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THE MICROWAVE SPECTRA OF HALOMETHYL-METHYLETHERS

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The microwave spectra of chloromethyl- and bromomethyl-methylether in the gauche form were studied in relation to their molecular structures and quadrupole coupling constant tensors, χ, for six isotopic species. The χ tensor elements were obtained from the hyperfine structures of the observed spectra.

Recently, we studied the microwave spectra of chloromethyl- and bromomethyl-methylether ($ClCH_2OCH_3$ and $BrCH_2OCH_3$) in relation to their molecular structures and quadrupole coupling constant tensors, χ.[1] The spectra of two isotopic species of the chlorine and bromine atoms for the normal and two deuterated species were measured in the frequency region from 8400 to 36000 MHz by a conventional Stark modulation spectrometer at the temperature of dry ice.

About twenty of the a-type R branch and c-type Q branch transitions were assigned for each isotopic species. With exception of low J transitions, most of the transitions were observed as quartets due to the quadrupole coupling effect of the chlorine and bromine nuclei. Either triplets or doublets were also observed for some of the transitions of $ClCH_2OCH_3$ because of smallness of the coupling constants. The observed hyperfine structures of the spectra were predicted by the first-order perturbation formula for $ClCH_2OCH_3$ and χ_{aa} and $\eta_a(=(\chi_{bb}-\chi_{cc})/\chi_{aa})$ were obtained by a least-squares analysis using all the measured splittings for each species.

For $BrCH_2OCH_3$, some of the observed spectra exhibited a considerable asymmetric splitting due to the second-order quadrupole coupling effect. Since the gauche form is expected for these molecules, all the three off-diagonal χ elements are non-vanishing in the inertial axes system. The asymmetry of splitting is defined and related to the off-diagonal χ elements in the following expression.

$$\begin{aligned}\delta\nu &= \nu(J'+1/2 \leftarrow J+1/2) + \nu(J'-3/2 \leftarrow J-3/2) - \nu(J'+3/2 \leftarrow J+3/2) - \nu(J'-1/2 \leftarrow J-1/2) \\ &= a\chi_{ab}^2 + b\chi_{ac}^2 + c\chi_{bc}^2 + d\chi_{aa}^2 + e\eta_a\chi_{aa}^2 + f\eta_a^2\chi_{aa}^2,\end{aligned}$$

where $\nu(J'+1/2 \leftarrow J+1/2)$ indicates a component of a quartet with $F' = J'+1/2$ and $F = J+1/2$ for higher and lower levels of the transition, respectively, and so on. The coefficients, a, b,..., and f obtained by the second-order perturbation theory, are the constants which depend on the rotational constants, the transition types, and the degree of accidental near-degeneracies of transition energy levels with the other levels. Since the estimated values of the off-diagonal elements, χ_{ab}, χ_{ac}, and χ_{bc} are about 300, 100, and 70 MHz, respectively, the level(E_J) of the transition receives the effect beyond the experimental error from the other levels ($E_{J'}$; $J' = J$, $J \pm 1$, and $J \pm 2$), if $E_{J'}$ exists within about 30000 MHz of E_J and belongs to appropriate symmetry species.

The second-order perturbation calculation was so tedious that the matrix elements of $(\Phi_{zg}\Phi_{zg'})$, $(g \neq g';\ g, g' = a, b, c)$ in the numerators of the perturbation sums were evaluated by using the symmetric rotor wave functions instead of the asymmetric rotor wave functions. This approximation is valid since this molecule is close to the symmetric top[2]. All the χ tensor elements were determined from

Table 1. The Rotational Constants and the Quadrupole Coupling Constant Tensor of $ClCH_2OCH_3$ and $BrCH_2OCH_3$ in the Inertial Principal Axes System[a].

species[b]	A(MHz)	B(MHz)	C(MHz)	χ_{aa}(MHz)	η_a	$\lvert\chi_{ab}\rvert$(MHz)
(35,H_3)	14233.14(63)	3481.36(15)	3032.91(18)	-27.3(5)	1.23 (6)	
(37,H_3)	14185.48(60)	3398.25(14)	2967.65(17)	-21.5(10)	1.21 (4)	
(35,D_3)	12484.28(50)	3174.79(12)	2771.23(14)	-23.0(9)	1.61 (9)	
(37,D_3)	12440.27(46)	3099.28(11)	2711.53(14)	-19.2(20)	1.56 (19)	
(35,D_2)	12214.08(65)	3434.84(16)	2960.05(19)	-27.7(10)	1.31 (7)	
(37,D_2)	12167.48(54)	3353.97(13)	2897.29(16)	-22.2(6)	1.26 (5)	
(79,H_3)	13312.38(61)	2306.30(8)	2081.51(9)	284.6(76)	0.6701(296)	320.4(168)
(81,H_3)	13305.16(58)	2288.24(8)	2066.63(5)	237.1(61)	0.6665(287)	270.1(188)
(79,D_3)	11646.13(88)	2109.02(11)	1903.77(11)	258.0(110)	0.8258(500)	350.6(177)
(81,D_3)	11639.64(78)	2092.13(10)	1889.82(10)	218.0(93)	0.8103(498)	299.3(108)
(79,D_2)	11397.86(58)	2276.57(8)	2035.26(8)	294.2(100)	0.6657(340)	321.2(178)
(81,D_2)	11391.21(59)	2258.52(8)	2020.61(8)	245.0(80)	0.6688(333)	272.8(179)

(79,H_3)	$\lvert\chi_{ac}\rvert$	109.3(232)MHz	$\lvert\chi_{bc}\rvert$	70.6(128)MHz
(81,H_3)	$\lvert\chi_{ac}\rvert$	91.4(57)MHz	$\lvert\chi_{bc}\rvert$	63.9(103)MHz

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

b) The symbols (35,H_3) and (79,D_3) indicate the $^{35}ClCH_2OCH_3$ and $^{79}BrCH_2OCD_3$ species, respectively, and so on.

all the measured splittings by a least-squares analysis so as to fit in with the first-order perturbation formula and the second-order perturbation formula described above for the ^{79}Br and ^{81}Br species of the normal species. As for the two deuterated species, only χ_{aa}, η_a, and χ_{ab} were determined since the transitions which exhibited the asymmetric splitting caused by χ_{ac} and χ_{bc} were not observed.

The rotational constants were obtained by a least-squares analysis using hypothetical unsplit frequencies which were evaluated from the observed frequencies and the χ values. For the two deuterated species of $BrCH_2OCH_3$, the values for the normal species were used for χ_{ac} and χ_{bc}. The rotational constants and the χ tensors are shown in Table 1.

For $ClCH_2OCH_3$, the principal χ values cannot be calculated from the determined χ diagonal elements in the inertial axes system without structural informations.

Table 2. Principal Values (MHz) of the Quadrupole Coupling Constant Tensors for $ClCH_2OCH_3$ and $BrCH_2OCH_3$[a].

	(35,H_3)	(37,H_3)	(79,H_3)		(81,H_3)	
			positive[b]	negative[b]	positive[b]	negative[b]
χ_{zz}[c]	-71.3(0.4)	-55.0(0.4)	502.4(27.9)	484.2(21.2)	422.3(22.9)	405.7(19.7)
χ_{xx}[c]	35.6	27.5	-241.3(17.2)	-125.3(10.8)	-201.8(10.4)	-100.9(11.2)
χ_{yy}[c]	35.6	27.5	-261.1(13.9)	-358.5(35.2)	-220.5(15.2)	-304.8(23.6)
η_z[c]	0	0	0.0395(.1174)	0.4823(.1388)	0.0442(.1148)	0.5027(.1097)
θ_{za}[d]	39°54'	39°34'	32°46'(1°57')	30°52'(1°48')	33°(1°48')	30°59'(1°53')
θ_{zb}[d]	127°35'	127°16'	120°51'(42')	120°28'(41')	121°(40')	120°37'(41')
θ_{zc}[d]	78°32'	78°37'	80° 2'(4°10')	85°24'(7°50')	79°49'(3°55')	85°39'(8°43')
ratio[e]	$\chi_{zz}(^{35}Cl)/\chi_{zz}(^{37}Cl)$ = 1.30(0.02)		$\chi_{zz}(^{79}Br)/\chi_{zz}(^{81}Br)$		= 1.190(0.131) positive[b] = 1.193(0.110) negative[b]	

a) Figures in parentheses indicate the uncertainties. For $ClCH_2OCH_3$, only the uncertainties of the χ_{aa} values were taken into account.

b) "positive" and "negative" indicate the cases where the signs of the product of the off-diagonal elements $\chi_{ab}\chi_{ac}\chi_{bc}$ are positive and negative, respectively.

c) For $ClCH_2OCH_3$, χ_{zz} was calculated by using the relation $\chi_{aa} = (\chi_{zz}/2)(3\cos^2\theta_{za} - 1)$ and it was assumed that $\eta_z = 0$ and the z axis coincided with the C-Cl bond. Then $\chi_{xx} = \chi_{yy} = -\chi_{zz}/2$.

d) The values for $ClCH_2OCH_3$ are those of the C-Cl bond direction calculated from the model structure shown in Table 3.

e) The quadrupole moment ratio of $^{35}Cl/^{37}Cl$ and $^{79}Br/^{81}Br$ are 1.2688 and 1.19707[3], respectively.

Therefore, the χ_{zz} values in Table 2 were calculated on two assumptions that 1) the z axis of the χ tensor coincides with the C-Cl bond, whose direction is calculated from the model structure described below, and 2) the χ tensor is cylindrically symmetric about the z axis.

For $BrCH_2OCH_3$, only the absolute values were determined for the off-diagonal χ elements so that two sets of the principal χ values which depend on the sign of the product $\chi_{ab}\chi_{ac}\chi_{bc}$ were calculated irrespective of the molecular structure. As is shown in Table 2, for the case of $\chi_{ab}\chi_{ac}\chi_{bc} > 0$ (the positive case), the asymmetry parameter η_z about the largest principal value χ_{zz} is nearly equal to zero, that is, the field gradient around the bromine nucleus is nearly cylindrically symmetric, while for the case of $\chi_{ab}\chi_{ac}\chi_{bc} < 0$ (the negative case), η_z has a large value. In the third-order perturbation formula, there exists a $\chi_{ab}\chi_{ac}\chi_{bc}$ dependent term which gives a contribution to the asymmetric splitting if an accidental degeneracy occurs among the transition energy level and the two other levels. Then, the sign of $\chi_{ab}\chi_{ac}\chi_{bc}$ is determined in accord with whether the contribution of this term is additive or subtractive. Unfortunately, it was found that the contributions were so small for these species that the determination of the sign of $\chi_{ab}\chi_{ac}\chi_{bc}$ was impossible from the splittings alone.

As the r_s structures of these molecules cannot be determined due to the lack of the data for a sufficient number of the isotopic species, the structures of these molecules were estimated from the observed rotational constants of the six isotopic species for each of the molecules.

In Table 3, the model structure has the structural parameters transferred from those of the reported r_s structures of dimethylether[4], ethylchloride[5] and bromide[6] except the skeletal dihedral angle τ which was adjusted so as to give the minimum root mean square deviation(RMS) which is defined in the following.

$$\mathrm{RMS} = \{(1/N)\sum_i[(\Delta A_i/A_i)^2 + (\Delta B_i/B_i)^2 + (\Delta C_i/C_i)^2]\}^{1/2} \times 10^2,$$

where ΔA_i, ΔB_i, and ΔC_i indicate the differences between the observed and calculated rotational constants for the i-th isotopic species and N is the number of the isotopic species.

The minimum RMS values of 1.29 and 1.67 were obtained at $\tau = 75°$ for $ClCH_2OCH_3$ and at $\tau = 77°30'$ for $BrCH_2OCH_3$, respectively, though large uncertainties in τ values were inevitable because RMS is a slow-varying function of τ ($\Delta(\mathrm{RMS})/\Delta\tau = 1.0/\pm 4°$). For $ClCH_2OCH_3$, $\tau = 74°$ and $71°$ were reported by Planje et al[7] from the electron diffraction study and by Ikeda et al 1) from the microwave spectroscopy, respectively.

Since the RMS values of the model structure were not so small as expected, trials were made for reducing the RMS values by adjusting the skeletal structural parameters. First, the three angles (τ, α_1(COC), and α_2(OCX), (X = Cl, Br)) were adjusted. However, it was found that in the range of the RMS values below 0.24, the two angles among the three were automatically settled by a given value of the other angle in a narrow range of the uncertainties. For example, for $ClCH_2OCH_3$, τ = 75° results in the increases of the α_1 and α_2 values from those of the model structure by 6°30' and -3°, respectively, and τ = 71° (the value reported by Ikeda et al 1)) results in those of the α_1 and α_2 values by 4°30' and 0°, respectively. The similar situation was found for the adjustments of the bond length of r(C-X) and the angles of τ and α_2(OCX).

From these trials, it is concluded that some of the six skeletal parameters should be determined by some means in order to reduce the RMS values and the uncertainties of the structure. Then, at present, the model structure in Table 3 is proposed as a tentative structure for these molecules. From this model structure, the C-Br bond for $^{79}BrCH_2OCH_3$ makes the angles of 33°36', 121°44', and 80°18' with the inertial axes, a, b, and c, respectively, which are compared with the angles of

Table 3. The Model Structures for $ClCH_2OCH_3$ and $BrCH_2OCH_3$.

CH_3 group		CH_2 group		Skeleton	
From $(CH_3)_2O$		For $ClCH_2OCH_3$ from $ClCH_2CH_3$		From $(CH_3)_2O$	
r(CH_s)	1.091 Å	r(CH)	1.089 Å	r(CH_3-O)	1.410 Å
r(CH_a)	1.100 Å	α(HCH)	109°12'	r(CH_2-O)	1.410 Å[c]
α(OCH_s)	107°14'	α(OCH)	111°36'[a]	α(COC)	111°43'
α(OCH_a)	110°50'	α(ClCH)	106°35'[b]	For $ClCH_2OCH_3$ from $ClCH_2CH_3$	
α(H_sCH_a)	109°33'	For $BrCH_2OCH_3$ from $BrCH_2CH_3$		r(CCl)	1.788 Å
α(H_aCH_a)	108°44'	r(CH)	1.087 Å	α(OCCl)	111° 2'[a]
Skeletal dihedral angle τ		α(HCH)	109°54'	For $BrCH_2OCH_3$ from $BrCH_2CH_3$	
$ClCH_2OCH_3$	75°	α(OCH)	112°15'	r(CBr)	1.950 Å
$BrCH_2OCH_3$	77°30'	α(BrCH)	105°25'	α(OCBr)	111° 2'[a]

a) Since these angles do not exist for ethyl halides, the corresponding α(CCH) and α(CCX) for ethyl halides were transferred.

b) The reported value is 106°41'. However, the value was adjusted in order to make the sum of the six angles around the carbon atom equal to six times the tetrahedral angle.

c) Assumed that r(CH_3-O) = r(CH_2-O).

θ_{za}, θ_{zb}, and θ_{zc} for the χ tensor in Table 2. It is noted that the C-Br bond direction is not sensitive to the structure. Actually, the C-Br bond directions calculated from the trial structures described above coincide with each other within the deviation of about 1°. Therefore, the positive case is preferable from this comparison, though the large uncertainties of θ_{za}, θ_{zb}, and θ_{zc} prevent the definite conclusion. Then, the field gradient around the C-Br bond of $BrCH_2OCH_3$ is probably nearly cylindrically symmetric in the similar manner as the reported molecules with the C-Br single bond such as bromomethylsilane$^{2)}$, ethylbromide$^{6)}$, and propargylbromide$^{8)}$.

The work is in progress on the other isotopic species and on analogous molecules such as fluoromethyl-methylether and the results will be published in the near future.

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1) Independent measurements on the ^{35}Cl and ^{37}Cl species of the normal species of chloromethyl-methylether have been reported by T. Ikeda and R. F. Curl, Jr. at the Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, (Paper No. T5, June 14, 1973). This paper appeared after our own measurements on the normal species of chloromethyl-methylether had been made and reported at the Symposium on Molecular Structure and Spectroscopy, Tohoku Institute of Technology, Sendai, (Papers No. 6D05 and No. 6D06, October 6, 1972). Their rotational constants and the χ_{aa} and η_a values of the ^{35}Cl species of $ClCH_2OCH_3$ are in fair agreement with ours. We deliberately delayed publication of our experimental results in order to obtain the results for the deuterated species of $ClCH_2OCH_3$ and the results for the bromomethyl-methylether including the analysis of the off-diagonal elements of the χ tensor.

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