28]	84.33	1102(17)	174.12
cis-trans CH_3CH_2ONO [29]	81.037	1082(2)	177.0
trans-cis $CH_3CH_2OCH{=}CH_2$ [this work]	81.683	1074.4(4)	175.253

Conclusion

We demonstrated that the determination of higher barriers to internal rotation is successful. The high resolution and precision of MB-FTMW spectroscopy provides the possibility. The sensitivity of the method, illustrated in Fig. 2, promises that the ^{13}C and ^{18}O isotopomers may be investigated in natural abundance. As the MB-FTMW spectroscopy usually enhances the observability of the most stable conformer, the present work confirms statements given in [2] and [6].

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