On the Structure of *Trans* Ethyl Methyl Ether and the W Form of Diethyl Ether

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We have measured the microwave spectra of ethyl methyl ether and its isotopically substituted species. Since the measurements have not been finished for ^{18}O and one of ^{13}C species, the r_s structure can not be obtained at present.

We found many weak spectra around the expected regions for the spectra of the ^{18}O and one of three ^{13}C species. Some of these spectra may be assigned to those of the vibrationally excited states of the molecule. Since these spectra are confusing, it is preferable to assign them before the assignments of the spectra are undertaken for the ^{18}O and the ^{13}C species. However, we have tried to determine a tentative structure of *trans* ethyl methyl ether which reproduces the observed rotational constants for the parent and nine isotopic species.

In Table 1 are shown the observed rotational constants and the differences between the observed and the calculated rotational constants which were calculated using the obtained structural parameters given in Table 2. Work is in progress with respect to both the *trans* and the *gauche* isomers on the electric dipole moment, the internal rotation of the CH_3CH_2 and OCH_3 groups and the skeletal torsion and spectra due to the vibrationally excited states.

We have also tried to measure the microwave spectra of diethyl ether based on the trial calculation for the rotational constants of four possible molecular forms of diethyl ether using the structural parameters given in Table 2. We could find a set of spectra assigned to the W form (or the *trans-trans* form) of the molecule. In order to reproduce the observed rotational constants, we have adjusted only the structural parameters of the skeleton. The best agreement is obtained when we reduce the ∠COC angle by about 1° from the values for *trans* ethyl methyl ether. The results are given in Table 1.

TABLE 1. THE OBSERVED ROTATIONAL CONSTANTS (MHz) AND THE DIFFERENCES BETWEEN THE OBSERVED AND PREDICTED ROTATIONAL CONSTANTS

Species		$A(\Delta A)$[a]	$B(\Delta B)$[a]	$C(\Delta C)$[a]
trans ethyl methyl ether				
$CH_3CH_2OCH_3$		27992.03 (13.96)	4159.61 (4.61)	3891.11 (0.06)
$CH_3CH_2OCH_2D$	sym[b]	27218.96 (5.98)	3956.97 (4.21)	3699.99 (−0.74)
	asym[b]	26194.77 (0.52)	4009.66 (6.49)	3765.02 (2.23)
$CH_3CHDOCH_3$		25040.20 (10.71)	4131.86 (4.86)	3843.20 (0.18)
$CH_3CD_2OCH_3$		22669.17 (10.70)	4095.93 (5.23)	3804.65 (0.05)
$CH_2DCH_2OCH_3$	sym[b]	27505.31 (7.36)	3937.57 (−0.39)	3683.49 (0.02)
	asym[b]	26057.29 (18.57)	4008.84 (4.44)	3760.41 (0.20)
$CH_3CH_2OCD_3$		23838.31 (0.85)	3704.12 (7.48)	3491.59 (3.02)
$^{13}CH_3CH_2OCH_3$[c]		27951.36 (17.20)	4041.94 (6.71)	3787.16 (2.23)
$CH_3CH_2O^{13}CH_3$[c]		27978.56 (16.60)	4051.52 (6.66)	3796.06 (2.16)
the W form of diethyl ether				
$(CH_3CH_2)_2O$		17955.83 (6.87)[d]	2244.15 (2.71)[d]	2101.73 (0.12)[d]
		(−114.65)[e]	(−0.27)[e]	(−4.15)[e]

a) $\Delta R = R_{calcld} - R_{obsd}$, $R = A, B, C$

b) "sym" and "asym" refer to the symmetric and asymmetric forms, respectively with respect to the molecular plane.

c) Since the Q branches of the transitions have only been measured at present for two ^{13}C species, the rotational constants are determined on the assumption that the difference of $I_a+I_b-I_c$ between the parent and the isotopic species is the same as that found in CH_3CH_2Br and $(CH_3)_2O$, respectively.

d) The difference between the observed and predicted rotational constants calculated from the adjusted structural parameters.

e) The difference between the observed and predicted rotational constants calculated from the structural parameters obtained for *trans* ethyl methyl ether.

TABLE 2. STRUCTURAL PARAMETERS OBTAINED FOR *trans* ETHYL METHYL ETHER

CH_3O		CH_3C		CH_2		Skeleton	
$r(CH_s)$	1.091Å	$r(CH_s)$	1.083Å	$r(CH)$	1.097Å	$r(CC)$	1.540Å
$r(CH_a)$	1.097Å	$r(CH_a)$	1.087Å			$r(CH_3O)$	1.412Å
$\angle H_aCH_a$	109°24′	$\angle H_aCH_a$	108°48′	∠HCH	107°30′	$r(CH_2O)$	1.412Å
$\angle H_aCH_s$	110°10′	$\angle H_aCH_s$	109°45′	∠HCC	110°51′	∠COC	111°23′
$\angle H_sCO$	107°13′	$\angle H_sCC$	109°30′	∠HCO	109°50′	∠OCC	107°57′
$\angle H_aCO$	110°5′	$\angle H_aCC$	109°30′				

locked angles for: CH_3O, 1°55′; CH_2O, 1°15′