CHEMISTRY LETTERS, pp. 1249-1252, 1975. Published by the Chemical Society of Japan

# MICROWAVE SPECTRA OF DIMETHYLETHER IN THE EXCITED TORSIONAL STATES

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Microwave spectra of dimethylether and its deuterated species, $(CD_3)_2O$, in the excited torsional states were studied in relation to the top-top coupling problem of internal rotation of two methyl groups. A preliminary analysis of the observed splittings of the spectra was carried out in order to evaluate $V_3$, V' and V" values in the potential function.

Microwave spectra of dimethylether and its isotopic species in the ground torsional state were extensively studied and its $r_s$ structure$^{1)}$ and the barrier to internal rotation of the methyl groups$^{2)}$ neglecting the top-top coupling terms were determined. Though the internal rotation analysis including the top-top coupling terms were reported for several molecules,$^{3)}$ $^{4)}$ for dimethylether, a similar analysis has not been made by the use of microwave data.

Recently we measured microwave spectra of dimethylether and its deuterated species, $(CD_3)_2O$, in the excited torsional states. The torsional states pertinent to our discussion will hereafter be designated as $(V_1\ V_2)$ where $V_i$ is the torsional quantum number of the i-th methyl torsional wave function. Though each one of the (0 1) and (0 2) states is doubly degenerate, presence of the top-top coupling terms produces two different states for each of them. They will be designated by the symbols + and −. [e.g. (0 1)+ and (0 2)−]. Furthermore, the (0 2)+ and (1 1) states give the influences with each other. The b-type Q and R branches of trasitions with $J \leqq 5$ could be assigned for the (0 0), (0 1)± states of $(CH_3)_2O$ and for the (0 0), (0 1)±, (0 2)± and (1 1) states of $(CD_3)_2O$. For the (0 1)± states of $(CD_3)_2O$, transitions with $J \leqq 8$ were also measured. The observed transitions were quartets or triplets due to internal rotation except those of the (0 0) state of $(CD_3)_2O$ which were singlets. Assignments of the observed spectra were done taking the statistical weights$^{5)}$ and the sum rule$^{6)}$ of the components of multiplets into our considerations. The rotational constants are listed in Table 1.

They were obtained from the observed frequencies of the AA components[7)] of the multiplets by a least-squares analysis so as to fit in with a rigid rotor expression.

A preliminary analysis of the observed splittings of the spectra for $(CH_3)_2O$ and $(CD_3)_2O$ was carried out by a method proposed by Hoyland.[4)] The kinetic part of the Hamiltonian was derived by the principal axis method and the usual internal rotation potential function[8) 9)] was used.

$$V(\alpha_1, \alpha_2) = (V_3/2)(2 - \cos 3\alpha_1 - \cos 3\alpha_2) + V'\cos 3\alpha_1 \cos 3\alpha_2 + V''\sin 3\alpha_1 \sin 3\alpha_2.$$

Spacings $\Delta\nu$ between components of multiplets due to internal rotation for $(CH_3)_2O$ type molecules can be written approximately as

$$\Delta\nu(\text{AA-EE}) = \Delta\nu^e + \Delta\nu_a{}^o + \Delta\nu_b{}^o,\ \Delta\nu(\text{AA-AE}) = 2\Delta\nu^e + 4\Delta\nu_b{}^o,\ \Delta\nu(\text{AA-EA}) = 2\Delta\nu^e + 4\Delta\nu_a{}^o$$

where $\Delta\nu$(AA-EE) means the spacing from AA to EE components. Since the so-called odd term contribution $\Delta\nu^o$ can be determined for each of the transitions independently if the observed spacings of a suitable pair of transitions are available, the so-called even term contribution $\Delta\nu^e$ can also be determined for each of the transitions. It was found that for the observed transitions, $\Delta\nu_b{}^o$ was so small and negligible that $\Delta\nu$(AA-AE) was practically equal to $2\Delta\nu^e$. $\Delta\nu^e$ can be written approximately as $\Delta\nu_a{}^{(2)} + \Delta\nu_b^{(2)}$ where $\Delta\nu_a{}^{(2)}$ and $\Delta\nu_b{}^{(2)}$ are contributions proportional to squares of the angular momentum components, $P_a{}^2$ and $P_b{}^2$, respectively. Then, from $\Delta\nu_a{}^{(2)}$ and $\Delta\nu_b{}^{(2)}$ for transitions, differences of the rotational constants A and B between AA and AE components can be obtained. In Table 1, differences of the A rotational constants, $\Delta A$, are shown. They were obtained from $\Delta\nu^e$ values of all the observed transitions by a least-squares analysis. For the B rotational constants, differences were so small as compared with the experimental uncertainties so that they could not be regarded as useful data. For the C rotational constants, differences were identically zero from symmetry.

In the theoretical calculations, first, the energy matrix was derived from the basis functions given by Hoyland and the pure torsional part of the Hamiltonian. Second, assuming $V_3$ and $V''$ values in $V(\alpha_1, \alpha_2)$, taking $V' = 0$, the pure torsional energies and their wave functions were obtained by solving the secular equations which were obtained from the energy matrix and were of the order 30 × 30 for pairs of the symmetry species, AA, and AE. Third, the second order perturbation sums were calculated from the torsional wave functions obtained and the torsion-rotation coupling terms of the Hamiltonian. Then the effective rotational constants for the AA and AE species were calculated. These procedures were repeated for $(CH_3)_2O$ and

$(CD_3)_2O$, separately, until the best fit was obtained between the calculated differences ΔA and the observed. The results are shown in Table 1.

Since some of the pure torsional energy differences can be determined by the observed torsional vibrations, reasonableness of $V_3$ and V" values can be tested by comparing the calculated frequencies with the observed. The observed torsional frequencies $\nu[(0\ 1)- \leftarrow (0\ 0)]$ were reported as 240.5 and 192 $cm^{-1}$ for $(CH_3)_2O$ and $(CD_3)_2O$, respectively, while they were calculated as 239 and 190 $cm^{-1}$ respectively. Then, a good agreement is found between the observed and calculated frequencies.

From the analysis, the followings can be concluded; 1) $V_3$ for $(CD_3)_2O$ is somewhat lower than that for $(CH_3)_2O$ in a similar manner as the results for the other molecules such as acetone6) and so on. 2) As is shown in Table 1, a change in $V_3$ produces shifts of the absolute values of ΔA, |ΔA| in the same direction for all the states, while a change in V" produces shifts of |ΔA| in the opposite directions for the ± states with each other. This is a favorable tendency for the determination of V" from the ± state splittings. 3) Though Rodolph10) pointed out that the determination of V' would require the (0 2)± state splittings, there are

Table 1. Rotational Constants (MHz) and Barrier to Internal Rotation of Dimethylether and its Deuterated Species[a)]

| species | state | A | B | C | $\Delta A_{obsd}$[b)] | δΔA[c)] | $\Delta(A/V_3)$[d)] | Δ(A/V")[d)] |
|---|---|---|---|---|---|---|---|---|
| | (0 0) | 38798.15( 63) | 10056.38(15) | 8886.80(14) | 1.76(11) | -0.14 | -0.08 | -0.01 |
| $(CH_3)_2O$ | (0 1)+ | 38797.55( 70) | 10024.95(17) | 8867.43(16) | -47.79(28) | -0.03 | -1.08 | 0.75 |
| | (0 1)- | 38770.74(100) | 9993.08(22) | 8870.23(21) | -45.68(35) | -0.08 | -1.10 | -0.50 |
| | (0 0) | 25696.37( 30) | 7483.76( 7) | 6798.08( 7) | —— | —— | —— | —— |
| | (0 1)+ | 25702.22( 29) | 7466.94( 7) | 6785.74( 7) | -0.48( 8) | 0.02 | -0.01 | 0.00 |
| $(CD_3)_2O$ | (0 1)- | 25675.27( 36) | 7448.73( 9) | 6793.79( 8) | -0.44( 3) | 0.02 | -0.02 | -0.01 |
| | (0 2)+ | 25723.88( 25) | 7448.79( 6) | 6772.79( 6) | 9.67(34) | 0.20 | -0.29 | 0.10 |
| | (0 2)- | 25697.75( 34) | 7433.64( 8) | 6776.72( 8) | 16.85(74) | 0.34 | -0.52 | -0.16 |
| | (1 1) | 25877.27( 31) | 7461.53( 7) | 6791.70( 6) | 0.99(43) | -5.71 | -0.25 | -0.22 |

| | $V_3$(cal/mol) | V"(cal/mol) | V' | states used |
|---|---|---|---|---|
| $(CH_3)_2O$ | 2605(14) | +17(17) | 0(assumed) | (0 0), (0 1)± |
| $(CD_3)_2O$ | 2580(64) | +17(17) | 0(assumed) | (0 1)±, (0 2)± |

a) Figures in parentheses indicate the uncertainties attached to the last significant figures calculated from 2.5 times the standard deviation.

b) Difference of the A rotational constants between AA and AE components of multiplets.

c) δΔA = ΔAobsd - ΔAcalctd. ΔAcalctd was calculated using $V_3$ and V" in the table.

d) Changes of the absolute value of ΔA with the increases of $V_3$ and V" by 10 cal/mole in MHz, respectively.

too small effects for ΔA in the (0 2)± states of $(CD_3)_2O$ and V' could not be determined. 4) For $(CD_3)_2O$, the observed ΔA for the (1 1) state has a large deviation from the calculated ΔA. Reasonable interpretations for this discrepancy can not be found at present. 5) The present sets of barrier parameters can be compared with those reported by Tuazon and Fateley[11)] who analyzed four $v = 0 \rightarrow 1$ infrared bands of $(CH_3)_2O$, $(CD_3)_2O$ and $CH_3OCD_3$. They obtained $V_{effective} = V_3 - 2V'$ $= 2705$, ($V_3 = 2591$), $V'' = 86$ and $V' = -57$ cal/mole by assuming a common $V_3$ for three isotopic species because of lack of sufficient data for the analysis. However, this assumption seems to be unfavorable as is pointed out in 1). Though the difference in $V_3$ is within the experimental uncertainties between our value and theirs, this makes a large influence on the V" value. Since a preliminary analysis for the (0 0), (0 1) and (1 0) state splittings of $CH_3OCD_3$ by an extended Bootstrap method[12)] gave $V_3 = 2597$ and $V'' = 0$ assuming $V' = 0$, then their V" value may be too large for dimethylether.

The work is in progress on the analysis by a more elaborate method using the data for the normal, $(CD_3)_2O$ and $CH_3OCD_3$ species.

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7) The components of multiplets should be named by considering the symmetry of the state, that is, for example, $A_1A_1$ for (0 0), (1 1) and (0 2)+ states, $A_1A_2$ for (0 1)+ state and so on. However, for simplicity, we will designate them as AA, EE, AE and EA, for all states hereafter.

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(Received October 3, 1975)