A Contribution to the Microwave Spectrum of Dimethylether-D6 in Excited Torsional States

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(Z. Naturforsch. **30 a,** 1782 [1975];
received September 29, 1975)

A number of rotational transitions of $(CD_3)_2O$ in the excited torsional states $\tilde{v}=1_1$ and $\tilde{v}=1_2$ were recorded in the region from 8.0 to 40.0 GHz. The potential parameter V_3 and the angle α between the axis of internal rotation and the *b*-axis were fitted to line splittings. The results are $V_3=2545$ cal/mole and $\alpha=60.8°$.

The spectra were recorded in the region from 8.0 to 40.0 GHz with a conventional microwave spectrometer[1, 2] equipped with an 8m-absorption cell and employing 33 kHz Stark-modulation. The sample pressure was 10 mT and the temperature approximately $-50\ °C$. The $(CD_3)_2O$ was supplied by Isocommerz GmbH, Leipzig.

The ground state spectrum of $(CD_3)_2O$ has been assigned earlier, but only a few lines were measured. We recorded additional lines and remeasured those given in[3] with higher accuracy. A splitting due to internal rotation was not observable in the ground torsional state $\tilde{v}=0_0$[4]. The rotational constants determined from seven lines up to $J=3$ are $A=25\,696.17\pm0.11$, $B=7483.80\pm0.03$, $C=6798.01\pm0.06$ MHz.

About 20 rotational transitions of both excited torsional states $\tilde{v}=1_1$ and $\tilde{v}=1_2$[4] were observed as triplets or quartets. The components of these multiplets are characterized by the A_1A_2, EE, A_1E, EA_2 and A_2A_1, EE, A_2E, EA_1 species of the group $C_{3V}^{-}\otimes C_{3V}^{+}$. The assignment of the multiplets was made by use of the Stark-effect. Furthermore the transitions of the torsional state $v=1_1$ appeared stronger in intensity than those of $\tilde{v}=1_2$. The $[A_iA_j-(A_iE, EA_j)]$-splittings of the rotational transitions were different for both torsional states.

The rotational constants calculated for the A_1A_2- and A_2A_1-species of the $v=1_1$ and $v=1_2$ states using the rigid rotor approximation are given in Table 1. For both torsional substates the same set of seven rotational transitions up to $J=3$ was used.

Table 1. Effective rotational constants[5] of the torsional states $\tilde{v}=1_1$ and $\tilde{v}=1_2$ ($A_i\,A_j$-species) in MHz.

	$\tilde{v}=1_1$ $A_1\,A_2$	$\tilde{v}=1_2$ $A_2\,A_1$
A	25 701.73 ± 0.09	25 674.80 ± 0.09
B	7 466.97 ± 0.03	7 448.76 ± 0.03
C	6 785.67 ± 0.05	6 793.73 ± 0.05

The potential barrier V_3 and the angle α between the axis of internal rotation of a top and the *b*-axis were calculated for 16 lines, using the average[5] of the $[A_{ij}-(A_iE, EA_j)]$-splittings for $\tilde{v}=1_1$ and $\tilde{v}=1_2$. This calculation * used second and fourth order perturbation neglecting the potential interaction terms V_{12}' and V_{12}[4]. The value for I_α used in this calculation was taken from Blukis et al.[3]. The results are given in Table 2. Values for $(CH_3)_2O$ calculated with the same program are included for comparison. These values were determined from the ground state spectrum of $(CH_3)_2O$ in cooperation with Lovas[6].

Table 2. Internal rotation parameters.

	$(CD_3)_2O$ $\tilde{v}=1_1, 1_2$	$(CH_3)_2O$ $\tilde{v}=0_0$
V_3	2545 cal/mole	2561 cal/mole
α [a]	60.8° ± 0.4	57.9° ± 0.4
I_α [b]	6.42742 amu A^2	3.20740 amu A^2
s	109.91 ± 0.6	60.99 ± 0.3
F	107.94 GHz	195.71 GHz
α_{r_s} [c]		58.38° ± 0.7
$\frac{1}{2}\sphericalangle$ COC		55.86° ± 0.3 [3]

[a] Definition see text,

[b] From U. Blukis et al.[3],

[c] Same angle as α, but derived from the r_s-structure[3] of $(CH_3)_2O$.

Further work on the determination of the potential coupling parameters V_{12} and V_{12}', also for $(CH_3)_2O$, is in progress. To determine V_{12} we hope to assign higher excited torsional states, of which we already have observed several lines.

We thank Prof. Dr. H. D. Rudolph for supplying his SPLIT 5 program. The 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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