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MICROWAVE SPECTRA AND STRUCTURE OF DICHLOROETHENES*

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ABSTRACT

The complete r_s structures for both 1,1- and *cis*-1,2-dichloroethenes have been derived from isotopic measurements for each isotopic position. The accuracy of the structural parameters obtained is discussed on the basis of isotope effect on bond lengths caused by zero-point vibrations, and it is suggested that more than 0.01 Å of additional uncertainty originating from the isotope effect must be considered for the bond lengths determined by means of the Kraitchman method. The quadrupole coupling constants are re-evaluated by use of the newly determined structures.

INTRODUCTION

A previous paper showed the systematic changes in bond lengths for the series of halogenomethanes containing chlorine and/or fluorine atoms [1]. The structures of halogenoethenes are of interest since they provide further information as to the changes in bond lengths resulting from multiple halogen substitution in simple hydrocarbons. For fluoro-derivatives of ethene, r_s structures have been determined for fluoroethene [2], 1,1-difluoroethene [3], and *cis*-1,2-difluoroethene [3] from the measurements of the microwave spectra for the normal and all the possible mono-substituted isotopic species. Comparison of the CC bond lengths in these molecules shows that the CC length in fluoroethene (1.329 Å) is clearly shortened in 1,1-difluoroethene (1.315 Å), while the shortening is very slight in *cis*-1,2-difluoroethene (1.324 Å). This fact suggests that the shortening depends largely on the position substituted rather than the number of substitution. It would be interesting to compare the above shortening with that in chloro-derivatives of ethene.

The complete r_s structure of chloroethene has been determined by Kivelson et al. [4]. Nakata and Kuchitsu [5] derived the r_z structure of 1,1-dichloroethene from a joint analysis of the electron diffraction intensity and the preliminary microwave data obtained in the present investigation. Later, Davis and

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*Dedicated to the memory of Professor Walter Gordy.

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Gerry [6] also determined the r_z structure from analysis of the rotational and centrifugal distortion constants obtained for several isotopic species combining the vibrational data. The microwave spectrum of *cis*-1,2-dichloroethene was observed by Flygare and Howe [7] only for the normal isotopic species and no determination of the molecular structure has been done by microwave spectroscopy. Since it is necessary to use consistent structural parameters for analysis of the change in bond length, in the present investigation the complete r_s structures have been determined by measurements of microwave spectra of enough isotopic species for both dichloroethenes.

EXPERIMENTAL

Samples of normal 1,1-dichloroethene and *cis*-1,2-dichloroethene were obtained from a commercial source and used without further purification. A mixture of deuterated *cis*- and *trans*-dichloroethenes was prepared in the following way

$$CaC_2 + D_2O \rightarrow DC{\equiv}CD + CaO$$

$$DC{\equiv}CD + 2Cl_2 \rightarrow CDCl_2CDCl_2$$

$$CDCl_2CDCl_2 + Zn \rightarrow CDCl{=}CDCl + ZnCl_2$$

The carbon-13 enriched sample was synthesized from 90% enriched $H^{13}C{\equiv}^{13}CH$ by the same method. Observation of the microwave spectra was made on the mixture of two isomers since the *trans* isomer gives rise to no absorption. The ^{13}C enriched sample of 1,1-dichloroethene was obtained as follows

$$CH_2{=}CH_2 + Cl_2 \rightarrow CH_2ClCH_2Cl$$

$$CH_2ClCH_2Cl \xrightarrow[(KOH)]{-HCl} CHCl{=}CH_2$$

$$CHCl{=}CH_2 + Cl_2 \rightarrow CHCl_2CH_2Cl$$

$$CHCl_2CH_2Cl \xrightarrow[(KOH)]{-HCl} CH_2{=}CCl_2$$

All the reactions were carried out in a closed vacuum system. Since 90% enriched 1-^{13}C ethene was used as the starting material, the final product obtained was a mixture of $^{13}CH_2{=}CCl_2$ (45%) and $CH_2{=}^{13}CCl_2$ (45%). The deuterated species ($CD_2{=}CCl_2$) was made from CD_2ClCD_2Cl by the same reactions.

The microwave spectra were observed by a conventional 100 kHz Stark modulation spectrometer with a cell cooled to dry-ice temperature.

ANALYSIS OF THE SPECTRA

The theory for the rotational spectrum of asymmetric top containing two nuclei of isotopic spin 3/2 presented by Robinson and Cornwell [8] shows that the four degenerate hyperfine components always exist at the unsplit position when the two quadrupole coupling constants are equivalent. The rotational constants, therefore, were obtained only from the measurements of these lines without any analysis of the hyperfine structure. Among the possible isotopic species $CH^{35}Cl{=}CH^{35}Cl$, $CH^{37}Cl{=}CH^{37}Cl$, $CD^{35}Cl{=}CD^{35}Cl$, and $^{13}CH^{35}Cl{=}{}^{13}CH^{35}Cl$ for *cis*-1,2-dichloroethene and $CH_2{=}C^{35}Cl_2$, $CH_2{=}C^{37}Cl_2$, $^{13}CH_2{=}C^{35}Cl_2$, $^{13}CH_2{=}C^{37}Cl_2$, $CH_2{=}{}^{13}C^{35}Cl_2$, $CH_2{=}{}^{13}C^{37}Cl_2$ and $CD_2{=}C^{35}Cl_2$ for 1,1-dichloroethene were chosen for this study, since the two quadrupole couplings of the chlorine atoms are equivalent in these isotopic species. Their spectra were readily assigned with the method described in a previous paper on the microwave spectrum of CCl_2F_2 [1]. In the analysis of the ^{13}C enriched sample of 1,1-dichloroethene, a pair of lines with the same intensities and the same quadrupole patterns due to $^{13}CH_2{=}CCl_2$ and $CH_2{=}{}^{13}CCl_2$ species were found for each transition and thereby quick assignments were possible for both species. The rotational and centrifugal distortion constants determined by least squares fitting are given in Tables 1 and 2.

MOLECULAR STRUCTURES

The coordinates of the atoms in the two dichloroethenes were calculated by the use of Kraitchman equations. The results are shown in Tables 3 and 4 with the structural parameters obtained from them. The values in parentheses indicate the limits of errors estimated from the uncertainties in rotational constants which are three times the standard deviations.

Since both molecules are planar, the three moments of inertia of each isotopic species provide only two independent relations. In this analysis a calculation was performed for each combination of the moments of inertia for the test of consistency. As shown in Tables 3 and 4, there are small discrepancies in the coordinates obtained from different combinations as a result of zero-point vibrations. The uncertainties introduced by these effects, however, are the same order of magnitude as those of experimental errors.

Since the r_s coordinate is affected by ambiguity of spectral data in inverse proportion to the absolute value of the coordinate, the effect of zero point vibrations is large for an atomic coordinate with a small value. Pierce [9] has proposed the double substitution method for the determination of such atomic coordinates and it was successfully applied to N_2O [9] and CH_3SiHF_2 [10].

Although any coordinate of the atom in both dichloroethenes is not small, as shown in Tables 3 and 4, a calculation by the double substitution method was carried out as a test of the accuracy of the bond lengths obtained by the

TABLE 1

Rotational and centrifugal distortion constants of 1,1-dichloroethene (MHz)

	$CH_2{=}C^{35}Cl_2$	$CH_2{=}C^{37}Cl_2$	$CH_2{=}{}^{13}C^{35}Cl_2$	$CH_2{=}{}^{13}C^{37}Cl_2$	$^{13}CH_2{=}C^{35}Cl_2$	$^{13}CH_2{=}C^{37}Cl_2$	$CD_2{=}C^{35}Cl_2$
A	7467.077(36)[b]	7378.987(15)	7443.099(19)	7353.716(10)	7126.533(16)	7039.655(17)	6440.353(40)
B	3411.561(18)	3229.457(9)	3411.881(9)	3229.768(6)	3411.544(6)	3229.445(10)	3370.578(19)
C	2339.088(14)	2243.907(9)	2336.878(7)	2241.710(3)	2304.536(5)	2211.438(14)	2210.209(18)
Δ^a	0.2400(24)	0.2435(15)	0.2402(12)	0.2440(7)	0.2445(9)	0.2483(14)	0.2476(32)
τ_{aaaa}	−0.0292(49)	[c]	−0.0314(26)	[c]	−0.0295(20)	[c]	−0.0240(38)
τ_{bbbb}	−0.00623(49)		−0.00631(24)		−0.00617(18)		−0.00888(60)
τ_{aabb}	0.0076(20)		0.0074(10)		0.0077(8)		0.0057(24)
τ_{abab}	−0.00617(97)		−0.00576(52)		−0.00586(36)		−0.00068(134)

[a] Inertia defect (uÅ^2). [b] The values in parentheses are three times the standard deviations. [c] Centrifugal distortion constants of $^{37}Cl_2$ species are fixed to those of corresponding $^{35}Cl_2$ species.

TABLE 2

Rotational and centrifugal distortion constants of *cis*-1,2-dichloroethene (MHz)

	$CH^{35}Cl=CH^{35}Cl$	$CH^{37}Cl=CH^{37}Cl$	$CD^{35}Cl=CD^{35}Cl$	$^{13}CH^{35}Cl={}^{13}CH^{35}Cl$
A	11518.176(86)[b]	11355.163(23)	9858.955(45)	11010.611(20)
B	2545.255(19)	2416.971(19)	2504.877(33)	2534.143(6)
C	2082.634(17)	1990.990(13)	1995.578(23)	2058.037(6)
Δ[a]	0.2294(38)	0.2305(35)	0.2305(58)	0.2364(13)
τ_{aaaa}	−0.107(74)			−0.1175(17)
τ_{bbbb}	−0.00845(62)			−0.00834(11)
τ_{aabb}	0.0224(80)	[c]	[c]	0.0249(13)
τ_{abab}	−0.023(40)			−0.00360(89)

[a] Inertia defect (uÅ^2). [b] The values in parentheses are three times the standard deviations. [c] Fixed to those of $^{13}CH^{35}Cl={}^{13}CH^{35}Cl$.

TABLE 3

Coordinates of atoms (in Å) and structural parameters (lengths in Å, angles in degrees) of 1,1-dichloroethene

		From I_a and I_b	From I_b and I_c	From I_c and I_a
Cl	a	±1.4462(2)	±1.4462(2)	±1.4465(4)
	b	−0.4592(3)	−0.4600(14)	−0.4592(26)
C	a	0	0	0
	b	0.4686(6)	0.4679(31)	0.4686(6)
C	a	0	0	0
	b	1.8047(2)	1.8058(3)	1.8047(2)
H	a	±0.9461(4)	±0.9461(4)	±0.9475(11)
	b	2.3396(1)	2.3401(5)	2.3396(1)
r(C=C)		1.3362(8)	1.3379(35)	1.3362(8)
r(C-H)		1.0868(9)	1.0866(19)	1.0880(15)
r(C-Cl)		1.7182(4)	1.7183(14)	1.7184(6)
r(C···H)		2.0967(9)	2.0977(14)	2.0973(8)
r(C···Cl)		2.6864(6)	2.6880(5)	2.6865(4)
r(H···H)		1.8922(7)	1.8922(7)	1.8950(22)
r(Cl···Cl)		2.8925(3)	2.8925(3)	2.8929(8)
∠CCH		119°29′(14′)	119°28′(34′)	119°27′(16′)
∠CCCl		122°40′(7′)	122°41′(23′)	122°41′(7′)
∠HCH		121°02′(14′)	121°05′(26′)	121°07′(31′)
∠ClCCl		114°39′(3′)	114°38′(10′)	114°39′(6′)
$\sum m_i b_i$		−0.1191	−0.1667	−0.1191

TABLE 4

Coordinates of atoms (in Å) and structural parameters (lengths in Å, angles in degrees) of *cis*-1,2-dichloroethene

		From I_a and I_b	From I_b and I_c	From I_c and I_a
Cl	*a*	±1.6245(2)	±1.6245(2)	±1.6245(4)
	b	−0.4054(2)	−0.4055(27)	−0.4054(2)
C	*a*	±0.6587(7)	±0.6587(7)	±0.6613(12)
	b	1.0144(1)	1.0161(3)	1.0144(1)
H	*a*	±1.2612(5)	±1.2612(5)	±1.2611(8)
	b	1.9356(1)	1.9355(8)	1.9356(1)
r(C=C)		1.3173(14)	1.3173(14)	1.3226(25)
r(C–H)		1.1007(12)	1.0992(26)	1.0992(20)
r(C–Cl)		1.7172(6)	1.7187(13)	1.7157(10)
r(C···H)		2.1294(12)	2.1286(14)	2.1317(10)
r(C···Cl)		2.6886(6)	2.6896(8)	2.6909(7)
r(H···H)		2.5224(9)	2.5224(9)	2.5221(17)
r(Cl···Cl)		3.2490(5)	3.2490(5)	3.2490(8)
∠CCH		123°11′(21′)	123°14′(29′)	123°04′(30′)
∠CCCl		124°13′(12′)	124°11′(16′)	124°09′(18′)
∠ClCH		112°33′(16′)	112°34′(22′)	112°47′(24′)
$\sum m_i b_i$		−0.1057	−0.0715	−0.1057

Kraitchman equations, since it was expected that the bond length determined by the double substitution method is less affected by zero-point vibrations. From the rotational constants of $CH_2=C^{35}Cl_2$, $CH_2=C^{37}Cl_2$, $CH_2={}^{13}C^{35}Cl_2$, and $CH_2={}^{13}C^{37}Cl_2$, the *b*-coordinate of the carbon atom attached to the chlorine atoms was determined as 0.468(20) Å, and that of another carbon atom as 1.799(21) Å from the rotational constants of $CH_2=C^{35}Cl_2$, $CH_2=C^{37}Cl_2$, ${}^{13}CH_2=C^{35}Cl_2$ and ${}^{13}CH_2=C^{37}Cl_2$. In this analysis the coordinates given by I_b and I_c are essentially the same as those by I_a. Although the uncertainties shown in parentheses which were calculated from the uncertainties of the rotational constants are fairly large, actual errors of the coordinates seem to be smaller, because the standard deviations given in the present calculation arise partly from the use of approximate equations for the centrifugal distortion effect and such systematic deviations are cancelled in the ΔIs. The CC bond length of 1,1-dichloroethene obtained from these coordinates is 1.331 Å, which is a little shorter than the value obtained by the Kraitchman equations.

QUADRUPOLE COUPLING CONSTANTS

Since the molecular structures of the two dichloroethenes are precisely determined in this study, the diagonalized χ tensor was obtained on the basis that

TABLE 5

Quadrupole coupling constants of 1,1-dichloroethene, *cis*-1,2-dichloroethene, and similar molecules (MHz)

	$CH_2{=}CCl_2$	*cis*-$CHCl{=}CHCl$		χ_{zz}	η^{b}
χ_{aa}	−42.48(10)	4.51(7)	$Cl_2C{=}O$	−78.7	−0.31
χ_{bb}	8.12(18)	−35.87(10)	$Cl_2C{=}CH_2$	−77.9	−0.12
χ_{cc}	34.36(15)	31.36(9)	Cl_2CH_2	−76.92	0.035
$\chi_{zz}{}^{a}$	−77.9(5)	−70.7(3)	$CHCl{=}CH_2$	−70.7	−0.11
$\chi_{xx}{}^{a}$	43.5(7)	39.3(3)	$CHCl{=}CHCl$	−70.2	−0.14
$\chi_{yy}{}^{a}$	34.36(15)	31.36(9)	CH_3CH_2Cl	−68.8	0.035

[a] z along C–Cl bond; y perpendicular to plane of molecule. [b] $\eta = (\chi_{xx} - \chi_{yy})/\chi_{zz}$.

the z axis of diagonalized χ tensor coincides with the CCl bond direction. The quadrupole coupling constants have been reported already as $\chi_{aa} = 3.7$ MHz, and $\chi_{cc} = 31.9$ MHz for *cis*-1,2-dichloroethene [7] and as $\chi_{zz} = -78.7$ MHz and $\eta = 0.12$ for 1,1-dichloroethene [11]. These constants were re-determined in the present study. Since the separations of hyperfine splitting observed in the series of Q-branch transitions of low-J levels with $K_{-1} = 0$ or 1 were large in *cis*-1,2-dichloroethene, the values of $\langle eQq \rangle_J$ for these transitions were determined precisely. Only from these values, however, were ambiguous quadrupole coupling constants in the principal axis system obtained, because the contributions of both the χ_{aa} and χ_{bb} to the splittings are almost the same in these transitions. For the precise determination of the constants it was necessary to observe the hyperfine structures of Q-branch transitions with large splittings and with different rates of contribution from χ_{aa} and χ_{bb}. The only transitions of this type suitable for the measurement were $2_{2,0}$–$2_{1,1}$ and $3_{2,1}$–$3_{1,2}$. The values obtained are slightly different from the previously reported ones, as shown in Table 5.

In 1,1-dichloroethene the splittings are small compared to those in *cis*-1,2-dichloroethene but the constants have been determined with fairly small uncertainties. They are also given in Table 5.

The χ_{zz} values of the two dichloroethenes are somewhat different. This difference is consistent with the general trend that the χ_{zz} of Cl in a $-CH_2Cl$ or $=CHCl$ group is smaller than in a $-CHCl_2$ or $=CCl_2$ group as shown in Table 5. The asymmetry parameters of the two dichloroethenes and vinylchloride are almost the same indicating that the effects of the carbon–carbon double bond on chlorine atom are similar in all the ethane derivatives.

DISCUSSION

The structural parameters of the chloro- and fluoro-derivatives of ethene derived from their microwave data are shown in Fig. 1. The comparison of the

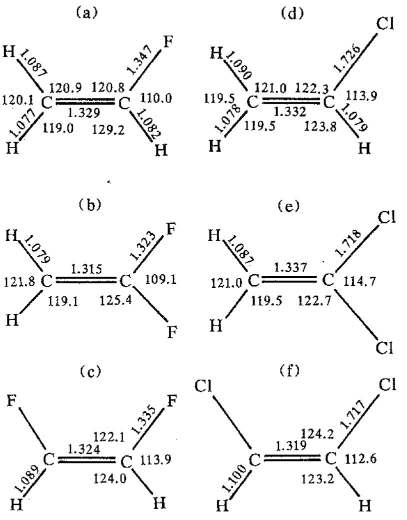

Fig. 1. Comparison of molecular structures of fluoro- and chloro-derivatives of ethene obtained by microwave spectroscopy: (a) ref. 2, (b) ref. 3, (c) ref. 3, (d) ref. 4, (e) this work, (f) this work.

bond lengths in Fig. 1 shows that the carbon–halogen distance is shortened when an additional halogen is added to the molecule, and that the CF shortening is more marked than the CCl. This shortening is almost the same as in halogen derivatives of methane. On the other hand, the regular shortening is not seen for CC distances. The CC distance in 1,1-dichloroethene is longer than that in vinylchloride. In addition, the trend of the change in CC length depending on the position of halogen atoms is inverse between difluoro- and dichloroethenes; 1,1-difluoroethene has a shorter CC length than *cis*-1,2-difluoroethene, while 1,1-dichloroethene has a rather longer CC bond length than *cis*-1,2-dichloroethene. This irregularity is too large to be ascribed to the experimental errors. It is difficult to attribute such a large discrepancy to the effect of zero-point vibrations. However, the discrepancy between the CC distances of 1,1-dichloroethene obtained by the single and double substitution methods suggests the presence of errors resulting from zero-point vibrations. Also, the r_z CC lengths reported in refs. 5 and 6 are 1.329(3) and 1.3282(5) Å, respectively; these are about 0.01 Å shorter than the r_s value.

It has been shown by Kuchitsu et al. [12, 13] that small isotopic differences in molecular structure resulting from zero-point vibrations cause an additional uncertainty originating from the solution of Kraitchman equations. Generally, the uncertainty caused by the above effect is about the same as that by experimental error. However, the error is multiplied by a large factor when an atom with a large mass exists far from the center of mass, or an atom is very close to one of the principal axes, as can be expected from the following expression for the error caused by isotope effect [13].

$$\Delta a_j = -\left(\sum_i m_i a_i \delta_i\right) / \Delta m_j a_j - \delta_j$$

where a_i denotes the coordinate of the ith atom and δ_i is the displacement of a_i due to isotopic substitution. Since the chlorine atom is fairly heavy, it is possible that the r_s coordinates of dichloroethenes have larger errors caused by isotopic shift of atoms than those of difluoroethenes.

One may notice in Table 1 that the B value for $H_2{}^{12}C{=}{}^{13}C^{35}Cl_2$ is considerably larger than that of normal species, in spite of the fact that the carbon atom exists on the b-principal axis. This difference shows that the effective Cl···Cl distance is shortened by the change in mass of the carbon atom, and the change of effective Cl···Cl distance is calculated to be 0.000138 Å. This value seems to be reasonable compared to the isotope effects obtained for diatomic [14] and triatomic [13] molecules. Similar effects are also seen between the carbon isotopic species of phosgene and dichloromethane, and the changes of Cl···Cl distances are calculated as nearly equal to the above value. If we assume that the change in Cl···Cl distances is ascribed to the shortening of the CCl bond, it is calculated to be 0.00008 Å. A similar isotope effect is also expected for the CC bond by the isotopic change of carbon atoms, and the magnitude of the shortening due to the substitution of ^{12}C for ^{13}C may be assumed to be 0.00005 Å. By assuming these two isotopic displacements the coordinates of the carbon atoms in both dichloroethenes were calculated, and the CC lengths were given as 1.331 Å for 1,1-dichloroethene and 1.335 Å for *cis*-1,2-dichloroethene. By this correction the CC length of *cis*-1,2-dichloroethene becomes slightly longer than that of 1,1-dichloroethene.

A similar calculation was tried on difluoroethenes and the CC length in *cis*-1,2 difluoroethene was calculated to be 1.331 Å, which is 0.007 Å longer than the value of 1.324 Å determined by the single substitution method. It should be noted that the correction of the isotope effect is 0.015 Å for *cis*-1,2-dichloroethene, while that for *cis*-1,2-difluoroethene is half this value. The large correction for *cis*-1,2-dichloroethene is due mainly to the large mass of the Cl atoms.

The CC length of 1,1-difluoroethene [3] has been determined with the aid of the center of mass and the moment of inertia conditions, because one of the carbon atoms lies close to the center of mass, and therefore the above method cannot be applied. If we calculate the CC length of 1,1-difluoroethene using only Kraitchman equations it becomes 1.338 Å which is abnormally longer than that in fluoroethene (1.329 Å). However, it is corrected to 1.328 Å by taking into account the same isotopic displacements as for *cis*-1,2-difluoroethene. If we adopt these CC lengths for difluoro- and dichloroethenes, the change in CC length between the two isomers of dihalogenoethene becomes very small. It is interesting to mention that a reasonable value of the coordinate may be obtained even when the atom is located very close to the center of mass if the proper isotope effects are taken into consideration.

Unfortunately, the correction with the exact isotope effects is not feasible for halogenoethenes since the isotopic differences in bond lengths cannot be obtained experimentally. However, the above calculations suggest that the different trends of the change in the r_s CC lengths between difluoro- and dichloroethenes are removed by considering the isotope effect. It seems likely that the regular shortening occurs by the chlorine and fluorine substitution for the series of halogenoethenes.

It has been thought that the Kraitchman equations give consistent structural parameters although the physical meaning of r_s is somewhat ambiguous, and they can be used for the critical test of the slight changes in bond lengths. However, the result of the above calculations shows that considerable errors must be considered in some cases because of isotope effects.

Although the CC length of 1,1-dichloroethene determined by the double substitution method has a fairly large uncertainty, the value of 1.331 Å seems quite reasonable if regular shortening of the CC bond in the series of halogenoethene is assumed. For more critical evaluation of the value derived by the double substitution method, it is necessary to reduce its uncertainty.

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