Torsion-Torsion Interaction in the Microwave Spectrum of Dimethylether

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We report an analysis of the torsional fine structure of rotational lines of $(CH_3)_2O$ in excited torsional states leading to the potential parameters V_3 and V'_{12} of a Hamiltonian for the overall- and internal rotation.

The microwave rotational spectrum of dimethylether, $(CH_3)_2O$, was recorded in the region from 8 to 40 GHz with a conventional microwave spectrometer[1, 2] equipped with an 8 m-absorption cell and employing 33 kHz-Stark-modulation. The sample pressure was about 10 mT and the temperature approximately $-50\,^\circ C$. The $(CH_3)_2O$ was supplied by Fluka GmbH, Neu-Ulm.

The ground state spectrum of $(CH_3)_2O$ has been assigned earlier[3]. Additional lines of the ground state were measured by F. J. Lovas[4], as the molecule is of radioastronomic interest. We measured six rotational transitions, which appear as quartets of both the excited torsional states $\tilde{v} = 1_1$ and $\tilde{v} = 1_2$[5]. They are given in Table 1. The Hamiltonian for the torsion and overall rotation is invariant to the group $C_{3v}^{-} \otimes C_{3v}^{+}$[6, 7]. The torsional substates may be specified by the group $C_{3v}^{-} \otimes C_{3v}^{+}$ as follows:

$$\tilde{v} = 1_1 : \bar{\sigma} : A_1A_2\,, EE, A_1E, EA_2\,,$$
$$\tilde{v} = 1_2 : \bar{\sigma} : A_1A_2\,, EE, A_2E, EA_1\,.$$

The spin statistical weights of the components of the measured quartets result as[5–7]:

$$\begin{array}{ccccccccccccccl}
A_1A_2 & : & A_2A_1 & : & EE & : & A_1E & : & A_2E & : & EA_2 & : & EA_1 & & \\
6 & : & 10 & : & 16 & : & 2 & : & 2 & : & 4 & : & 4 & & \text{for } K_- K_+ = \text{ee} \longleftrightarrow \text{oo-} \quad \text{and} \\
10 & : & 6 & : & 16 & : & 6 & : & 6 & : & 4 & : & 4 & & \text{for } K_- K_+ = \text{eo} \longleftrightarrow \text{oe-}
\end{array}$$

transitions.

The assignment of the quartet lines was made by their Stark-effect and by observing the intensity ratio given by the spin weights. Furthermore transitions in the torsional state $\tilde{v} = 1_1$ appeared stronger in intensity than those of $\tilde{v} = 1_2$.

The rotational constants of the A_iA_j-species rototional lines for both excited states are calculated by a least square fit using rigid rotor approximation. Only lines up to $J = 4$ were used. The results are given in Table 2. Similar measurements on $(CD_3)_2O$ were reported recently[8].

The analysis of the torsional fine structure is based on a Hamiltonian given in[5]. As adjustable parameters were taken the hindering potential V_3, the potential interaction parameter V_{12}' and the angle ϑ between the methyl top and the b axis. The numerical evaluation used a computer program MELIT, written by Trinkaus[5] and Tan, which we adapted to the TR 440 of the Hamburg and the PDP 10 of the Kiel computer center. The v-diagonalisation is made to second order by a van Vleck-transformation aiming at the combined $\tilde{v} = 1_1$ and $\tilde{v} = 1_2$ torsional submatrix. The effective rotational hamiltonian matrix is diagonalised by a Householder procedure. The least square fit was made to the experimental splittings $\Delta\nu\,(EE - A_iA_j)$, $\Delta\nu\,(A_iE - A_iA_j)$, and $\Delta\nu\,(EA_j - A_iA_j)$ simultaneously. The parameters are given in Table 3, the calculated $\Delta\nu$ in Table 1. The accuracy of the calculation was checked by variing the number of torsional basis functions according to Trinkaus et al.[5]. The fit was made with $v_{\max} = 8$. Using the resulting parameters the mean square deviation of the splittings does not improve significantly when using $v_{\max} = 9$. The correlation of the three fitted parameters is low.

When we had finished this work we noticed an independent work of Hayashi and Imachi[9]. Their V'_{12} value, calculated by an approximation proposed by Hoyland[10], agrees with ours in the error limit, the V_3 values are different. But we believe that our analysis of the torsional fine structure and the evaluation of V_3 and V'_{12} is less approximative, as we used the complete Hamiltonian. The results of this work differ also from those given in[8] as the approximation of the evaluation procedure and the selection of torsional states is different. The differences exceed the standard errors.

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Tab. 1. Rotational transitions of $(CH_3)_2O$ in the excited torsional states $\tilde{v}=1_1$ and $\tilde{v}=1_2$. $\bar{\sigma}$ indicates the torsional substate $\Gamma\Gamma'$. * AA stands for A_1A_2 or A_2A_1. Standard deviation of splittings of 0.16 MHz.

$J_{K_-K_+}-J'_{K'_-K'_+}$	$\tilde{v}$	$\bar{\sigma}$	exp. frequency [MHz]	exp. splitting $\Delta\nu_{\mathrm{exp.}}=$ $\nu_{\Gamma\Gamma'}-\nu_{\mathrm{AA}}$* [MHz]	calc. splitting $\Delta\nu_{\mathrm{calc.}}$ [MHz]	error $\Delta\nu_{\mathrm{exp.}}-$ $\Delta\nu_{\mathrm{calc.}}$ [MHz]
$1_{01}-1_{10}$	1_1	A_1A_2	29 929.979	0.0		
		EE	29 957.060	27.081	27.05	0.03
		A_1E	29 977.927	47.978	47.74	0.24
		EA_2	29 990.262	60.283	60.38	−0.10
	1_2	A_2A_1	29 900.276	0.0		
		EE	29 926.222	25.944	25.82	0.12
		A_2E	29 946.153	45.877	45.66	0.22
		EA_1	29 958.051	57.775	57.46	0.31
$2_{02}-2_{11}$	1_1	A_1A_2	31 121.932	0.0		
		EE	31 147.428	25.496	25.46	0.04
		A_1E	31 170.863	48.931	48.79	0.14
		EA_2	31 174.941	53.009	53.00	0.01
	1_2	A_2A_1	31 055.554	0.0		
		EE	31 079.945	24.391	24.35	0.04
		A_2E	31 102.353	46.799	46.70	0.10
		EA_1	—	—	—	—
$1_{11}-2_{02}$	1_1	A_1A_2	8 978.337	0.0		
		EE	8 959.123	−19.214	−19.16	−0.05
		A_1E	8 933.668	−44.669	−44.68	0.01
		EA_2	8 946.033	−32.304	−31.99	−0.32
	1_2	A_2A_1	8 917.192	0.0		
		EE	8 898.789	−18.403	−18.39	−0.01
		A_2E	8 874.392	−42.800	−42.70	−0.10
		EA_1	8 886.424	−30.768	−30.91	0.14
$2_{12}-3_{03}$	1_1	A_1A_2	28 890.842	0.0		
		EE	28 870.718	−20.124	−20.26	0.14
		A_1E	28 848.524	−42.318	−42.67	0.34
		EA_2	28 852.695	−38.147	−38.33	0.18
	1_2	A_2A_1	28 773.941	0.0		
		EE	28 754.634	−19.307	−19.41	0.11
		A_2E	28 733.355	−40.586	−40.79	0.21
		EA_1	28 737.363	−36.578	−36.81	0.23
$3_{03}-3_{12}$	1_1	A_1A_2	32 973.397	0.0		
		EE	32 999.106	25.709	25.70	0.01
		A_1E	33 023.837	50.440	50.37	0.07
		EA_2	33 025.766	52.369	52.41	−0.04
	1_2	A_2A_1	32 848.287	0.0		
		EE	32 872.879	24.610	24.63	−0.02
		A_2E	32 896.516	48.229	48.26	−0.03
		EA_1	32 898.396	50.109	50.19	−0.08
$4_{04}-4_{13}$	1_1	A_1A_2	35 558.525	0.0		
		EE	35 585.053	26.528	26.54	−0.01
		A_1E	35 611.021	52.496	52.48	0.02
		EA_2	35 612.063	53.538	53.64	−0.10
	1_2	A_2A_1	35 348.404	0.0		
		EE	35 373.746	25.342	25.46	−0.12
		A_2E	35 398.543	50.139	50.35	−0.21
		EA_1	35 399.572	51.168	51.45	−0.28

Tab. 2. Effective rotational constants of the torsional states $\tilde{v}=1_1$ and $\tilde{v}=1_2$ for $(CH_3)_2O$ calculated from lines up to J=4. The errors are standard errors of the fit.

$\tilde{v}=1_1$ Torsional symmetry species A_1A_2 .

$A = 38\,797.34 \pm 0.30$ MHz;
$B = 10\,024.95 \pm 0.05$ MHz;
$C = 8\,867.34 \pm 0.10$ MHz.

$\tilde{v}=1_2$ Torsional symmetry species A_2A_1 .

$A = 38\,770.43 \pm 0.30$ MHz;
$B = 9\,993.07 \pm 0.05$ MHz;
$C = 8\,870.13 \pm 0.10$ MHz.

Tab. 3. Internal rotation parameters for $(CH_3)_2O$. The values of the second column result from an analysis of ground state lines alone (without top-top interaction)[8]. The F values are different by theoretical reasons and influence the V_3 values considerably. * taken from [3]. ** assumed. Errors are three times standard errors.

V_3	2654 ±2	2561	cal/mole	Correlation		
s	59.90 ± 0.03	60.99		matrix		
V_{12}	0.0 **	—	cal/mole	s	ϑ	V_{12}'
V_{12}'	14 ±3	—	cal/mole	1	.76	−.28
I_α	3.2074 *	3.2074 *	amu Å²		1	.1
F	206.47	195.71	GHz			1
F'	−43.70	—	GHz			
ϑ	60.11 ± 0.3	57.9 ± 0.4	°			

made in the Rechenzentrum der Universität Hamburg on a Telefunken TR 440 computer. The final calculations were made with the PDP 10 of the Rechenzentrum der Universität Kiel. We gratefully acknowledge the financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemie.

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