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# The $r_s$ Structures of Fluoromethyl, Chloromethyl Ethers, and Methyl 2-Propynyl Ether

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$^{18}$O enriched samples of chloromethyl methyl ether and chloromethyl ethyl ether were prepared and their microwave spectra were measured. The $r_S$ structures of fluoromethyl methyl ether, fluoromethyl ethyl ether, chloromethyl methyl ether, chloromethyl ethyl ether, and methyl 2-propynyl ether were re-evaluated from the observed rotational constants obtained under the common constraints and assumptions on the structures of the molecules. A comparison of the $r_S$ structures was made between the five molecules and between the molecules and their related molecules.

In previous papers, reports were given on the $r_S$ structures of chloromethyl methyl ether,$^{1)}$ chloromethyl ethyl ether,$^{2)}$ and fluoromethyl ethyl ether.$^{3)}$ Studies on fluoromethyl methyl ether$^{4)}$ and methyl 2-propynyl ether$^{5)}$ have been completed, the $r_S$ structures of these molecules being determined.

The most populated isomer for these five molecules is the gauche isomer around the $CH_2$–O bond. Since several atoms in the molecules are situated close to the principal axes, solutions of the Kraitchman equation for these atoms are not reliable for coordinates having small absolute values. Moreover, a fluorine atom has no stable isotope, and thus the coordinate values of the fluorine atom should be computed from the coordinate values of the other atoms by means of the first moment equations.

The coordinate values of the oxygen atom were also obtained from those of other atoms with certain assumptions on the structure since no $^{18}$O enriched samples were available.$^{1,2)}$ After our results for these molecules had been reported, we succeeded in preparing $^{18}$O enriched samples. Three coordinate values for the oxygen atom could then be obtained by means of the Kraitchman equation. Since we are interested in comparison of the structures of these molecules it is important to re-evaluate their structures under a common set of constraints and assumptions on the five molecules by using new additional data. This paper deals with the structures obtained under different constraints and assumptions for each molecule. They are compared in order to find the most reliable $r_S$ structures obtained by means of the common set of constraints and assumptions on these five molecules.

Interesting features of the structural parameters for halomethyl ethers and their related molecules are given. The dipole moment, nuclear quadrupole coupling constant tensor and internal rotation are not dealt with.

For the sake of convenience, the names of the molecules referred to are abbreviated as follows: fluoromethyl methyl ether, [F, Me]; fluoromethyl ethyl ether, [F, Et]; chloromethyl methyl ether, [Cl, Me]; chloromethyl ethyl ether, [Cl, Et]; and methyl 2-propynyl ether, [Pr, Me].

The conventional terms, trans and gauche, are used instead of the IUPAC nomenclature, antiperiplanar and synclinal, respectively, since they were used in previous papers.

## Experimental

$^{18}$O enriched samples of [Cl, Me] and [Cl, Et] were prepared by the reaction of $^{18}$O enriched methanol or ethanol and paraformaldehyde with hydrochloric acid.

$^{18}$O enriched methanol was prepared by the method of Sawyer.$^{6)}$ Tributyl orthoformate was mixed with $^{18}$O enriched water (70 atom % $^{18}$O, Prochem.) in the presence of hydrochloric acid in diglyme. The resulting butyl formate-carbonyl-$^{18}$O was reduced by lithinum aluminum hydride. The methanol obtained contains *ca.* 60 atom % $^{18}$O.

$^{18}$O enriched ethanol was obtained by mixing acetaldehyde with $^{18}$O enriched water and the resulting aldehyde was reduced with lithium aluminum hydride. The ethanol obtained was found to contain *ca.* 30 atom % $^{18}$O.

The microwave spectra were measured in the range 8500—34000 MHz with a conventional Stark modulation spectrometer at dry ice temperature. Observed frequencies and rotational constants are given in Tables 1 and 2.

## Determination of $r_s$ Structures

In spite of sufficient data for determining the $r_S$ structures of the four halomethyl ethers by the substitution method, there are several unreliable Kraitchman atom coordinate values for each molecule. The coordinate value obtained by the Kraitchman equation is hereafter referred to as the *K*-value. The identification symbols of the atoms for the $XCH_2OCH_3$ and $XCH_2OCH_2CH_3$ type molecules are shown in Fig. 1 where the hydrogen atoms situated on the same side as the X atom with respect to the COC plane have

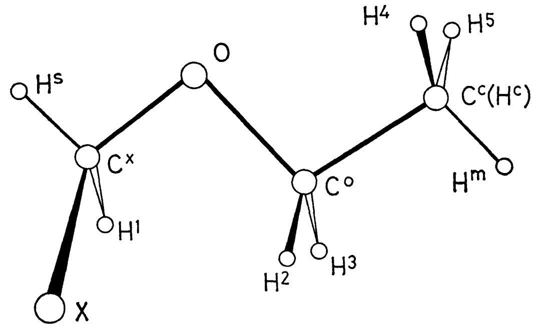

Fig. 1. Identification number of atoms in $XCH_2OCH_2CH_3$.
The symbols in parentheses indicate the atom symbols for $XCH_2OCH_3$.

TABLE 1. OBSERVED AND HYPOTHETICAL UNSPLIT FREQUENCIES[a] AND ROTATIONAL CONSTANTS[b] OF THE $^{18}$O SPECIES OF CHLOROMETHYL METHYL ETHER (MHz)

| $F$ | $J+3/2$ | $J+1/2$ | $J-1/2$ | $J-3/2$ | $\nu_0$ | $\Delta\nu$ $(J+3/2)$ | $\Delta\nu$ $(J+1/2)$ | $\Delta\nu$ $(J-1/2)$ | $\Delta\nu$ $(J-3/2)$ |
|---|---|---|---|---|---|---|---|---|---|
| $3_{03}\leftarrow 2_{02}$ | 19100.02 | 19100.02 | 19098.12 | 19098.12 | 19099.60(−7) | 0.42( 1) | 0.42( 24) | −1.48(−1) | −1.48(−24) |
| $3_{13}\leftarrow 2_{12}$ | 18493.49 | 18491.75 | 18490.63 | ··· | 18492.53(−1) | 0.96( 2) | −0.78( 6) | −1.90(−6) | — |
| $3_{12}\leftarrow 2_{11}$ | 19796.18 | 19794.37 | 19795.27 | ··· | 19795.57( 10) | 0.61( 4) | −1.20( 1) | −0.30(−4) | — |
| $4_{04}\leftarrow 3_{03}$ | 25405.69 | 25405.45 | 25404.69 | ··· | 25405.39( 3) | 0.30(−4) | 0.06( 3) | −0.70( 1) | — |
| $4_{14}\leftarrow 3_{13}$ | 24642.23 | 24641.47 | 24640.73 | 24641.47 | 24641.70(−5) | 0.53(−2) | −0.23(−2) | −0.97( 4) | −0.23( 2) |
| $4_{13}\leftarrow 3_{12}$ | 26378.16 | 26377.46 | 26377.46 | 26378.16 | 26377.82(−1) | 0.34( 2) | −0.36( 9) | −0.36(−3) | 0.34( −9) |
| $5_{05}\leftarrow 4_{04}$ | 31660.81 | 31660.49 | 31660.07 | 31660.49 | 31660.56( 1) | 0.25(−5) | −0.07( 0) | −0.49( 0) | −0.07( 5) |
| $5_{15}\leftarrow 4_{14}$ | 30779.24 | 30778.78 | 30778.35 | 30778.78 | 30778.91( 5) | 0.33(−4) | −0.13(−7) | −0.56( 6) | −0.13( 6) |
| $5_{14}\leftarrow 4_{13}$ | 32945.73 | 32945.38 | 32945.38 | 32945.73 | 32945.57(−5) | 0.16(−6) | −0.19( 4) | −0.19( 6) | 0.16( −4) |
| $3_{22}\leftarrow 3_{12}$ | 31033.47 | ··· | ··· | ··· | 31033.90(−6) | −0.43( 2) | — | — | — |
| $4_{23}\leftarrow 4_{13}$ | 30182.75 | 30182.12 | ··· | ··· | 30182.53( 13) | 0.22(−5) | −0.41( 5) | — | — |
| $5_{24}\leftarrow 5_{14}$ | 29128.46 | 29126.74 | 29127.16 | 29128.88 | 29127.77(−8) | 0.69( 3) | −1.03( 3) | −0.61(−3) | 1.11( −3) |
| $6_{25}\leftarrow 6_{15}$ | 27879.27 | 27876.98 | ··· | 27879.83 | 27878.37( 1) | 0.90( 0) | −1.39(−3) | — | 1.46( 3) |
| $7_{26}\leftarrow 7_{16}$ | 26446.33 | 26443.73 | 26444.26 | 26446.84 | 26445.26( 25) | 1.07( 2) | −1.53(−2) | −1.00(−1) | 1.58( 1) |
| $8_{27}\leftarrow 8_{17}$ | 24844.61 | 24841.87 | 24842.34 | 24845.03 | 24843.43( 70) | 1.18( 3) | −1.56( 1) | −1.09(−1) | 1.60( −3) |
| $9_{28}\leftarrow 9_{18}$ | 23093.97 | 23091.20 | 23091.57 | 23094.39 | 23092.76(158) | 1.21( 2) | −1.56( 3) | −1.19(−5) | 1.63( 0) |
| $10_{29}\leftarrow 10_{19}$ | 21219.53 | 21216.76 | 21217.10 | 21219.88 | 21218.30(278) | 1.23( 3) | −1.54( 3) | −1.20(−3) | 1.58( −2) |

$A=13968.12(12)$, $B=3409.25(4)$, $C=2974.86(4)$, $d_J=1.95(74)\times10^{-3}$, $d_{JK}=-1.72(43)\times10^{-2}$, $\chi_{aa}=-27.7(35)$, $\eta\chi_{aa}=-31.5(21)$

a) Since the observed components were restricted to those expected under the rule of $\Delta F=\Delta J$, the component can be designated by the $F$ value of the lower level alone. For example, the component of the $J+1\leftarrow J$ transition labeled $F=J+3/2$ indicates the component of $F'=J+5/2\leftarrow F=J+3/2$ and so on. Dotted line indicates that the corresponding component is overlapped with the other strong line. $\nu_0$ is the hypothetical unsplit frequency where the figures in parentheses indicate the deviations of the observed frequency from the calculated. $\Delta\nu(J+3/2)$ indicates the difference of the $F=J+3/2$ component from $\nu_0$ where the figures in parentheses indicate the deviation of the observed frequency from the calculated one. b) Figures in parentheses indicate the uncertainties attached to the last significant figures calculated from 2.5 times the standard deviation.

TABLE 2. OBSERVED AND HYPOTHETICAL UNSPLIT FREQUENCIES AND ROTATIONAL CONSTANTS OF THE $^{18}$O SPECIES OF CHLOROMETHYL ETHYL ETHER (MHz)[a]

| $F$ | $J+3/2$ | $J+1/2$ | $J-1/2$ | $J-3/2$ | $\nu_0$ | $\Delta\nu$ $(J+3/2)$ | $\Delta\nu$ $(J+1/2)$ | $\Delta\nu$ $(J-1/2)$ | $\Delta\nu$ $(J-3/2)$ |
|---|---|---|---|---|---|---|---|---|---|
| $3_{03}\leftarrow 2_{02}$ | 10334.40 | 10334.40 | ··· | ··· | 10334.34( −3) | 0.06( −7) | 0.06( −7) | — | — |
| $3_{13}\leftarrow 2_{12}$ | 10113.80 | 10113.80 | 10111.99 | 10111.99 | 10113.44(−15) | 0.36(−11) | 0.36( 28) | −1.45( 3) | −1.45(−35) |
| $3_{12}\leftarrow 2_{11}$ | 10568.18 | 10568.18 | ··· | ··· | 10568.48( 18) | −0.30(−16) | −0.30( 23) | — | — |
| $4_{04}\leftarrow 3_{03}$ | 13770.14 | 13770.14 | 13770.14 | 13770.14 | 13770.16( 2) | −0.02(−15) | −0.02( 7) | −0.02( 19) | −0.02( −2) |
| $4_{14}\leftarrow 3_{13}$ | 13482.70 | 13482.70 | 13481.72 | 13481.72 | 13482.43( −8) | 0.27( −3) | 0.27( 17) | −0.71( −2) | −0.71(−21) |
| $4_{13}\leftarrow 3_{12}$ | 14088.63 | 14088.63 | ··· | ··· | 14088.80( 9) | −0.17( −8) | −0.17( 11) | — | — |
| $5_{05}\leftarrow 4_{04}$ | 17198.33 | 17198.33 | 17198.33 | 17198.33 | 17198.34( 12) | −0.01(−15) | −0.01( 11) | −0.01( 17) | −0.01( −9) |
| $5_{15}\leftarrow 4_{14}$ | 16849.60 | 16849.60 | 16849.12 | 16849.12 | 16849.46( −5) | 0.14( −7) | 0.14( 7) | −0.34( 7) | −0.34( −6) |
| $5_{14}\leftarrow 4_{13}$ | 17606.98 | 17606.98 | 17606.98 | 17606.98 | 17606.95(−11) | 0.03( 8) | 0.03( 22) | 0.03(−16) | 0.03(−30) |
| $6_{06}\leftarrow 5_{05}$ | 20616.91 | 20616.91 | 20616.91 | 20616.91 | 20616.92( 13) | −0.01(−17) | −0.01( 15) | −0.01( 17) | −0.01(−14) |
| $6_{16}\leftarrow 5_{15}$ | 20214.18 | 20214.18 | 20214.18 | 20214.18 | 20214.21( 2) | −0.03(−19) | −0.03( −8) | −0.03( 25) | −0.03( 13) |
| $6_{15}\leftarrow 5_{14}$ | 21122.66 | 21122.66 | 21122.66 | 21122.66 | 21122.64(−14) | 0.02( 4) | 0.02( 17) | 0.02( −9) | 0.02(−21) |
| $3_{22}\leftarrow 3_{12}$ | 26462.83 | 26457.41 | ··· | ··· | 26460.99( 24) | 1.84( 8) | −3.58(−10) | — | — |
| $4_{23}\leftarrow 4_{13}$ | 26162.29 | 26156.96 | ··· | ··· | 26160.39( 3) | 1.90(−15) | −3.43( 16) | — | — |
| $5_{24}\leftarrow 5_{14}$ | 25788.27 | 25782.77 | 25784.44 | 25789.91 | 25786.20( 1) | 2.07(−17) | −3.43( 15) | −1.76( 18) | 3.71(−17) |
| $6_{25}\leftarrow 6_{15}$ | 25341.45 | 25335.44 | 25336.75 | 25342.82 | 25339.01(−16) | 2.44( 8) | −3.57( −2) | −2.26(−11) | 3.81( 5) |
| $7_{26}\leftarrow 7_{16}$ | 24823.03 | ··· | 24817.80 | ··· | 24820.33(−22) | 2.70( 25) | — | −2.53(−25) | — |
| $8_{27}\leftarrow 8_{17}$ | 24234.21 | ··· | ··· | 24235.37 | 24231.75(−14) | 2.46(−12) | — | — | 3.62( −2) |
| $9_{28}\leftarrow 9_{18}$ | 23577.69 | 23571.72 | ··· | 23578.65 | 23575.14( 3) | 2.55( −1) | −3.42( −6) | — | 3.51( 0) |
| $10_{29}\leftarrow 10_{19}$ | 22855.56 | 22849.42 | 22850.31 | ··· | 22852.85( 22) | 2.71( 18) | −3.43( −7) | −2.54( −3) | — |

$A=10694.92(20)$, $B=1799.47(3)$, $C=1647.90(4)$, $d_J=0.68(94)\times10^{-3}$, $d_{JK}=1.54(32)\times10^{-2}$, $\chi_{aa}=-5.7(77)$, $\eta\chi_{aa}=-50.7(54)$

a) See footnote to Table 1.

even numbers and those on the opposite side, odd numbers. For the unreliable $K$-values, the values should be solved by means of certain constraints and/or assumptions. However, since several different sets of constraints and/or assumptions are usually possible, a preferable set is selected by certain criterions. When

TABLE 3. KRAITCHMAN VALUES OF THE ATOM COORDINATES FOR FLUOROMETHYL AND CHLOROMETHYL ETHERS IN Å[a)]

| Atom[b)] | $x_a$ | $x_b$ | $x_c$ | $x_a$ | $x_b$ | $x_c$ |
|---|---|---|---|---|---|---|
| | $FCH_2OCH_3(X=F)$ | | | $ClCH_2OCH_3(X=Cl)$ | | |
| X | −1.3427( 33)[c)] | 0.4847( 43)[c)] | d) | −1.3485( 10) | 0.2480( 55) | $\underline{-0\ 0402(339)}$ |
| $C^x$ | −0.5532( 44) | −0.5804( 42) | 0.2965( 85) | $\underline{e)}$ | −0.8498( 27) | 0.2905( 80) |
| $H^1$ | −0.4705( 42) | −0.4854( 37) | 1.3924( 15) | $\underline{0.1663(108)}$ | −0.8251( 20) | 1.3829( 14) |
| $H^s$ | −1.0682( 20) | 1.4955( 15) | $\underline{\pm0.0636(401)^{f)}}$ | $\underline{-0.2582(\ 88)}$ | −1.8280( 13) | $\underline{\pm0.0770(352)^{f)}}$ |
| O | 0.6636( 18) | −0.5536( 22) | −0.3156( 40) | 1.1989( 10) | −0.4674( 26) | −0.3668( 34) |
| $C^o$ | 1.4950( 15) | 0.5185( 44) | 0.1176(195) | 1.7853( 15) | 0.7249( 38) | 0.1359(205) |
| $H^2$ | 1.0311( 23) | 1.4900( 17) | $\underline{-0.1705(169)}$ | 1.0783( 19) | 1.5877( 14) | $\underline{\pm0.0777(306)^{f)}}$ |
| $H^3$ | 1.6230( 13) | 0.4735( 45) | 1.2104( 19) | 1.9915( 11) | 0.6106( 36) | 1.2156( 20) |
| $H^c$ | 2.4503( 9) | 0.4041( 56) | −0.3684( 62) | 2.7118( 12) | 0.8726( 38) | −0.3930( 88) |
| | $FCH_2OCH_2CH_3(X=F)$ | | | $ClCH_2OCH_2CH_3(X=Cl)$ | | |
| X | d) | d) | d) | −1.7842( 17) | 0.4133( 77) | $\underline{-0\ 0443(729)}$ |
| $C^x$ | −1.1684( 28) | −0.5774( 56) | 0.2312(145) | −0.5928( 97) | −0.9500( 61) | 0.1922(311) |
| $H^1$ | 1.2076( 26) | −0.5714( 50) | 1.3308( 25) | −0.6225(104) | −1.0956( 56) | 1.2817( 54) |
| $H^s$ | −1.7098( 18) | −1.4257( 23) | $\underline{-0.1960(186)}$ | −1.0339( 46) | −1.8002( 27) | −0.3327(165) |
| O | $\underline{0.0635(259)}$ | −0.6061( 27) | −0.2408( 72) | 0.6310( 52) | −0.6843( 48) | −0.3052(112) |
| $C^o$ | 0.9736( 30) | 0.3494( 84) | 0.3763( 80) | 1.3701( 34) | 0.2929(158) | 0.4336(108) |
| $H^2$ | 0.4618( 64) | 1.3726( 22) | $\underline{0.2364(145)}$ | 0.6439( 94) | 1.2789( 48) | 0.4300(151) |
| $H^3$ | 0.9765( 30) | $\underline{0.1515(169)}$ | 1.4609( 21) | 1.4597( 36) | $\underline{e)}$ | 1.4816( 36) |
| $C^c$ | 2.3711( 12) | 0.1355(224) | −0.1671(181) | 2.7498( 18) | 0.4018(124) | −0.1798(278) |
| $H^4$ | 2.7135( 10) | −0.8686( 33) | $\underline{0.1508(361)}$ | 3.2662( 23) | −0.5402(146) | $\underline{0.1974(402)}$ |
| $H^5$ | 2.3784( 12) | $\underline{0.2734(\ 93)}$ | −1.2509( 23) | 2.6732( 28) | 0.7117(105) | −1.2241( 66) |
| $H^m$ | 3.0622( 10) | 0.8474( 38) | $\underline{0\ 2824(118)}$ | 3.3404( 22) | 1.1456( 67) | 0.3447(234) |

a) Figures in parentheses indicate the 99% reliability intervals attached to the last significant figures. Underlined figures indicate unreliable Kraitchman values. b) Indentification symbol is shown in Fig. 1. c) Coordinate value can be determined by means of the first moment equation. d) Coordinate value can be determined by means of the first moment equation, but will be influenced by other coordinate values to be solved with other constraints. e) Kraitchman coordinate value is imaginary. f) Kraitchman coordinate value is so small that the sign of the value is also uncertain.

the moments of inertia are calculated from atom coordinate values containing the values solved by the set of the constraints and/or assumptions, a useful criterion is the root mean square deviation of the observed and calculated moments of inertia for all the species measured (referred to as RMS).

*Chloromethyl Ethyl Ether (Gauche-Trans Isomer) [Cl, Et]*. Owing to the lack of data for the $^{18}O$ species, three coordinate values of the oxygen atom had to be solved from the coordinate values of the other atoms as well as three unreliable *K*-values.[2)] The *K*-values of the oxygen atom are regarded as reliable ones (Table 3). The coordinate values to be solved are then those of $x_b(H^3)$, $x_c(Cl)$, and $x_c(H^4)$. $x_b(H^3)$ can be solved with the aid of the first moment equation. The $x_c(H^4)$ value is obtained in two ways: 1) by assuming $\alpha(CCH^4)=\alpha(CCH^5)$, and 2) under the $I_{ac}=0$ constraint. In both cases, $x_c(Cl)$ is solved by means of the first moment equation. Since the hydrogen atom $H^m$ corresponds to the in-plane hydrogen if the molecule has the plane of symmetry, 1) gives a symmetric methyl group (Table 4, Structure I), while 2) gives an asymmetric methyl group (Structure II).

The structure of the $CCH_3$ part of the molecule is obtained by the assumption that the $x_c(H^5)$ *K*-value is reliable. The reported structure[2)] (Table 4) is close to Structure II for the $CCH_3$ part of the molecule. As regards the other part of the molecule, Structure II is better irrespective of the choice of assumptions for the $CCH_3$ part of the molecule, since the reported structure was obtained under several assumptions on the structure.

It is difficult to decide which of I and II is reliable. The constraint imposed on II ($I_{ac}=0$) is not applicable to the case of [F, Et]. Thus I having a symmetric methyl group is preferable to II for [Cl, Et].

*Chloromethyl Methyl Ether (Gauche Isomer) [Cl, Me]*. There are six unreliable *K*-values for [Cl, Me].[1)] The *K*-values of the oxygen atom obtained from newly additional data for the $^{18}O$ species seem to be reliable. For the $x_c$ coordinates, three unreliable *K*-values are situated at the same positions as those found for [F, Me] (Table 3). The constraints used for the case of [F, Me] may also be applicable to this molecule. Then three $x_c$ coordinates, $x_c(Cl)$, $x_c(H^s)$, and $x_c(H^2)$ are solved by the first moment equation, the $I_{bc}=0$ constraint and the $\alpha(OCH^2)=\alpha(OCH^3)$ assumption, respectively. The solutions for the $x_c$ coordinates thus obtained are independent of the uncertainties due to three unreliable $x_a$ *K*-values since all the $x_a$ and $x_b$ values related to the $\alpha(OCH^2)=\alpha(OCH^3)$ assumption are reliable.

In order to obtain the three $x_a$ coordinate values, the first moment equation for the $x_a$ coordinates, $\sum(x_a)_i m_i=0$ and the $I_{ab}=0$ and $I_{ac}=0$ constraints might be useful besides the assumptions on the structure. However, use of the $I_{ac}=0$ constraint may produce large uncertainties since some of the $x_c$ coordinate

TABLE 4. STRUCTURAL PARAMETERS OF CHLOROMETHYL ETHYL ETHER[a)]

| | Structure I (Proposed) | Structure II | Reported |
|---|---|---|---|
| Coordinate values (Å) obtained under the set of constraints and assumptions | | | |
| $x_b(\mathrm{H}^3)$ | −0.1417(1138) | −0.1417 | 0 |
| $x_c(\mathrm{C}^1)$ | −0.0677( 157) | −0.0648 | −0.0740 |
| $x_c(\mathrm{H}^4)$ | −0.0999( 538) | −0.2005 | −0.1974 |
| Inertia product (amu·Å$^2$) for the normal species | | | |
| $I_{ab}$ | 0.6841 | 0.6841 | 0.6842 |
| $I_{ac}$ | −0.5124 | 0 | −0.7339 |
| $I_{bc}$ | 0.0675 | −0.0293 | 0.0699 |
| Difference of the observed and calculated moment of inertia for the normal species (amu·Å$^2$) | | | |
| $\Delta I_a$ | 0.0859 | 0.0678 | 0.0377 |
| $\Delta I_b$ | 0.9416 | 0.9244 | 0.8509 |
| $\Delta I_c$ | 1.0407 | 1.0419 | 0.6453 |
| RMS(amu·Å$^2$) | 0.8085 | 0.8011 | 0.6172 |
| Skeleton | | | |
| $r$(CCl) (Å) | 1.829(11) | 1.829 | 1.830 |
| $r(\mathrm{OC}^x)$ (Å) | 1.347(16) | 1.347 | 1.348 |
| $r(\mathrm{OC}^o)$ (Å) | 1.431(14) | 1.431 | 1.421 |
| $r$(CCC) (Å) | 1.514(13) | 1.514 | 1.514 |
| $\alpha$(ClCO) | 113° 5′( 54′) | 113° 7′ | 113°44′ |
| $\alpha$(COC) | 114°24′(1°25′) | 114°24′ | 114°58′ |
| $\alpha$(OCC) | 108° 6′( 58′) | 108° 6′ | 108°10′ |
| $\tau$(ClCOC) | 71°49′(2°35′) | 71°44′ | 70°18′ |
| $\tau$(COCC) | 175°41′(3°20′) | 175°41′ | 176°50′ |
| Cl–CH$_2$–O group | | | |
| $r(\mathrm{CH}^1)$ (Å) | 1.100(31) | 1.100 | 1.100 |
| $r(\mathrm{CH}^s)$ (Å) | 1.092(18) | 1.092 | 1.092 |
| $\alpha(\mathrm{ClCH}^1)$ | 102°49′(1°29′) | 102°43′ | 103°00′ |
| $\alpha(\mathrm{ClCH}^s)$ | 104°24′(1° 2′) | 104°27′ | 104°18′ |
| $\alpha(\mathrm{OCH}^1)$ | 114°36′(2°10′) | 114°36′ | 113°38′ |
| $\alpha(\mathrm{OCH}^s)$ | 110° 3′(1°23′) | 110° 3′ | 110°21′ |
| $\alpha(\mathrm{H}^1\mathrm{CH}^s)$ | 111°14′(2°36′) | 111°14′ | 111°14′ |
| O–CH$_2$–C group | | | |
| $r(\mathrm{CH}^2)$ (Å) | 1.225(15) | 1.225 | 1.225 |
| $r(\mathrm{CH}^3)$ (Å) | 1.138(45) | 1.138 | 1.092 |
| $\alpha(\mathrm{OCH}^2)$ | 104°00′(1° 8′) | 104°00′ | 104°40′ |
| $\alpha(\mathrm{OCH}^3)$ | 104°47′(3°10′) | 104°47′ | 109°58′ |
| $\alpha(\mathrm{CCH}^2)$ | 118°46′(1°28′) | 118°46′ | 118°46′ |
| $\alpha(\mathrm{CCH}^3)$ | 109°11′(3°26′) | 109°11′ | 109°28′ |
| $\alpha(\mathrm{H}^2\mathrm{CH}^3)$ | 110°54′(7°36′) | 110°54′ | 105°31′ |
| CH$_3$ group | | | |
| $r(\mathrm{CH}^4)$ (Å) | 1.077(17) | 1.074 | 1.074 |
| $r(\mathrm{CH}^5)$ (Å) | 1.092(28) | 1.092 | 1.092 |
| $r(\mathrm{CH}^m)$ (Å) | 1.085(20) | 1.085 | 1.085 |
| $\alpha(\mathrm{CCH}^4)$ | 110° 7′(1°41′) | 112°30′ | 112°26′ |
| $\alpha(\mathrm{CCH}^5)$ | 110° 7′(1°41′) | 110° 7′ | 110° 7′ |
| $\alpha(\mathrm{CCH}^m)$ | 110°27′(1°19′) | 110°27′ | 110°27′ |
| $\alpha(\mathrm{H}^4\mathrm{CH}^m)$ | 107°37′(2°28′) | 110°24′ | 110°19′ |
| $\alpha(\mathrm{H}^5\mathrm{CH}^m)$ | 107°48′(2°47′) | 107°48′ | 107°48′ |
| $\alpha(\mathrm{H}^4\mathrm{CH}^5)$ | 110°39′(3°54′) | 105°18′ | 105°28′ |

a) Figures in parentheses indicate 99% reliability intervals. For bond lengths, the figures are attached to the last significant figures.

values are already solved by the other constraints and assumptions.

For this molecule, all the unreliable $x_a$ values are the coordinates in the ClCH$_2$O part of the molecule. Since all the $K$-values of the ClCH$_2$O part are reliable for [Cl, Et] except the $x_c$(Cl) value, the structural parameters of this part of [Cl, Et] are considered to be reliable except those related to the chlorine atom.

Since the structure of the ClCH$_2$O part of [Cl, Me] does not seem to be much affected by the substitution of OCH$_3$ with OCH$_2$CH$_3$, the structural parameters can be transferred between these two molecules.

Though four bond lengths and six angles belong to the ClCH$_2$O part, seven parameters related to the Cl and H$^s$ atoms cannot be used in order to evaluate the $x_a$ values irrespective of the evaluation of the $x_c$ values. The structural parameters of the skeleton are more important than the other parameters for our purpose so that the transfer of the $r(\mathrm{C}^x\mathrm{O})$ value is not preferable. $r(\mathrm{CH}^1)$ and $\alpha(\mathrm{OCH}^1)$ are thus are the best parameters for the transfer.

Usually, the $K$-values for hydrogen atoms are regarded as unreliable for values less than 0.3 Å. However, they sometimes give reasonable structural parameters even when the values are less than 0.3 Å. Thus it is better to calculate structural parameters by using the unreliable $K$-values. If the structural parameters thus calculated are reasonable, the $K$-values used will be considered to be reliable.

Taking the above discussion into consideration, we tested ten possible sets of constraints and/or assumptions. 1) Use of the first moment equation and the $I_{ab}=0$ constraint requires one additional assumption on the coordinate value or structural parameter, there being four choices of assumption: i) the $x_a(\mathrm{H}^s)$ $K$-value is reliable, ii) the $x_a(\mathrm{H}^1)$ $K$-value is reliable, iii) the $r(\mathrm{CH}^1)$ value is transferred, and iv) $\alpha(\mathrm{OCH}^1)$ is transferred from that of [Cl, Et]. However, the results obtained from these four sets can be rejected since i) gives a too large $x_a(\mathrm{H}^1)$ value and ii), iii), and iv) very small $\alpha(\mathrm{ClCH}^s)$ values. Thus use of the $I_{ab}=0$ constraint is regarded to be inadequate. 2) Use of the first moment equation and two transferred structural parameter values, $r(\mathrm{CH}^1)$ and $\alpha(\mathrm{OCH}^1)$ also give a too large $x_a(\mathrm{H}^s)$ value. 3) Use of the first moment equation and the $x_a(\mathrm{H}^1)$ $K$-value assumed to be reliable requires one transferred parameter, either $r(\mathrm{CH}^1)$ or $\alpha(\mathrm{OCH}^1)$. These sets, however, give too small values of $\alpha(\mathrm{OCH}^s)$ or $\alpha(\mathrm{ClCH}^s)$ and can be rejected. 4) Use of the first moment equation, the $x_a(\mathrm{H}^s)$ $K$-value assumed to be reliable requires one transferred parameter, either $r(\mathrm{CH}^1)$ or $\alpha(\mathrm{OCH}^1)$, (Table 5, Structures I and II). 5) The $x_a(\mathrm{H}^1)$ values solved by the two sets of 4) are very close to the $K$-value. If we regard the $K$-values of $x_a(\mathrm{H}^1)$ and $x_a(\mathrm{H}^s)$ as reliable, the structural parameters obtained are close to those of Structures I and II. This set of structural parameters (Structure III) is obtained without transfer of the parameter values from the other molecules. Therefore, this is considered to be the most reliable set of parameters for [Cl, Me]. The structure reported[1)] is also given in Table 5 for the sake of comparison.

TABLE 5. STRUCTURAL PARAMETERS OF CHLOROMETHYL METHYL ETHER[a)]

| | Structure I | Structure II | Reported | Structure III (Proposed) |
|---|---|---|---|---|
| Coordinate values (Å) obtained under the set of constraints and assumptions | | | | |
| $x_a(C^x)$ | 0.0665 | 0.0700 | 0.0560 | 0.0684( 37) |
| $x_a(H^1)$ | 0.1886 | 0.1478 | 0.1780 | 0.1663(108) |
| $x_a(H^s)$ | −0.2582 | −0.2582 | −0.2941 | −0.2582( 88) |
| $x_c(Cl)$ | −0.0392 | −0.0392 | −0.0402 | −0.0392( 78) |
| $x_c(H^s)$ | −0.0830 | −0.0830 | −0.0466 | −0.0830(294) |
| $x_c(H^2)$ | −0.0173 | −0.0173 | −0.0471 | −0.0173(371) |
| Inertia product (amu·Å²) for the normal species | | | | |
| $I_{ab}$ | 0.1501 | 0.1511 | 0.1931 | 0.1506 |
| $I_{ac}$ | 0.4104 | 0.4554 | 0.4831 | 0.4350 |
| $I_{bc}$ | 0 | 0 | 0.0937 | 0 |
| Difference of the observed and calculated moment of inertia for the normal species (amu·Å²) | | | | |
| $\Delta I_a$ | 0.1349 | 0.1352 | 0.0440 | 0.1351 |
| $\Delta I_b$ | 0.5766 | 0.5849 | 0.1798 | 0.5816 |
| $\Delta I_c$ | 0.7173 | 0.7252 | 0.1855 | 0.7220 |
| RMS (amu·Å²) | 0.5391 | 0.5484 | 0.1508 | 0.5446 |
| Skeleton | | | | |
| $r(CCl)$ (Å) | 1.821 | 1.824 | 1.813 | 1.822( 5) |
| $r(OC^x)$ (Å) | 1.364 | 1.361 | 1.379 | 1.362( 5) |
| $r(OC^o)$ (Å) | 1.421 | 1.421 | 1.422 | 1.421( 8) |
| $\alpha(ClCO)$ | 112°52′ | 112°52′ | 113°22′ | 112°52′( 21′) |
| $\alpha(COC)$ | 114° 2′ | 114° 2′ | 113°37′ | 114° 2′( 35′) |
| $\tau(ClCOC)$ | 70°35′ | 70°40′ | 69°40′ | 70°37′(1°33′) |
| $-CH_2-$ group | | | | |
| $r(CH^1)$ (Å) | 1.100 | 1.096 | 1.100 | 1.097( 8) |
| $r(CH^s)$ (Å) | 1.096 | 1.097 | 1.092 | 1.097(11) |
| $\alpha(ClCH^1)$ | 104°38′ | 102°49′ | 104°41′ | 103°39′( 44′) |
| $\alpha(ClCH^s)$ | 104°14′ | 104° 2′ | 103°45′ | 104° 7′( 39′) |
| $\alpha(OCH^1)$ | 112°20′ | 114°36′ | 111°55′ | 113°34′( 45′) |
| $\alpha(OCH^s)$ | 109°23′ | 109°31′ | 111°24′ | 109°27′( 53′) |
| $\alpha(H^1CH^s)$ | 113° 2′ | 112°22′ | 111°14′ | 112°41′(2°24′) |
| $CH_3$ group | | | | |
| $r(CH^2)$ (Å) | 1.126 | 1.126 | 1.130 | 1.126( 7) |
| $r(CH^3)$ (Å) | 1.105 | 1.105 | 1.105 | 1.105(20) |
| $r(CH^c)$ (Å) | 1.077 | 1.077 | 1.077 | 1.077(11) |
| $\alpha(OCH^2)$ | 109°37′ | 109°37′ | 109°30′ | 109°37′( 46′) |
| $\alpha(OCH^3)$ | 109°37′ | 109°37′ | 109°24′ | 109°37′(1° 5′) |
| $\alpha(OCH^c)$ | 107°14′ | 107°14′ | 106°54′ | 107°14′( 44′) |
| $\alpha(H^2CH^c)$ | 111°36′ | 111°36′ | 110°43′ | 111°36′(1° 4′) |
| $\alpha(H^3CH^c)$ | 109°28′ | 109°28′ | 109°28′ | 109°28′(1°32′) |
| $\alpha(H^2CH^3)$ | 109°13′ | 109°13′ | 110°43′ | 109°13′(2°32′) |

a) See footnote to Table 4.

*Fluoromethyl Methyl Ether (Gauche Isomer) [F, Me].* Of the five molecules mentioned, [F, Me] is the most favorable for the determination of its $r_s$ structure. There are only two unreliable *K*-value, $x_c(H^s)$ and $x_c(H^2)$, (Table 3). For the $x_c(H^s)$ coordinate, the *K*-value is so small that the sign of the coordinate value is also uncertain. Three coordinate values of the fluorine atom have to be solved by means of the first moment equations.

The $x_c(H^s)$ value is found to be very sensitive to the $I_{bc}$ inertia product but not to the $I_{ac}$ product. On the other hand, the effect of the $x_c(H^2)$ value on the $I_{bc}$ and $I_{ac}$ values is reverse to that of the $x_c(H^s)$ value. In order to find the adequacy of the use of the $I_{bc}$ and $I_{ac}=0$ constraints, the following calculations were carried out. 1) The $x_c(H^s)$ value is evaluated by $I_{bc}=0$ on the assumption that the $x_c(H^2)$ *K*-value is reliable (Table 6, Structure I). 2) The $x_c(H^2)$ value is evaluated by $I_{ac}=0$ with the sign of the $x_c(H^s)$ *K*-value taken as a) plus, (Structure II) and b) minus. Since the latter gives a very large $\alpha(H^1CH^s)$ value, a great increase of the absolute $I_{bc}$ value and a large RMS, the structure obtained by this assumption can be rejected.

Parameter differences between Structures I and II are found mainly in the $OCH_3$ group. For the former, both the $\alpha(OCH^3)$ and $\alpha(OCH^2)$ values are larger than the $\alpha(OCH^c)$ value and are close to each other, while three $\alpha(HCH)$ values are close to each other. The $CH^c$ bond is much shorter than the other two CH bonds which can be regarded to be equal if the experimental error is taken into account. Since the $H^c$ hydrogen atom corresponds to the hydrogen atom in the molecular plane if the molecule has the plane of symmetry, the relations on the structure indicate that the symmetric methyl group tilts towards the direction of the lone pair electrons on the oxygen atom. Thus, Structure I is essentially equal to the structure obtained on the assumption $\alpha(OCH^2)=\alpha(OCH^3)$ and the $I_{bc}=0$ constraint whose parameters are listed in Table 6 as III.

On the other hand, Structure II gives an asymmetric methyl group. It is difficult to judge which structure is more reliable. The sets of constraints applied to Structures I and II cannot be used for the case of [Cl, Me]. Structure III is thus considered to be better than the other structures when a comparison of structures is made between these molecules.

*Fluoromethyl Ethyl Ether (Gauche-Trans Isomer) [F, Et].* The GT isomer of [F, Et] is the most unfavorable molecule of the four halomethyl ethers for the determination of the $r_s$ structure. There are seven unreliable *K*-values and three coordinate values of the fluorine atom should be solved by means of the first moment equations.

First, the reliability of the unreliable *K*-values was tested in order to reduce the number of coordinate values to be evaluated. For the $CCH_3$ part of the molecule, the unreliable *K*-values are $x_b(H^5)$, $x_c(H^4)$, and $x_c(H^m)$. Since the calculations indicate that the structural parameters containing $x_b(H^5)$ and $x_c(H^m)$ give quite reasonable values as compared with the corresponding parameter values of [Cl, Et], the *K*-values of $x_b(H^5)$ and $x_c(H^m)$ can be regarded as reliable. On the other hand, the calculated parameter values related to $x_c(H^4)$ give a very small $r(CH^4)$ and a very large $\alpha(CCH^4)$. The $x_c(H^4)$ *K*-value should thus be evaluated by some other means.

A similar test indicates that the $x_a(O)$ *K*-value is doubtful, while the $x_c(H^s)$ *K*-value is quite reliable though the absolute value is small.

As regards the two *K*-values of $x_c(H^2)$ and $x_b(H^3)$, the test gives no conclusive result and they should be evaluated by other means.

TABLE 6. STRUCTURL PARAMETERS OF FLUOROMETHYL METHYL ETHER[a)]

| | Structure I | Structure II | Structure III (Proposed) |
|---|---|---|---|
| Coordinate values (Å) obtained under the set of constraints and assumptions | | | |
| $x_c(F)$ | −0.1048 | −0.1140 | −0.1059(142) |
| $x_c(H^s)$ | −0.0091 | 0.0492 | −0.0026(304) |
| $x_c(H^2)$ | −0.1705 | −0.0557 | −0.1578(425) |
| Inertia product (amu·Å$^2$) for the normal species | | | |
| $I_{ab}$ | −0.0768 | −0.0768 | −0.0768 |
| $I_{ac}$ | 0.2908 | 0 | 0.2585 |
| $I_{bc}$ | 0 | 0 | 0 |
| Difference of the observed and calculated moment of inertia for the normal species (amu·Å$^2$) | | | |
| $\Delta I_a$ | 0.1840 | 0.1685 | 0.1840 |
| $\Delta I_b$ | 0.6224 | 0.6081 | 0.6226 |
| $\Delta I_c$ | 0.7849 | 0.7861 | 0.7852 |
| RMS(amu·Å$^2$) | 0.5884 | 0.5843 | 0.5890 |
| Skeleton | | | |
| $r$(CF) (Å) | 1.385 | 1.388 | 1.385( 7) |
| $r$(OC$^x$) (Å) | 1.362 | 1.362 | 1.362( 6) |
| $r$(OC$^o$) (Å) | 1.424 | 1.424 | 1.424( 7) |
| $\alpha$(FCO) | 111°19′ | 111° 6′ | 111°18′( 33′) |
| $\alpha$(COC) | 113°33′ | 113°33′ | 113°33′( 36′) |
| $\tau$(FCOC) | 69°11′ | 69°29′ | 69°13′(1°38′) |
| –$CH_2$– group | | | |
| $r$(CH$^1$) (Å) | 1.103 | 1.103 | 1.103( 9) |
| $r$(CH$^s$) (Å) | 1.094 | 1.079 | 1.092(10) |
| $\alpha$(FCH$^1$) | 105°19′ | 105°41′ | 105°21′(1° 2′) |
| $\alpha$(FCH$^s$) | 107° 6′ | 108° 9′ | 107°13′( 43′) |
| $\alpha$(OCH$^1$) | 112°11′ | 112°11′ | 112°11′( 40′) |
| $\alpha$(OCH$^s$) | 108° 9′ | 109°53′ | 108°20′( 43′) |
| $\alpha$(H$^1$CH$^s$) | 112°38′ | 109°40′ | 112°18′(2°19′) |
| $CH_3$ group | | | |
| $r$(CH$^2$) (Å) | 1.115 | 1.090 | 1.111(12) |
| $r$(CH$^3$) (Å) | 1.101 | 1.101 | 1.101(19) |
| $r$(CH$^c$) (Å) | 1.078 | 1.078 | 1.078( 9) |
| $\alpha$(OCH$^2$) | 109°32′ | 111°57′ | 109°48′( 47′) |
| $\alpha$(OCH$^3$) | 109°48′ | 109°48′ | 109°48′(1° 3′) |
| $\alpha$(OCH$^c$) | 107°28′ | 107°28′ | 107°28′( 39′) |
| $\alpha$(H$^2$CH$^c$) | 110°10′ | 113°34′ | 110°33′(1° 5′) |
| $\alpha$(H$^3$CH$^c$) | 109°52′ | 109°52′ | 109°52′(1°23′) |
| $\alpha$(H$^2$CH$^3$) | 109°54′ | 104° 5° | 109°16′(3°11′) |

a) See footnote to Table 4.

The original set of $K$-values gave the RMS value of 3.4283 amu·Å$^2$ and the large inertia products ($I_{ab}$, $I_{ac}$, $I_{bc}$)=(−0.6012, 0.4859, −0.2993) amu·Å$^2$ (Table 7).

Since the $x_c(H^4)$ $K$-value was also unreliable for [Cl, Et], it was obtained on the assumption $\alpha(CCH^4)=\alpha(CCH^5)$. The same assumption is also applied to $x_c(H^4)$ of the present molecule. The RMS and $I_{bc}$ values are reduced to 3.4056 and 0.0179 amu·Å$^2$, respectively, the structural parameters of the $CCH_3$ part becoming reasonably closer to those of [Cl, Et]. The $x_c(H^4)$ value thus obtained is used in all the trial calculations.

In order to evaluate the most unreliable three coordinate values, $x_a(O)$, $x_b(H^3)$, and $x_c(H^2)$, the set of the $I_{ab}=0$, $I_{ac}=0$, and $I_{bc}=0$ constraints and the three first moment equations might be applied on the assumption that the other four unreliable $K$-values are regarded as reliable. However, simultaneous use of the zero inertia product constraints seems dangerous for the present molecule where many unreliable $K$-values exist in all the $x_a$, $x_b$, and $x_c$ coordinates.

The $x_a(O)$ value is evaluated by i) $I_{ab}=0$ or ii) $I_{ac}=0$ constraint on the assumption that the $K$-values of $x_b(H^s)$ and $x_c(H^2)$ and the other unreliable $K$-values are regarded as reliable. The $x_a(O)$ value obtained from ii) is too large, that from i) being reasonable. The RMS value for the structure from i) is 1.8570 amu·Å$^2$.

Since the $I_{bc}=0$ constraint was successfully used for the $x_c(H^s)$ value of [F, Me], it is applied to one of the $x_c(H^2)$ and $x_b(H^3)$ values. The parameters related to the oxygen atom for these two cases are essentially equal to those obtained from i) but the RMS values are reduced slightly. The parameters (Structure I, Table 7) are obtained for the case where the $x_c(H^2)$ value is obtained from the $I_{bc}=0$ constraint. For Structure I, the RMS and $I_{ac}$ values are fairly large. We see that the RMS and $I_{ac}$ values strongly depend on the $x_a(O)$ and $x_a(F)$ values which are related with each other by means of the first moment equation.

The $x_a(O)$ value can be solved on the assumptions that the $x_b(H^3)$ and $x_c(H^2)$ values of Structure I as reliable and one of the skeletal parameter values related to the oxygen atom for analogous molecules can be transferred to that of [F, Et]. First, the $\alpha$(OCC) value of [Cl, Et] is transferred. The parameter values obtained are listed under Structure II. The RMS, $I_{ab}$ and $I_{ac}$ values of Structure II are fairly large. Though the structure is also obtained by use of the transferred $r$(C$^o$O) value of [Cl, Et], the parameter values obtained are found to be very close to those of Structure II. The $r$(C$^o$O) value of [Cl, Et] is inadequate to be transferred since the influence of the substitution of the chlorine atom with the fluorine atom seems to be too serious.

The plausible structures of [Cl, Me] and [Cl, Et] indicate that the $\alpha$(COC) values of these two molecules are relatively close to each other (Table 8). On the assumption that the situation is the same for [F, Me] and [F, Et], the $\alpha$(COC) value of [F,Me] is transferred (Structure III, Table 7). Though the RMS value of Structure III is satisfactorily small, the $I_{ab}$ and $I_{ac}$ values are fairly large. Furthermore, the skeletal parameter values of Structure III do not always seem to be reasonable, when a comparison is made between the plausible structures of fluoromethyl and chloromethyl ethers. For example, the difference between $r$(C$^x$O) and $r$(C$^o$O) for [Cl, Et] is larger than that for [Cl, Me], while the difference for [F, Et] is smaller than that for [F, Me].

Since the (COC) value of [Cl, Et] is slightly larger (22′) than that of [Cl, Me], the $\alpha$(COC) value of [F, Et] is assumed to be larger by 22′ than that of [F, Me]. By this slight change in the $\alpha$(COC) value, the RMS, $I_{ab}$ and $I_{ac}$ values are much reduced and the difference of two CO bond lengths becomes close to that of Structure II. From the above discussion, it is

TABLE 7. STRUCTURAL PARAMETERS OF FLUOROMETHYL ETHYL ETHER[a)]

| | Original[b)] | Structure I (Proposed) | Structure II | Structure III (Reported) |
|---|---|---|---|---|
| Coordinate values (Å) obtained under the set of constraints and assumptions | | | | |
| $x_a(O)$ | 0.0635 | 0.0952 | 0.1057 | 0.1216 |
| $x_b(H^3)$ | 0.1515 | 0.1515(169) | 0.1515 | 0.1515 |
| $x_c(H^2)$ | 0.2364 | 0.2588(145) | 0.2588 | 0.2588 |
| $x_a(F)$ | −1.7822 | −1.8088 | −1.8177 | −1.8311 |
| $x_b(F)$ | 0.5804 | 0.5804(157) | 0.5804 | 0.5804 |
| $x_c(F)$ | −0.1663 | −0.1790(169) | −0.1790 | −0.1790 |
| Inertia product (amu·Å²) for the normal species | | | | |
| $I_{ab}$ | −0.6012 | 0 | 0.1996 | 0.5026 |
| $I_{ac}$ | 0.4859 | −0.5175 | −0.5071 | −0.4913 |
| $I_{bc}$ | −0.2993 | 0 | 0 | 0 |
| Difference of the observed and calculated moment of inertia for the normal 1 species (amu·Å²) | | | | |
| $\Delta I_a$ | 0.1300 | 0.0518 | 0.0520 | 0.0532 |
| $\Delta I_b$ | 4.1963 | 2.2158 | 1.5718 | 0.5804 |
| $\Delta I_c$ | 4.2044 | 2.3105 | 1.6668 | 0.6768 |
| RMS (amu·Å²) | 3.4283 | 1.8484 | 1.3233 | 0.5164 |
| Skeleton | | | | |
| $r(CF)$ (Å) | 1.369 | 1.385 | 1.389 | 1.396 |
| $r(C^xO)$ (Å) | 1.319 | 1.349 | 1.359 | 1.374 |
| $r(C^oO)$ (Å) | 1.456 | 1.437 | 1.431 | 1.421 |
| $r(CC)$ (Å) | 1.515 | 1.515( 8) | 1.515 | 1.515 |
| $\alpha(FCO)$ | 109°27′ | 110°19′ | 110°41′ | 111°14′ |
| $\alpha(COC)$ | 114°40′ | 114° 4′ | 113°52′ | 113°33′ [c)] |
| $\alpha(OCC)$ | 109°22′ | 108°25′ | 108° 6′ [c)] | 107°36′ |
| $\tau(FCOC)$ | 70°10′ | 70°22′ | 70°16′ | 70° 8′ |
| $\tau(COCC)$ | 175°15′ | 175°41′ | 175°49′ | 176° 1′ |
| F–$CH_2$– group | | | | |
| $r(CH^1)$ (Å) | 1.100 | 1.100( 15) | 1.100 | 1.100 |
| $r(CH^s)$ (Å) | 1.093 | 1.093( 10) | 1.093 | 1.093 |
| $\alpha(FCH^1)$ | 105°38′ | 105°57′ | 105°53′ | 105°47′ |
| $\alpha(FCH^s)$ | 108°42′ | 107°41′ | 107°26′ | 107° 4′ |
| $\alpha(OCH^1)$ | 113° 3′ | 112°31′ | 112°22′ | 112° 8′ |
| $\alpha(OCH^s)$ | 107°48′ | 108° 5′ | 108°11′ | 108°20′ |
| $\alpha(H^1CH^s)$ | 112° 8′ | 112° 8′(1°50′) | 112° 8′ | 112° 8′ |
| O–$CH_2$– group | | | | |
| $r(CH^2)$ (Å) | 1.153 | 1.150( 9) | 1.150 | 1.150 |
| $r(CH^3)$ (Å) | 1.102 | 1.102( 9) | 1.102 | 1.102 |
| $\alpha(OCH^2)$ | 104°40′ | 106° 0′ | 106°16′ | 106°40′ |
| $\alpha(OCH^3)$ | 107°30′ | 107°44′ | 107°49′ | 107°56′ |
| $\alpha(CCH^2)$ | 119°26′ | 119°58′(1°23′) | 119°58′ | 119°58′ |
| $\alpha(CCH^3)$ | 108°58′ | 108°58′(1°15′) | 108°58′ | 108°58′ |
| $\alpha(H^2CH^3)$ | 106°15′ | 105° 8′(1°27′) | 105° 8′ | 105° 8′ |

$CH_3$ group Structural parameters are common to Structures I—III

| | $r(CH^4)$ (Å) | $r(CH^5)$ (Å) | $r(CH^m)$ | $\alpha(CCH^4)$ | $\alpha(CCH^5)$ |
|---|---|---|---|---|---|
| Original | 1.061 | 1.093 | 1.089 | 115°12′ | 110° 8′ |
| Others | 1.086(23) | 1.093(18) | 1.089(17) | 110° 8′(1°22′) | 110° 8′(1° 5′) |
| | $\alpha(CCH^m)$ | $\alpha(H^4CH^m)$ | $\alpha(H^5CH^m)$ | $\alpha(H^4CH^5)$ | $\tau(OCCH^m)$ |
| Original | 110°11′ | 114° 2′ | 108°49′ | 97°36′ | 180°17′ |
| Others | 110°11′( 57′) | 108°23′(1°51′) | 108°49′(1°46′) | 109° 7′(3°48′) | 179°55′ |

a) See footnote to Table 4. b) The structure obtained from the original Kraitchman coordinate values and the three first moment equations. c) Assumed. See text.

found that assurance is necessary for the transferability of the skeletal parameter value in order to transfer the parameter values.

In spite of the large RMS and $I_{ac}$ values, Structure I is considered to be plausible for the structure of [F, Et], since this structure is obtained with no assumption on the skeletal structure. It may be favorable for Structure I that the parameter values obtained are reasonable when a comparison of their values is made with those of the other three halomethyl ethers (Table 8).

TABLE 8. PLAUSIBLE STRUCTURAL PARAMETERS OF HALOMETHYL ETHERS[a)]

| | FCH$_2$OCH$_3$ | FCH$_2$OCH$_2$CH$_3$ | ClCH$_2$OCH$_3$ | ClCH$_2$OCH$_2$CH$_3$ | HC≡CCH$_2$OCH$_3$ |
|---|---|---|---|---|---|
| Skeleton (X=F, Cl, HC≡C) | | | | | |
| *r*(CX) (Å) | 1.385( 7) | 1.385 | 1.822( 5) | 1.829(11) | 1.459 |
| *r*(C$^x$O) (Å) | 1.362( 6) | 1.349 | 1.362( 5) | 1.347(16) | 1.410 |
| *r*(C$^o$O) (Å) | 1.424( 7) | 1.437 | 1.421( 8) | 1.431(14) | 1.410(17) |
| *r*(CC) (Å) | | 1.515 | | 1.514(13) | |
| α(XCO) | 111°18′( 33′) | 110°19′ | 112°52′( 21′) | 113° 5′( 54′) | 112°29′ |
| α(COC) | 113°33′( 36′) | 114° 4′ | 114° 2′( 35′) | 114°24′(1°25′) | 113°30′ |
| α(OCC) | | 108°25′ | | 108° 6′( 58′) | |
| τ(XCOC) | 69°13′(1°38′) | 70°22′ | 70′37′(1°33′) | 71°49′(2°35′) | 67°30′ |
| τ(COCC) | | 175°41′ | | 175°41′(3°20′) | |
| XCH$_2$ group (X=F, Cl, HC≡C) | | | | | |
| *r*(CH$^1$) (Å) | 1.103( 9) | 1.100(15) | 1.097( 8) | 1.100(31) | 1.101 |
| *r*(CH$^s$) (Å) | 1.092(10) | 1.093(10) | 1.097(11) | 1.092(18) | 1.101 |
| α(XCH$^1$) | 105°21′(1° 2′) | 105°57′ | 103°39′( 44′) | 102°49′(1°29′) | 108°44′ |
| α(XCH$^s$) | 107°13′( 43′) | 107°41′ | 104° 7°( 39′) | 104°24′(1° 2′) | 108°44′ |
| α(OCH$^1$) | 112°11′( 40′) | 112°31′ | 113°34′( 45′) | 114°36′(2°10′) | 109°49′ |
| α(OCH$^s$) | 108°20′( 43′) | 108° 5′ | 109°27′( 53′) | 110° 3′(1°23′) | 109°49′ |
| α(H$^1$CH$^s$) | 112°18′(2°19′) | 112° 8′(1°50′) | 112°41′(2°24′) | 111°14′(2°36′) | 107°13′ |
| OCH$_2$Y group (Y=H, C) | | | | | |
| *r*(CH$^2$) (Å) | 1.111(12) | 1.150( 9) | 1.126( 7) | 1.225(15) | 1.170( 9) |
| *r*(CH$^3$) (Å) | 1.101(19) | 1.102( 9) | 1.105(20) | 1.138(45) | 1.110(34) |
| α(OCH$^2$) | 109°48′( 47′) | 106° 0′ | 109°37′( 46′) | 104° 0′(1° 8′) | 109°51′(1°31′) |
| α(OCH$^3$) | 109°48′(1° 3′) | 107°44′ | 109°37′(1° 5′) | 104°47′(3°10′) | 109°51′(2° 2′) |
| α(YCH$^2$) | 110°33′(1° 5′) | 119°58′(1°22′) | 111°36′(1° 4′) | 118°46′(1°28′) | 113° 1′(1°48′) |
| α(YCH$^3$) | 109°52′(1°23′) | 108°58′(1°15′) | 109°28′(1°32′) | 109°11′(3°26′) | 108°52′(2°42′) |
| α(H$^2$CH$^3$) | 109°16′(3°11′) | 105° 8′(1°27′) | 109°13′(2°32′) | 110°54′(7°36′) | 107°50′(3°18′) |
| *r*(CH$^c$) (Å) | 1.078( 9) | | 1.077(11) | | 1.078(19) |
| α(OCH$^c$) | 107°28′( 39′) | | 107°14′( 44′) | | 107°23′(1°28′) |
| τ(COCH$^c$) | 175°48′(1°47′) | | 174°39′(2°24′) | | 180.0(assumed) |
| CCH$_3$ group | | | | | |
| *r*(CH$^4$) (Å) | | 1.086(23) | | 1.077(17) | |
| *r*(CH$^5$) (Å) | | 1.093(18) | | 1.092(28) | |
| *r*(CH$^m$) (Å) | | 1.089(17) | | 1.085(20) | |
| α(CCH$^4$) | | 110° 8′(1°22′) | | 110° 7′(1°41′) | |
| α(CCH$^5$) | | 110° 8′(1° 5′) | | 110° 7′(1°40′) | |
| α(CCH$^m$) | | 110°11′( 57′) | | 110°27′(1°19′) | |
| α(H$^4$CH$^m$) | | 108°23′(1°51′) | | 107°37′(2°28′) | |
| α(H$^5$CH$^m$) | | 108°49′(1°46′) | | 107°48′(2°47′) | |
| α(H$^4$CH$^5$) | | 109° 7′(3°48′) | | 110°39′(3°54′) | |
| τ(OCCH$^m$) | | 179°49′(2°55′) | | 180°47′(3°52′) | |
| RMS(amu·Å$^2$) | 0.5890 | 1.8484 | 0.5446 | 0.8085 | 0.7000 |

a) See footnote to Table 4.

Structure III was proposed as the plausible structure because of the smallest RMS value.[3)] However, its parameter values cannot be regarded to be adequate from a comparison of their values with those of the other three halomethyl ethers.

The large values of RMS and $I_{ac}$ for Structure I can be understood when the experimental errors of the $x_b$ and $x_c$ coordinate values of the C$^c$ carbon atom are taken into account. Experimental errors of the $x_b$ and $x_c$ *K*-values of the C$^c$ atom are fairly large, while its absolute $x_a$ value is large (Table 3). The experimental errors of $x_b$ and $x_c$ values induce large uncertainties on the $x_a$ values of the oxygen and fluorine atoms through the inertia product constraint ($I_{ab}=0$) and the first moment equation. Actually, when $x_b$(C$^c$) and $x_c$(C$^c$) values are shifted by about one-fifth of the experimental errors of the *K*-values (+0.005 and +0.003 Å, respectively), the RMS and $I_{ac}$ values of the structure obtained by the same procedure as Structure I are reduced to 1.2360 and −0.1160 amu·Å$^2$, while the parameters obtained are not much shifted.

The uncertainties for the "A" rotational constants of the normal and FCH$_2$OCH$_2$$^{13}$CH$_3$ species are as small as those of the other species. However, the uncertainties on the "A" rotational constants are amplified in the uncertainties on the $x_b$ and $x_c$ values due to the fact that the difference of the moments of inertia $\Delta I_a$ between the normal and $^{13}$C species is accidentally very small (0.0444 amu·Å$^2$). Thus, we cannot reduce the experimental errors in the $x_b$ and $x_c$

*K*-values though it is inevitable in order to reduce the RMS and $I_{ac}$ values of Structure I.

*Methyl 2-Propynyl Ether (Gauche Isomer) [Pr, Me].* A report has been given on the microwave spectra of the gauche isomer of [Pr, Me].[5] For this molecule, the $r_s$ structure cannot be obtained without serious assumptions on the structure since many coordinates having small absolute values exist in the $HC≡CCH_2$– part of the molecule. However, only one unreliable *K*-value exists for $OCH_3$ part of the molecule. This coordinate is $x_c(H^2)$. When the assumption $\alpha(OCH^2)=\alpha(OCH^3)$ is applied to this value as in the case of the halomethyl ethers, the $r_s$ structure of the $OCH_3$ part can be obtained irrespective of the uncertainties of the other part of the molecule, for which the parameters are adjusted so as to reproduce the observed moments of inertia. The results are given in Table 8.

*Summary of the Applied Constraints and/or Assumptions.* So far we have re-evaluated the $r_s$ structures of halomethyl ethers and the $OCH_3$ part of methyl 2-propynyl ether considering several sets of constraints and/or assumptions.

The sets used for the proposed structures of these molecules are given in the following, the coordinate values obtained by each constraint being shown in square brackets:

[F, Me]

The three first moment equations, $[x_a(F), x_b(F), x_c(F)]$; $\alpha(OCH^2)=\alpha(OCH^3)$, $[x_c(H^2)]$; $I_{bc}=0$, $[x_c(H^s)]$.

[Cl, Me]

The two first moment equations, $\sum mx_a=0$ and $\sum mx_c=0$, $[x_a(C^x), x_c(Cl)]$; $\alpha(OCH^2)=\alpha(OCH^3)$, $[x_c(H^2)]$; $I_{bc}=0$, $[x_c(H^s)]$; The assumption that the $x_a(H^1)$ and $x_a(H^s)$ *K*-values are reliable.

[F, Et]

The first moment equations, $[x_a(F), x_b(F), x_c(F)]$; $\alpha(CCH^4)=\alpha(CCH^5)$, $[x_c(H^4)]$; $I_{ab}=0$, $[x_a(O)]$; $I_{bc}=0$, $[x_c(H^2)]$; The assumption that the $x_b(H^3)$, $x_c(H^5)$, $x_b(H^5)$, and $x_c(H^m)$ *K*-values are reliable.

[Cl, Et]

The two first moment equations, $\sum mx_b=0$ and $\sum mx_c=0$, $[x_b(H^3), x_c(Cl)]$; $\alpha(CCH^4)=\alpha(CCH^5)$, $[x_c(H^4)]$.

[Pr, Me], $OCH_3$ group

$\alpha(OCH^2)=\alpha(OCH^3)$, $[x_c(H^2)]$

The above sets indicate that the plausible $r_s$ structures of these molecules can be obtained by use of the common constraints and/or assumptions on these five molecules. As is the case of [F, Et], even when many unreliable *K*-values are contained in the atom coordinates of a molecule to which usually no reliable $r_s$ structure can be obtained, the proposed structure seems to be fairly reliable.

## Discussion on Molecular Structures

The structures of four halomethyl ethers and [Pr, Me] have different reliabilities. However, their parameters (Table 8) exhibit interesting features when comparison is made with each other or with those of the other series of molecules.

Hereafter, for the quoted parameter values, figures in parentheses indicate the experimental uncertainties, while figures with ± such as 1.391±0.002 Å indicate the dispersion of the value, *viz.*, the value between 1.393 and 1.389 Å. The value referred to as that for alkyl ethers is the value taken from those for *trans*-ethyl methyl ether,[7] dimethyl ether,[8] TT-diethyl ether,[9] and TT-methyl propyl ether,[10] where TT indicates the trans-trans isomer.

*Skeleton.* 1) The $r(CF)$ value of $FCH_2OR(R=CH_3, CH_2CH_3)$ is close to that of methyl fluoride (1.384(1) Å)[11] but smaller than that of ethyl fluoride (1.398(5) Å).[12] On the other hand, the $r(CCl)$ value of $ClCH_2OR$ is larger than those of methyl chloride (1.781(1) Å)[13] and ethyl chloride (1.788(2) Å).[14] 2) The averages of the two $r(CO)$ values are nearly constant for all halomethyl ethers (1.391±0.002 Å) and smaller than those of alkyl ethers (1.410±0.002 Å). The value for [Pr, Me] is close to those of alkyl ethers. 3) $r(CO)$ attached to the halogen atom is much smaller than the other $r(CO)$ which is slightly larger than that of alkyl ethers. The difference between two $r(CO)$ values (0.073±0.015 Å) is much larger than that found in alkyl ethers such as *trans*-ethyl methyl ether (0.011 Å), the difference for $XCH_2OCH_2CH_3$ being larger than that for $XCH_2OCH_3$. For [Pr, Me], two $r(CO)$ values may be nearly equal to each other. 4) $r(CC)$ of $XCH_2OCH_2CH_3$ is smaller than that of propane,[15] *trans*-ethyl methyl ether and ethyl chloride, is nearly equal to that of diethyl ether, being larger than that of ethyl fluoride though the experimental uncertainty is fairly large. 5) $\alpha(COC)$ of halomethyl ethers is nearly equal to each other (114°±28′) and smaller than that of alkyl ethers by about 2°. $\alpha(COC)$ of [Pr, Me] is smaller than that of alkyl ethers. 6) $\alpha(FCO)$ of $FCH_2OR$ is smaller by *ca.* 1.5° than $\alpha(ClCO)$ of $ClCH_2OR$. 7) $\alpha(OCC)$ of $XCH_2OCH_2CH_3$ is nearly equal to that of alkyl ethers. 8) Skeletal dihedral angle $\tau(XCOC)$ increases in the order [F, Me], [F, Et], [Cl, Me], and [Cl, Et], the values being much larger (about 10°) than 60° which is presumed usual for the dihedral angle value of the gauche configuration of the molecules. For [Pr, Me], this angle is smaller by *ca.* 2° than that of halomethyl ethers. 9) Skeletal dihedral angle $\tau(COCC)$ of $XCH_2OCH_2CH_3$ is not 180° which is presumed for the value of the trans configuration, being smaller by *ca.* 4° than 180°. Since the difference from 180° is beyond the experimental error, the methyl group is situated not on the C–O–C plane but on the same side of the C–O–C plane where the halogen atom is found.

*$XCH_2O$ Group.* 1) $r(CH^1)$ (1.100±0.003 Å) related to the out-of-plane hydrogen $H^1$ might be larger than the $r(CCH^s)$ on the C–O–C plane (1.094±0.003 Å). 2) The average of two $\alpha(XCH)$ values is much smaller than the tetrahedral angle, the average for $ClCH_2OR$ (103°45′±9′) being smaller than that of $FCH_2OR$ (106°33′±16′). $\alpha(XCH)$ related to the in-plane hydrogen $H^s$ is larger than that related to the out-of-plane hydrogen $H^1$. On the other hand, the $\alpha(OCH)$ value related to the out-of plane hydrogen $H^1$ is much larger than the tetrahedral angle.

*$OCH_2Y$ Group.* 1) $r(CH)$, which is nearly

parallel to the CX bond, is much larger than the usual $r$(CH) value except for that of [F, Me] where all the CH bonds have the usual $r$(CH) value. On the other hand, the other $r$(CH) has the usual $r$(CH) value within experimental error. 2) $\alpha(CCH^2)$ of $XCH_2OCH_2CH_3$ (119°22′±36′) is much larger than the tetrahedral angle, while the corresponding angle $\alpha(H^cCH^2)$ of $XCH_2OCH_3$ is somewhat larger than the tetrahedral angle. 3) The dihedral angle $\tau(COCH^c)$ of $XCH_2OCH_3$ is smaller by about 4° than 180° as in the case of the $\tau$(COCC) value of $XCH_2OCH_2CH_3$.

Halomethyl ethers exhibit specific chemical properties. For example, the reaction velocity of these molecules on hydrolysis strongly depends on the polarity of the solvent. They are known as material having carcinogenic activity.

Since the molecular structure attained by the isotopic substitution method sometimes shows fairly large vibrational effects, we cannot conclude that irregular or unusual structural parameter values for a molecule are directly related to its chemical properties. However, as regards halomethyl ethers, specific features of the structural parameters are found for a group of molecules considered to have different vibrational effects. These specific features seem to afford some evidence of the chemical properties of halomethyl ethers.

## References

1) M. Hayashi and H. Kato, *J. Mol. Spectrosc.*, **76**, 412 (1979); M. Hayashi, K. Kuwada, and H. Imaishi, *Chem. Lett.*, **1974**, 913.

2) M. Hayashi and H. Kato, *J. Mol. Struct.*, **53**, 179 (1979).

3) M. Hayashi, H. Kato, and M. Oyamada, *J. Mol. Spectrosc.*, in press.

4) J. Nakagawa, H. Kato, and M. Hayashi, *J. Mol. Spectrosc.*, in press; J. Nakagawa and M. Hayashi, *Chem. Lett.*, **1976**, 349.

5) M. Hayashi, J. Nakagawa, and H. Kato, *J. Mol. Spectrosc.* in press.

6) C. B. Sawyer, *J. Org. Chem.*, **37**, 4225 (1972).

7) M. Hayashi and K. Kuwada, *J. Mol. Struct.*, **28**, 147 (1975).

8) U. Blukis, P. H. Kasai, and R. J. Myers, *J. Chem. Phys.*, **38**, 2753 (1963).

9) M. Hayashi and K. Kuwada, *Bull. Chem. Soc. Jpn.*, **47**, 3006 (1974).

10) H. Kato, J. Nakagawa, and M. Hayashi, *J. Mol. Spectrosc.*, **80**, 272 (1980).

11) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).

12) L. Nygaard, *Spectrochim. Acta*, **22**, 1261 (1966).

13) R. H. Schwendeman and J. D. Kelley, *J. Chem. Phys.*, **42**, 1132 (1965).

14) R. H. Schwendeman and G. D. Jacobs, *J. Chem. Phys.*, **36**, 1245 (1962).

15) D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1514 (1961).