The Millimeter and Submillimeter-Wave Spectrum of Dimethylether

W. Neustock and A. Guarnieri

Abteilung Chemische Physik, Institut für Physikalische Chemie der Universität Kiel, West Germany

J. Demaison and G. Wlodarczak

Laboratoire de Spectroscopie Hertzienne associé au C.N.R.S., Université de Lille I, France

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We report the analysis of the rotational spectrum of dimethylether measured between 60 and 400 GHz. Rotational and quartic centrifugal distortion constants are given. Internal rotation splittings are analysed with the IAM method. The value of I_α is compared to the values obtained for similar molecules.

Introduction

Dimethylether was the first two-tops molecule whose microwave spectrum was analyzed taking into account the internal rotation effects: the microwave spectrum of dimethylether was first studied by Kasai and Myers [1] who assigned some low J transitions of $(CH_3)_2O$ and $(CD_3)_2O$. These authors extended their measurements to transitions with $J<6$ for normal species and isotopic species [2]. They determined a structure of the molecule and measured the dipole moment ($\mu_b=1.302(1)$ D). Further studies of normal and deuterated species $(CD_3)_2O$ and CH_3OCD_3 in the ground state and the first and second excited torsional states were carried out by different groups in the frequency range 10–40 GHz [3–8]. The internal rotation was analyzed with the PAM method, and the potential barrier V_3 as well as the top-top coupling term V'_{12} were determined. A complete analysis of all existing data for the ground state of $(CH_3)_2O$, which includes new measurements in the millimeter-wave range (40–105 GHz), was made by Lovas, Lutz, and Dreizler [9]. Internal rotation analysis was made by the IAM method and a centrifugal distortion analysis was performed for the first time. The rotational Zeeman effect has been investigated on dimethylether by Benson and Flygare [10].

Dimethylether was also detected in the interstellar medium, first in Orion A [11] and then in $SgrB_2$ [12]. These detections were then confirmed by a more detailed search in these two molecular clouds [13]. Lovas, Lutz, and Dreizler [9] published a list of predicted frequencies up to 300 GHz for transitions with $J<16$, allowing the identification of many lines of dimethylether in the various millimeter-wave surveys of Orion A and $SgrB_2$ [14–16].

The aim of this work is to extend the previous ground state measurements to the millimeter and submillimeter frequency range and to improve the accuracy of the derived molecular constants. Another goal of this work is to determine experimentally the moment of inertia I_α of the methyl top. In the previous studies its value has always been kept fixed to a value calculated from the structure. It is well known that the structure of a methyl group is difficult to obtain with accuracy. On the other hand from the analysis of the internal rotation splittings it is often possible to determine I_α with good accuracy if the barrier is not too high.

Experimental Details

The sample of dimethylether was obtained from Fluka AG. (Buchs–Switzerland) and was used without further purification. The lines between 60 and 120 GHz were measured with the millimeter-wave spectrometer in Kiel [17]. The higher frequency measurements were performed in Lille. The millimeter- and submillimeter-wave spectrometers are described elsewhere [18, 19]. The accuracy of the measurements is typically 50 kHz. The measured frequencies are reported in Table 1.

Reprint request to Dr. G. Wlodarczak, Laboratoire de Spectroscopie Hertzienne, Bat. P5, Université de Lille I, F 59655 Villeneuve d'Ascq Cedex, France.

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Table 1. Measured rotational frequencies of dimethylether in the ground vibrational state.

J	K_-	K_+	J'	K'_-	K'_+	$\Gamma\Gamma'$	Exp. freq. (MHZ)	Unpert. freq. (exp.-calc.)	Exp. splitting (MHz)	Splitting (exp.-calc.)
3	3	1	4	2	2	AA	70 321.083	0.576		
3	3	1	4	2	2	EE			8.789	0.300
3	3	1	4	2	2	AE			18.404	1.050
3	3	1	4	2	2	EA			7.930	0.726
3	3	0	4	2	3	AA	70 844.458	0.071		
3	3	0	4	2	3	EE			−1.207	0.076
3	3	0	4	2	3	EA			7.138	−0.071
4	3	2	3	2	1	AA	222 254.582	−0.062		
4	3	2	3	2	1	EE			7.124	0.029
4	3	2	3	2	1	AE			15.669	−0.280
4	3	1	3	2	2	AA	222 433.706	0.011		
4	3	1	3	2	2	AE			−1.673	−0.438
5	0	5	4	1	4	AA	70 118.840	−0.058		
5	0	5	4	1	4	EE			−0.642	0.030
5	0	5	4	1	4	AE+EA			−1.291	0.053
5	1	5	4	0	4	AA	115 545.679	−0.040		
5	1	5	4	0	4	EE			0.847	0.025
5	1	5	4	0	4	AE+EA			1.709	0.065
6	2	4	5	1	5	AA	212 751.971	0.119		
6	2	4	5	1	5	EE			2.974	0.260
6	2	4	5	1	5	EA			5.648	0.206
7	4	4	7	3	5	AA	204 940.741	−0.114		
7	4	4	7	3	5	EE			7.716	−0.160
7	4	4	7	3	5	AE			15.866	−0.272
8	4	5	8	3	6	AA	204 847.175	−0.088		
8	4	5	8	3	6	EE			6.535	−0.124
8	4	5	8	3	6	EA			7.482	−0.133
8	4	5	8	3	6	AE			14.543	−0.225
9	4	5	9	3	6	AA	204 160.063	−0.078		
9	4	5	9	3	6	EE			2.229	−0.004
9	4	5	9	3	6	EA			7.315	−0.123
9	4	5	9	3	6	AE			2.229	−0.423
9	4	6	9	3	7	AA	204 741.765	0.004		
9	4	6	9	3	7	EE			5.181	−0.019
9	4	6	9	3	7	EA			7.375	−0.053
9	4	6	9	3	7	AE			12.085	−0.129
9	2	8	9	1	9	AA	115 077.722	0.128		
9	2	8	9	1	9	EE			2.810	0.025
9	2	8	9	1	9	AE+EA			5.620	0.050
9	1	8	9	0	9	AA	63 297.989	−0.021		
9	1	8	9	0	9	EE			1.379	−0.004
9	1	8	9	0	9	AE+EA			2.756	−0.010
10	4	6	10	3	7	AA	203 573.141	0.022		
10	4	6	10	3	7	EE			2.931	−0.030
10	4	6	10	3	7	EA			7.120	−0.114
10	4	6	10	3	7	AE			4.700	−0.063
11	4	7	11	3	8	AA	202 726.330	0.026		
11	4	7	11	3	8	EE			3.209	−0.004
11	4	7	11	3	8	EA			6.982	−0.026
11	4	7	11	3	8	AE			5.822	−0.038
11	4	8	11	3	9	AA	204 556.360	−0.044		
11	4	8	11	3	9	EE			3.741	−0.043
11	4	8	11	3	9	EA			6.885	−0.101
11	4	8	11	3	9	AE			8.051	−0.083
11	3	8	10	2	9	AA	361 877.701	−0.136		
11	3	8	10	2	9	EE			3.278	−0.013
11	3	8	10	2	9	AE+EA			6.544	−0.058
12	4	9	12	3	10	AA	204 524.862	−0.007		
12	4	9	12	3	10	EE			3.464	−0.037
12	4	9	12	3	10	EA			6.690	−0.041
12	4	9	12	3	10	AE			7.204	−0.066
12	0	12	11	1	11	AA	212 756.041	−0.093		
12	3	10	11	2	9	AA	359 387.657	−0.054		
12	3	10	11	2	9	EE			3.032	−0.030
12	3	10	11	2	9	AE+EA			6.102	−0.010
12	3	9	11	2	10	AA	383 955.616	0.052		

Table 1 (continued)

J	K_-	K_+	J'	K'_-	K'_+	$\Gamma\Gamma'$	Exp. freq. (MHZ)	Unpert. freq. (exp.-calc.)	Exp. splitting (MHz)	Splitting (exp.-calc.)
12	3	9	11	2	10	EE			3.228	0.009
12	3	9	11	2	10	AE+EA			6.416	−0.032
12	2	10	11	1	11	AA	382 333.893	−0.158		
12	2	10	11	1	11	EE			3.319	−0.026
12	2	10	11	1	11	AE+EA			6.615	−0.075
12	1	12	11	2	9	AA	68 986.627	−0.042		
12	1	12	11	2	9	EE			−3.026	−0.029
12	1	12	11	2	9	AE+EA			−6.045	−0.050
13	4	10	13	3	11	AA	204 579.137	0.013		
13	4	10	13	3	11	EE			3.299	0.003
13	4	10	13	3	11	AE+EA			6.674	−0.042
13	3	11	12	2	10	AA	373 470.195	0.099		
13	3	11	12	2	10	EE			2.887	−0.013
13	3	11	12	2	10	AE+EA			5.720	−0.080
14	4	11	14	3	12	AA	204 761.738	0.049		
14	4	11	14	3	12	EE			3.134	0.021
14	4	11	14	3	12	AE+EA			6.232	0.076
14	3	12	13	2	11	AA	386 800.237	−0.114		
14	3	12	13	2	11	EE			2.512	−0.212
14	3	12	13	2	11	EA			5.434	−0.013
14	3	11	13	4	10	AA	68 779.306	0.698		
14	3	11	13	4	10	EE			−3.103	0.103
14	3	11	13	4	10	EA			−6.175	0.100
14	3	11	13	4	10	AE			−6.175	0.382
15	4	12	15	3	13	AA	205 121.288	0.215		
15	4	12	15	3	13	EE			2.982	0.045
15	4	12	15	3	13	EA			6.568	0.730
16	2	14	15	3	13	AA	203 624.994	0.141		
16	2	14	15	3	13	EE			−1.832	−0.028
16	2	14	15	3	13	AE+EA			−3.657	−0.048
16	3	13	16	2	14	AA	115 295.577	−0.027		
16	3	13	16	2	14	EE			1.994	0.047
16	3	13	16	2	14	AE+EA			3.986	0.093
17	3	15	16	4	12	AA	115 775.994	0.032		
17	3	15	16	4	12	EE			−2.587	−0.014
17	3	15	16	4	12	AE+EA			−5.166	−0.020
17	4	13	16	5	12	AA	63 930.711	0.097		
17	4	13	16	5	12	EE			−2.739	0.037
17	4	13	16	5	12	AE			−5.803	0.085
17	4	13	16	5	12	EA			−5.134	0.075
18	2	16	18	1	17	AA	114 007.004	0.039		
18	2	16	18	1	17	EE			1.560	0.027
18	2	16	18	1	17	AE+EA			3.122	0.055
20	4	17	20	3	18	AA	211 497.507	0.086		
20	4	17	20	3	18	EE			2.090	0.059
20	4	17	20	3	18	AE+EA			4.178	0.115
20	3	17	19	4	16	AA	214 360.532	0.319		
20	3	17	19	4	16	EE			−1.846	−0.070
20	3	17	19	4	16	AE+EA			−3.693	−0.141
21	1	20	21	0	21	AA	213 461.628	0.229		
21	1	20	21	0	21	EE			4.007	0.100
21	1	20	21	0	21	AE+EA			7.990	0.177
21	4	18	21	3	19	AA	214 072.572	0.022		
21	4	18	21	3	19	EE			1.914	0.064
21	4	18	21	3	19	AE+EA			3.830	0.130
21	2	20	21	1	21	AA	222 037.059	−0.156		
21	2	20	21	1	21	EE			4.117	0.111
21	2	20	21	1	21	AE+EA			8.225	0.212
22	4	19	22	3	20	AA	217 193.170	−0.031		
22	4	19	22	3	20	EE			1.746	0.072
22	4	19	22	3	20	AE+EA			3.493	0.146
23	4	20	23	3	21	AA	220 895.000	−0.076		
23	4	20	23	3	21	EE			1.589	0.0.85
23	4	20	23	3	21	AE+EA			3.185	0.178
24	4	20	23	5	19	AA	220 846.525	−0.332		
24	4	20	23	5	19	EE			−1.116	−0.058
24	4	20	23	5	19	AE+EA			−2.239	−0.123

Table 2. Ground state molecular constants of dimethylether.

		This work	Ref. [9]
A	(MHz)	38 788.1768 (89)[a]	[b]
B	(MHz)	10 056.4742 (20)	
C	(MHz)	8 886.8263 (25)	
Δ_J	(kHz)	9.0641 (51)	
Δ_{JK}	(kHz)	−26.833 (30)	
Δ_K	(kHz)	342.18 (27)	
δ_J	(kHz)	1.77032 (92)	
δ_K	(kHz)	−14.183 (54)	
V_3	(cal. mol^{-1})	2 700.000 (80)	2583.000 (20)
I_α	(u. Å^2)	3.2626 (66)	3.2267[c]
$\alpha(b, i)$	(°)	59.000 (89)	57.794 (10)

[a] Standard deviation in parentheses, shown in units of the last digit.
[b] Rotational and distortion constants from a fit of AA lines are given in [9] and are not directly comparable to our parameters.
[c] Fixed to a value calculated from the structure.

Table 3. Methyl top moment of inertia for dimethylether and related molecules.

Molecule	I_α (u. Å^2)	Ref.
Mean value	3.197 (37)	[23]
CH_3OCH_3	3.26265 (66)	this work[a]
CH_3OCCH	3.328 (2)	[24][a]
$HCOOCH_3$	3.239 (9)	[25][a]
$CH_3OCH_2CH_2OH$	3.24 (5)	[26][a]
$CH_3OCH_2CH_2NH_2$	3.23 (3)	[27][a]
CH_3OCH_2F	3.250	[28][b]
CH_3OCH_2Cl	3.312	[29][b]
CH_3OCH_2CN	3.207	[30][b]
CH_3OCH_2CCH	3.3872	[31][b]
$CH_3OCH_2SiH_3$	3.2064	[32][b]
CH_3OCHCH_2	3.2266	[33][b]
CH_3ONO	3.261 (26)	[34][b]

[a] Value determined from the analysis of experimental A-E splittings.
[b] Value calculated from the structure.

Analysis

Dimethylether belongs to the symmetry point group C_{2v}, the C_2 axis being the axis of the intermediate moment of inertia. The two methyl groups are then equivalent and the rotation-internal rotation hamiltonian is invariant under the operations of the group $C_{3v} \cdot C_{3v}$ [20, 21]. Each ground state transition is split into four components labelled AA:EE:AE:EA, the relative intensities of which depend on the parity of the $K_- K_+$ labels, 6:16:4:2 for the ee-oo transitions and 10:16:4:6 for the eo-oe transitions. The constants of Lovas et al. [9] were used for the first prediction of the spectrum. The predicted splittings and the relative intensities of the components were a great help in the analysis.

The splittings were first fitted to internal rotation parameters (w_1 (s), I_α, and θ), the rotational constants being kept fixed. These calculations were made with an IAM hamiltonian originally written by Woods and modified by Kasten [22]. The internal rotation contributions were then subtracted from the experimental frequencies, and the unperturbed frequencies were fitted to a rigid rotor hamiltonian (Watson's A reduction, I^r representation). This two-step procedure was repeated until convergence was reached. The data from (9) were also included in our analysis. The derived parameters are reported in Table 2 and compared with the previous values from Lovas et al. [9].

The quality of our fit allows us to predict the ground state rotational transitions of dimethylether up to 400 GHz for higher J values and with a better accuracy than the previous studies. This might be of interest for radioastronomers in the assignment of interstellar lines in the millimeter and submillimeter domain.

I_α is determined for the first time with accuracy. Its value is higher than the values used in the previous internal rotation analyses. This high value of I_α may be compared with that found for other ethers or esters, see Table 3. It appears that in all cases $I_\alpha(CH_3-O)$ is higher than the mean value $I_\alpha = 3.197$ u.Å^2 obtained from the analysis of 48 molecules with internal methyl rotors [23]. These high values of I_α can be explained by a trans effect of the lone pairs of electrons of the oxygen atom. The C–H bonds which are in a trans position to the lone pairs are weakened, i.e. the corresponding bond lengths are increased and the methyl group becomes asymmetric. For dimethylether we have $\Delta r(Ha-Hs) = 0.010$ Å, a value obtained from the correlation relation between r(C–H) and the frequency of the stretching mode of the C–H bond (35). This value is further confirmed by ab initio calculations. The order of magnitude of this effect is in good agreement with our experimental value of I_α.

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