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

H. Lutz and H. Dreizler

Abt. Chemische Physik im Institut
für Physikalische Chemie der Universität Kiel

(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.

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_a 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 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

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_a [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.

Reprint requests to Prof. Dr. H. Dreizler, Institut für Physikal. Chemie der Universität Kiel, Abt. Chem. Physik, *D-2300 Kiel*, Olshausenstraße 40–60.

[1] H. D. Rudolph, Z. Angew. Phys. **13**, 401 [1961].

[2] U. Andresen and H. Dreizler, Z. Angew. Phys. **30**, 207 [1970].

[3] U. Blukis, P. H. Kasai, and R. J. Myers, J. Chem. Phys. **38**, 2753 [1963].

[4] A. Trinkaus, H. Dreizler, and H. D. Rudolph, Z. Naturforsch. **28 a**, 750 [1973].

[5] H. Dreizler and G. Dendl, Z. Naturforsch. **20 a**, 1431 [1965].

* Program SPLIT 5 from H. D. Rudolph, Department of Physical Chemistry, University of Ulm, Germany.

[6] Private Communication F. J. Lovas, National Bureau of Standards Washington D.C.