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Microwave Spectrum, Molecular Structure, and Quadrupole Coupling Constants of 2-Chloropropane*†

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The microwave spectra of $(CH_3)_2CHCl^{35}$, $(CH_3)_2CHCl^{37}$, $(CH_3)_2CDCl^{35}$, $(CH_3)_2C^{13}HCl^{35}$, $C^{13}H_3CHCl^{35}CH_3$, $CH_2DCl^{35}CH_3$ (3 species), and $CD_3CDCl^{35}CH_3$ have been examined and a complete structure has been obtained by the substitution method. The parameters obtained are as follows: $r(CC)=1.522$ Å, $r(CCl)=1.798$ Å, $r(CH_{sec})=1.091$ Å, $r(CH_{methyl})=1.092$ Å, $\angle CCC=112.7°$, $\angle CCCl=109.4°$, $\angle CCH_{sec}=109.9°$, $\angle CCH_\alpha=110.9°$, $\angle CCH_{\beta,\gamma}=109.7°$.

The quadrupole coupling constants in the principal axis system of $(CH_3)_2CHCl^{35}$ have been determined to be $\chi_{aa}=-61.49$ Mc/sec, $\chi_{bb}=34.81$ Mc/sec, and $\chi_{cc}=26.68$ Mc/sec. These values are consistent with $\chi_{zz}=-69.61$ Mc/sec assuming a cylindrical charge distribution near the Cl nucleus, or with $\chi_{zz}=-67.82$ Mc/sec and $\eta=0.0275$ assuming that the z axis and the CCl internuclear line coincide.

From the absence of observable splitting in certain high J transitions in $CD_3CDCl^{35}CH_3$, it has been concluded that the potential barrier hindering internal rotation of the methyl groups is greater than 3450 cal/mole.

AS part of a study in our laboratory of the molecular structure and quadrupole coupling constants of small halogenated hydrocarbons, the microwave spectra of several isotopic species of 2-chloropropane have been examined. Our original interest in 2-chloropropane stemmed from a desire to compare the carbon–chlorine bond length and chlorine quadrupole coupling constants with the corresponding quantities in ethyl chloride,[1] methyl chloride,[2] and cyclopropyl chloride.[3]

Two studies of the molecular structure of 2-chloropropane by electron diffraction have been reported.[4,5] The results of the two studies, however, are given with rather large uncertainties.

In order to determine the structure completely by the substitution method proposed by Kraitchman[6] we have prepared isotopic species with substitution at every nonequivalent atom site and examined the rotational spectra.

EXPERIMENTAL

The spectra were examined at −78°C with a conventional Hughes–Wilson microwave spectrometer using 100 kc/sec Stark modulation and phase-sensitive detection. The frequencies were measured by comparison with marker frequencies generated from a 1-Mc/sec crystal-controlled oscillator monitored by the 10 Mc/sec signal of radio station WWV. The transitions were either displayed on an oscilloscope (with sweep reversal) or by means of pen-and-ink recording. The uncertainty in the frequencies of the stronger lines is believed to be less than 0.05 Mc/sec.

The $(CH_3)_2CHCl^{35}$ and $(CH_3)_2CHCl^{37}$ spectra were examined in natural abundance using a sample as received from the Eastman Kodak Company. The sample of $CH_2DCHClCH_3$ was prepared by the reaction of DCl with propylene in the presence of $AlCl_3$.[7] The $(CH_3)_2CDCl$ was prepared in a similar manner by the reaction of HCl with 2-deuteropropene. The two enriched C-13 species were prepared by reductions[8] of $(CH_3)_2C^{13}O$ and $CH_3CH_2C^{13}O_2H$ with $LiAlH_4$ in diethylene-glycol-diethyl ether, followed by liberation of the alcohols, $(CH_3)_2C^{13}HOH$ and $CH_3CH_2C^{13}H_2OH$, with ethylene-glycol-monophenyl ether, and then by chlorination of the alcohols with PCl_5. The resulting $CH_3CH_2C^{13}H_2Cl$ was rearranged to $C^{13}H_3CHClCH_3$ over anhydrous $AlCl_3$.[9] The sample of $CH_3CH_2C^{13}O_2H$ used in one of the reductions was provided by Roy Foley. The sample of $(CH_3)_2C^{13}O$ used in the second reduction was prepared by the following series of reactions[10,11]:

$$KC^{13}N \xrightarrow{CH_3I} CH_3C^{13}N \xrightarrow[2)\ H_2SO_4]{1)\ NaOH}$$

$$CH_3C^{13}O_2H \xrightarrow{Ba(OH)_2}$$

$$(CH_3C^{13}O_2)_2Ba \xrightarrow[vacuum]{500°C} (CH_3)_2C^{13}O.$$

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The final C-13 samples were approximately 18% enriched. The sample of $CD_3CDClCH_3$ was prepared by chlorination with PCl_5 of a sample of $CD_3CDOHCH_3$ which was a gift from Chester Orzech.

MICROWAVE SPECTRA

Figure 1 is a picture of a model of 2-chloropropane identifying the sec, α, β, and γ H atoms and Fig. 2 is a projection of the molecule in the plane of symmetry showing the location of the principal axes. The CCl bond line forms an angle of approximately 14° with the a inertial axis and only the expected a-type transitions were observed. The asymmetry of the various species (asymmetry parameter $\kappa = -0.34$ to -0.47) is sufficient to allow the determination of the A rotational constant to within an uncertainty of tenths of a megacycle. In most of the transitions studied a resolvable hyperfine structure appeared due to the interaction of the over-all rotation with the quadrupole moment of the chlorine nucleus. Table I is a list of the hypothetical unsplit frequencies observed for the various species and Table II compares the measured and calculated frequencies of the hyperfine components for transitions in $(CH_3)_2CHCl^{35}$. The hyperfine splittings were computed as described below.

The rotational constants were obtained by fitting the frequencies of the $J=1 \rightarrow J=2$, $J=2 \rightarrow J=3$, $6_{16} \rightarrow 6_{15}$, and $5_{05} \rightarrow 5_{24}$ (when measured) transitions by means of least squares. The two high J Q-branch transitions were added to give some extra A dependence. There is probably some uncertainty in the rotational constants due to neglect of centrifugal distortion, but since the same transitions were used to obtain the constants for the various species, the effects of centrifugal distortion should tend to cancel in the use of the Kraitchman equations. The rotational constants and the moments of inertia derived from them are listed in Table III.

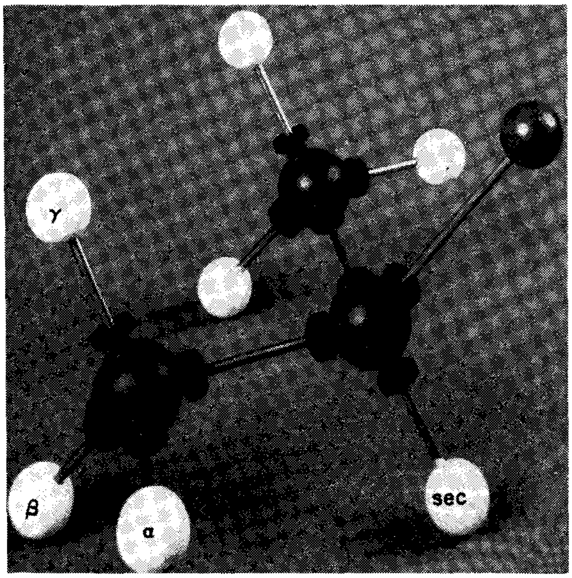

FIG. 1. A model of 2-chloropropane identifying the hydrogen atoms.

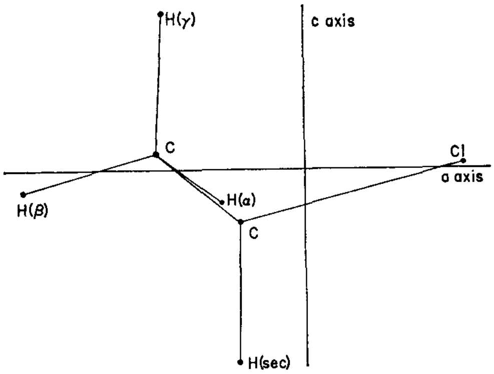

FIG. 2. A projection of 2-chloropropane in the ac plane of symmetry.

MOLECULAR STRUCTURE

Determination

Since rotational constants have been obtained for species with single isotopic substitution at every nonequivalent site, a complete structure determination can be made by the substitution method.[6] According to this method, the a coordinate of the sth atom (a_s) is given by

$$|a_s| = \left\{\mu^{-1}\left[(P_{aa}' - P_{aa})\left(1+\frac{P_{bb}'-P_{bb}}{P_{bb}-P_{aa}}\right)\times\left(1+\frac{P_{cc}'-P_{cc}}{P_{cc}-P_{aa}}\right)\right]\right\}^{\frac{1}{2}}, \quad (1)$$

where P_{aa}, P_{bb}, and P_{cc} are the principal second moments of one species designated the parent species, and P_{aa}', P_{bb}', and P_{cc}' are the principal second moments of a species which differs from the parent in that the sth atom has been substituted isotopically. The principal second moments are easily obtained from the experimental rotational constants of the two species. The reduced mass $\mu = M(M'-M)/M'$, where M and M' are the molecular weights of the two species. The coordinates b_s and c_s may be determined by means of equations obtained from Eq. (1) by cyclic permutation of the subscripts. The coordinates listed in Table IV were obtained by direct application of these equations using the moments of inertia given in Table III.

It has been pointed out by Laurie[12] that the substitution method nearly always tends to give coordinates which are too small, and that the error is particularly serious for atoms near a principal plane. In 2-chloropropane the c coordinates of the Cl atom and the end carbon atoms are 0.0409 Å and 0.1222 Å, respectively. Since only two heavy-atom coordinates are involved,

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TABLE I. Hypothetical unsplit frequencies (Mc/sec) in 2-chloropropane.

Transition	$(CH_3)_2CHCl^{35}$	$(CH_3)_2CHCl^{37}$	$(CH_3)_2C^{13}HCl^{35}$	$C^{13}H_3CHCl^{35}CH_3$	$(CH_3)_2CDCl^{35}$
$1_{11}\rightarrow 2_{12}$	14 193.54	13 898.83			14 075.17
$1_{01}\rightarrow 2_{02}$	15 229.64	14 908.71			15 044.26
$1_{10}\rightarrow 2_{11}$	16 920.10	16 505.91			16 611.82
$2_{12}\rightarrow 3_{13}$	21 105.42	20 681.51	21 058.97	20 748.20	
$2_{02}\rightarrow 3_{03}$	22 134.22	21 715.56	22 084.23	21 749.69	21 913.75
$2_{21}\rightarrow 3_{22}$	23 335.18	22 803.52	23 267.63		23 015.17
$2_{20}\rightarrow 3_{21}$	24 535.96	23 891.16	24 451.17	24 221.03	24 116.32
$2_{11}\rightarrow 3_{12}$	25 144.47	24 549.42	25 062.64	24 786.83	
$3_{21}\rightarrow 4_{22}$			33 263.37	32 958.63	
$3_{22}\rightarrow 4_{23}$	30 855.22	30 173.23	30 769.42	30 379.80	
$5_{05}\rightarrow 5_{24}$	23 820.25	23 645.74			22 382.95
$6_{15}\rightarrow 6_{16}$	25 251.36	24 457.45	25 061.48	25 092.66	23 576.88

Transition	$CH_2DCHCl^{35}CH_3(\alpha)$	$CH_2DCHCl^{35}CH_3(\beta)$	$CH_2DCHCl^{35}CH_3(\gamma)$	$(CH_3)_2CHCl^{35}(v=1)$
$1_{11}\rightarrow 2_{12}$	13 871.56			14 172.24
$1_{01}\rightarrow 2_{02}$	14 901.13	14 604.13	14 895.50	15 206.70
$1_{10}\rightarrow 2_{11}$	16 752.54	16 190.10	16 533.85	16 893.23
$2_{12}\rightarrow 3_{13}$	20 578.83	20 246.20	20 678.96	21 073.68
$2_{02}\rightarrow 3_{03}$	21 505.31	21 256.88	21 642.44	22 101.87
$2_{21}\rightarrow 3_{22}$	22 968.11	22 349.55		23 298.90
$2_{20}\rightarrow 3_{21}$	24 430.71	23 441.95	24 020.58	24 495.87
$2_{11}\rightarrow 3_{12}$	24 823.32	24 073.68	24 564.88	25 104.98
$3_{21}\rightarrow 4_{22}$	33 240.50	31 890.16	32 666.19	
$3_{22}\rightarrow 4_{23}$	30 298.78	29 566.16	30 185.01	
$6_{15}\rightarrow 6_{16}$	25 617.57	24 132.43	24 143.36	

the first-moment relation, $\sum m_i c_i=0$, and the product-of-inertia relation, $\sum m_i a_i c_i=0$, may be used to compute the values of these two coordinates. The results are compared in Table V with the values obtained from Kraitchman's equations. Table VI lists the bond distances and bond angles for three structures: I using the coordinates in Table V; II using coordinates in Table V except the c coordinates from Table VI; and III an average structure.

Uncertainty

Since the Kraitchman equations are exact if there are no changes in the relative positions of the atoms upon isotopic substitution, values of the principal second moments for the equilibrium configuration, $P_{aa}^{(e)}$, $P_{aa}^{(e)\prime}$, etc., may be used to obtain exact coordinates of the atoms in the equilibrium configuration. Unfortunately, equilibrium second moments are not available for molecules as complicated as 2-chloropropane. However, we may write

$$2P_{aa}^{(e)}=(I_b+I_c-I_a)+\Delta_{aa}=2P_{aa}+\Delta_{aa}, \qquad (2)$$

where I_a, I_b, I_c are moments of inertia obtained by inverting the ground state rotational constants, and Δ_{aa} is a quasi-inertial defect. By substitution of Eq. (2) into Eq. (1), it is found that

$$\begin{aligned} |a^{(e)}|-|a|=|2a\mu|^{-1}\Bigg\{&\left[1+\frac{P_{bb}'-P_{bb}}{P_{bb}-P_{aa}}\right] \\ &\times\left[1+\frac{P_{cc}'-P_{cc}}{P_{cc}-P_{aa}}\right]\left[\frac{\Delta_{aa}'-\Delta_{aa}}{2}\right] \\ &+\tfrac{1}{2}(P_{aa}'-P_{aa})\left(1+\frac{P_{cc}'-P_{cc}}{P_{cc}-P_{aa}}\right)\left(\frac{\Delta_{bb}'-\Delta_{bb}}{P_{bb}-P_{aa}}\right) \\ &+\tfrac{1}{2}(P_{aa}'-P_{aa})\left(1+\frac{P_{bb}'-P_{bb}}{P_{bb}-P_{aa}}\right)\left(\frac{\Delta_{cc}'-\Delta_{cc}}{P_{cc}-P_{aa}}\right)\Bigg\}. \qquad (3)\end{aligned}$$

Terms involving products of changes in the inertial defects have been ignored as have the differences between equilibrium and effective second moments in the denominators in Eq. (1). Such terms are ordinarily much smaller than those retained.

TABLE II. Calculated and observed frequencies (Mc/sec) for the hyperfine components in $(CH_3)_2CHCl^{35}$.

Transition	$F\rightarrow F'$	Observed frequency	Calculated frequency
$1_{11}\rightarrow 2_{12}$	$5/2\rightarrow 7/2$	14 197.18	14 197.18
	$3/2\rightarrow 5/2$	14 181.84	14 181.81
	$1/2\rightarrow 3/2$	14 202.20	14 202.22
	$5/2\rightarrow 5/2$	14 190.49	14 190.50
	$3/2\rightarrow 3/2$	14 186.96[a]	14 186.57
	$1/2\rightarrow 1/2$	14 208.94	14 208.90
$1_{01}\rightarrow 2_{02}$	$5/2\rightarrow 7/2$	15 230.70	15 230.70
	$3/2\rightarrow 5/2$	15 231.64	15 231.60
	$1/2\rightarrow 3/2$	15 214.27	15 214.27
	$5/2\rightarrow 5/2$	15 216.24	15 216.23
	$3/2\rightarrow 3/2$	15 241.94	15 241.94
	$1/2\rightarrow 1/2$	15 228.70	15 228.74
$1_{10}\rightarrow 2_{11}$	$5/2\rightarrow 7/2$	16 923.94	16 923.84
	$3/2\rightarrow 5/2$	16 908.53	16 908.47
	$1/2\rightarrow 3/2$	16 926.80	16 926.70
	$5/2\rightarrow 5/2$	16 915.19	16 915.15
	$3/2\rightarrow 3/2$	16 914.71	16 914.68
	$1/2\rightarrow 1/2$	16 935.51	16 935.39
$2_{12}\rightarrow 3_{13}$	$7/2\rightarrow 9/2$	21 106.94	21 106.98
	$1/2\rightarrow 3/2$		21 107.01
	$5/2\rightarrow 7/2$	21 103.34	21 103.37
	$3/2\rightarrow 5/2$		21 103.40
$2_{02}\rightarrow 3_{03}$	$7/2\rightarrow 9/2$	22 134.57	22 134.64
	$5/2\rightarrow 7/2$	22 135.60	22 135.63
	$3/2\rightarrow 5/2$	22 131.55	22 131.58
	$1/2\rightarrow 3/2$	22 130.50	22 130.60
$2_{21}\rightarrow 3_{22}$	$7/2\rightarrow 9/2$	23 339.55	23 339.55
	$5/2\rightarrow 7/2$	23 324.20	23 324.18
	$3/2\rightarrow 5/2$	23 335.15	23 335.16
	$1/2\rightarrow 3/2$	23 350.60	23 350.53
$2_{20}\rightarrow 3_{21}$	$7/2\rightarrow 9/2$	24 540.77	24 540.80
	$5/2\rightarrow 7/2$	24 524.35	24 524.45
	$3/2\rightarrow 5/2$	24 535.57	24 535.66
	$1/2\rightarrow 3/2$	24 551.92	24 552.02
$4_{04}\rightarrow 4_{23}$	$11/2\rightarrow 11/2$	20 516.14	20 516.04
	$9/2\rightarrow 9/2$	20 523.00	20 522.92
	$7/2\rightarrow 7/2$	20 520.51	20 520.51
	$5/2\rightarrow 5/2$	20 513.65	20 513.62
$5_{05}\rightarrow 5_{24}$	$13/2\rightarrow 13/2$	23 818.64	23 818.81
	$11/2\rightarrow 11/2$	23 821.61	23 821.59
	$9/2\rightarrow 9/2$	23 822.69	23 822.68
	$7/2\rightarrow 7/2$	23 817.66	23 817.72

[a] Partly obscured by interfering transition.

Equation (3) demonstrates the well-known fact that evaluation of the changes in the quasi-inertial defect upon isotopic substitution would enable the determination of the structure of a molecule in its equilibrium configuration. Even though it is not now possible to evaluate such changes, estimation of their magnitude may be used to estimate the uncertainty in coordinates which have been determined ignoring such changes. An objection to such a procedure is that the uncertainty obtained is the uncertainty in the coordinates

TABLE III. Rotational constants (Mc/sec) and moments of inertia (amu-Å^2)[a] for 2-chloropropane.

Species	A	B[b]	C[b]	I_a	I_b	I_c
$(CH_3)_2CHCl^{35}$	8068.09±0.05	4570.82	3207.57	62.6580	110.5997	157.6056
$(CH_3)_2CHCl^{37}$	8067.62±0.1	4452.33	3148.82	62.6617	113.5430	160.5461
$(CH_3)_2CDCl^{35}$	7793.09±0.1	4470.01	3201.70	64.8691	113.0938	157.8947
$(CH_3)_2C^{13}HCl^{35}$	8048.41±0.3	4553.49	3202.40	62.8113	111.0205	157.8599
$C^{13}H_3CHCl^{35}CH_3$	7872.19±0.3	4513.08	3148.72	64.2174	112.0146	160.5515
$CH_2DCHCl^{35}CH_3(\alpha)$	7512.61±0.4	4548.26	3107.78	67.2856	111.1486	162.6659
$CH_2DCHCl^{35}CH_3(\beta)$	7876.46±0.3	4370.13	3079.69	64.1825	115.6788	164.1500
$CH_2DCHCl^{35}CH_3(\gamma)$	7693.18±0.7	4461.66	3148.87	65.7116	113.3056	160.5438

[a] Conversion factor used: 5.05531×10^5 Mc/sec-amu Å^2.

[b] The estimated uncertainty in the B and C rotational constants is ±0.02 Mc/sec.

TABLE IV. Coordinates of the atoms in the $(CH_3)_2CHCl^{35}$ principal axis system.

Atom	a	b	c
Cl	1.2286 Å	0	0.0409 Å
C (center)	−0.5128	0	−0.4021
C (end)	−1.1695	±1.2666 Å	0.1222
H (secondary)	−0.5303	0	−1.4929
H(α)	−0.6664	±2.1546	−0.2588
H(β)	−2.2184	±1.2891	−0.1796
H(γ)	−1.1136	±1.2833	1.2203

$\sum_i m_i a_i = -0.1473$ amu-Å

$\sum_i m_i c_i = -0.3902$ amu-Å

$\sum_i m_i a_i c_i = -0.0118$ amu-Å^2

TABLE V. Comparison of the c coordinates of the Cl and end C atoms determined by Kraitchman's equations or by assuming $\Sigma m_i c_i = 0$ and $\Sigma m_i a_i c_i = 0$.

Atom	Kraitchman's equations	Assuming $\Sigma m_i c_i = 0$ and $\Sigma m_i a_i c_i = 0$
Cl	0.0409 Å	0.0462 Å
C (end)	0.1222 Å	0.1308 Å

as values for the equilibrium structure, and for many purposes these may be pessimistic.

Calculation of the three terms on the right-hand side of Eq. (3) for the coordinates of the atoms of 2-chloropropane shows that if the magnitudes of $(\Delta_{aa}'-\Delta_{aa})$, etc., are comparable, the last two terms may be ignored, being at least 10 times smaller than the first term in every case. Thus, $a^{(e)}-a$ is proportional to $\Delta_{aa}'-\Delta_{aa}$, $b^{(e)}-b$ is proportional to $\Delta_{bb}'-\Delta_{bb}$, etc. In Table VII are listed values of $a^{(e)}-a$, etc., for $\Delta_{aa}'-\Delta_{aa}$, etc., equal to 0.001 amu-Å^2. This value was chosen because it is probably within one order of magnitude of the correct value in each case, and also because of the simplicity of converting the numbers in Table VII into actual uncertainties.

If experimental values of the moments of inertia are used in Eq. (2), the changes in the quasi-inertial defects will contain a contribution from experimental error in addition to the contribution from zero-point vibration. We estimate the contribution from experimental error to be less than ±0.002 amu-Å^2. Thus, the strictly experimental uncertainty in the coordinates is equal to twice the values listed in Table VII.

Estimation of the probable contribution of vibrational effects to changes in the inertial defect is a considerably more difficult problem. The only available values are for substitution in a plane of symmetry of a molecule for which one $P^{(e)}$ value does not change. In Table VIII are listed the values of P_{bb} for several species of 2-chloropropane involving substitution in the ac plane of symmetry. The values of $\Delta_{bb}'-\Delta_{bb}$ shown are typical of values which have been obtained for other molecules. Changes in the quasi-inertial defects with isotopic substitution may also be estimated by a method described below. Our estimates for 2-chloropropane are 0.001 amu-Å^2 multiplied by the factors given in parentheses in Table VII.

TABLE VI. Bond distances (Å) and bond angles (degrees) for 2-chloropropane.

	I[a]	II[b]	III[c]		
r(CCl)	1.7968	1.7982	1.798	+0.008	−0.004
r(CC)	1.5200	1.5230	1.521	+0.004	−0.006
$r(CH_{sec})$	1.0909	1.0909	1.091	+0.003	−0.002
$r(CH_{methyl})$	1.0920	1.0920	1.092	±0.008	
∠CCC	112.9	112.5	112.7	+0.7	−0.3
∠CCCl	109.5	109.3	109.4	+0.3	−0.4
$\angle CCH_{sec}$	109.8	110.1	109.9	±0.4	
$\angle ClCH_{sec}$	105.2	105.4	105.3	±0.7	
$\angle CCH_{\alpha}$	111.0	110.7	110.9	±0.7	
$\angle CCH_{\beta\text{ and }\gamma}$	109.6	109.7	109.7	±0.6	
$\angle H_{\alpha}CH_{\beta} = \angle H_{\beta}CH_{\gamma}$	109.1	109.1	109.1	±0.7	
$\angle H_{\alpha}CH_{\gamma}$	108.3	108.7	108.5	±0.8	
I_a	62.3516 amu-Å^2	62.4219 amu-Å^2			
I_b	110.2004	110.2707			
I_c	156.9412	156.9412			

[a] Using the coordinates in Table IV.

[b] Using the coordinates in Table IV except c coordinates of Cl and methyl C atoms from Table V.

[c] Average of I and II.

TABLE VII. Differences (in Å) between substitution coordinates and equilibrium coordinates assuming 0.001 amu·Å^2 increase in quasi-inertial defects upon isotopic substitution.

Atom	$a^{(e)}-a$	$b^{(e)}-b$	$c^{(e)}-c$
Cl	0.00012 (6)[a]	···	0.00320 (2)
C (center)	−0.00049 (8)	···	−0.00063 (2)
C (end)	−0.00022 (2)	±0.00022 (2)	0.00215 (2)
H (sec)	−0.00047 (8)	···	−0.00018 (8)
H (α)	−0.00035 (8)	±0.00014 (8)	−0.00108 (8)
H (β)	−0.00013 (8)	±0.00023 (8)	−0.00152 (8)
H(γ)	−0.00023 (8)	±0.00021 (8)	−0.00023 (8)

[a] The numbers in parentheses are the factors by which the differences were multiplied to determine the uncertainties in Table VI.

To relate the uncertainties in the coordinates to uncertainties in the bond distances and angles, the changes in the various parameters are expanded in terms of changes in the coordinates of the atoms involved. For example, if r_{st} is the distance between atoms s and t,

$$\delta r_{st}=\frac{\partial r_{st}}{\partial a_s}\delta a_s+\frac{\partial r_{st}}{\partial a_t}\delta a_t+\frac{\partial r_{st}}{\partial b_s}\delta b_s+\cdots+\frac{\partial r_{st}}{\partial c_t}\delta c_t,$$

where a_s, b_s, c_s, a_t, b_t, c_t are the coordinates of the atoms. Changes in angles will involve the coordinates of three atoms. Now, as mentioned above, Laurie has pointed out that we can be reasonably certain that the signs of the δa's, δb's, etc., resulting from vibrational contributions will be such as to increase the absolute value of the corresponding coordinate. The signs resulting from experimental uncertainty will ordinarily be unknown. The largest possible δr_{st} would occur if all of the contributions with one sign were of maximum value, and all the contributions with the other sign were zero. Thus, the maximum positive uncertainty is the sum of the positive contributions to δr_{st} and the maximum negative uncertainty is the sum of the negative contributions. The uncertainties given for the parameters of the average structure in Table VI were computed in this way.

Laurie[13] has suggested another approach to the estimation of uncertainty in the structure. It is apparent that upon isotopic substitution the effective bond distances and bond angles change, and it is plausible to assume that the most important changes involve the parameters of the atoms substituted. Laurie estimates that the interatomic distances from the substituted atom to other heavy atoms decrease several hundred-thousandths of an angstrom unit upon substitution of a heavier isotope. The distances to a hydrogen atom are estimated to change by a smaller amount. Substitution of deuterium for hydrogen results in a decrease

TABLE VIII. P_{bb} values in 2-chloropropane.

Species	P_{bb}
$CH_3CHCl^{35}CH_3$	54.8320 amu-Å^2
$CH_3CHCl^{37}CH_3$	54.8324
$CH_3C^{13}HCl^{35}CH_3$	54.8254
$CH_3CDCl^{35}CH_3$	54.8349

TABLE IX. Comparison of coordinates and structural parameters for 2-chloropropane with values computed assuming reductions in bond lengths upon isotopic substitution.

Coordinate or parameter	No reduction upon substitution	0.00005 Å reduction
a(Cl)	1.2219 Å	1.2210 Å
b(Cl)	0	0
c(Cl)	0.0466	0.0463
a(C, middle)	−0.5176	−0.5119
b(C, middle)	0	0
c(C, middle)	−0.4084	−0.4082
a(C, end)	−1.1663	−1.1660
b(C, end)	1.2659	1.2652
c(C, end)	0.1329	0.1330
r(CCl)	1.7980 Å	1.7915 Å
r(CC)	1.5220	1.5236
∠CCC	112°34′	112°17′
∠CCCl	108°48′	108°59′

TABLE X. Quadrupole coupling constants for $(CH_3)_2CHCl^{35}$.

eQq_m	−61.49±0.11 Mc/sec	
$eQq_m\eta$	8.13±0.49 Mc/sec	
η[a]	−0.1322±0.0082	
χ_{aa}	−61.49±0.11 Mc/sec	
χ_{bb}	34.81±0.25 Mc/sec	
χ_{cc}	26.68±0.25 Mc/sec	
	I[b]	II[c]
χ_{zz}	−67.82±0.12 Mc/sec	−69.61±0.50 Mc/sec
η_{bond}[d]	0.0275±0.003	0
θ_z[e]	14°26′	16°12′±30′
I	23%	22%

[a] $\eta=(\chi_{bb}-\chi_{cc})/\chi_{aa}$.

[b] Assuming the z axis of the quadrupole tensor and the CCl internuclear line coincide.

[c] Assuming cylindrical charge distribution.

[d] $\eta_{\text{bond}}=(\chi_{xx}-\chi_{yy})/\chi_{zz}$; the y axis is perpendicular to the plane of symmetry.

[e] The angle between the a and z axis.

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[13] V. W. Laurie, Symposium on Molecular Structure and Spectroscopy, Ohio State University, June 1963.

TABLE XI. Rotational constants (Mc/sec) and moments of inertia (amu-Å^2)[a] of 2-chloropropane species used in internal rotation study.

Torsional state vv'	A	B[b]	C	I_a	I_b	I_c
$CD_3CDCl^{35}CH_3(0, 0)$	6869.21±0.7	4152.48	2938.53	73.5937	121.7418	172.0353
$CD_3CDCl^{35}CH_3(1, 0)$	6861.67±0.7	4146.49	2935.11	73.6746	121.9178	172.2358
$CD_3CDCl^{35}CH_3(0, 1)$	6851.55±1.2	4148.51	2934.37	73.7834	121.8584	172.2792
$(CH_3)_2CHCl^{35}(v=1)$	8060.24±2.0	4563.43	3202.87	62.7191	110.7787	157.8369

[a] Conversion factor used: 5.05531×10^5 Mc/sec-amu-Å^2.

[b] Uncertainty in B and C is ±0.07 Mc/sec.

of the interatomic distance to the H atom of about 0.003 Å. The importance of these apparently negligible changes is the way in which they are magnified by the substitution method.

For 2-chloropropane the second moments of the parent species have been calculated assuming the parameters listed under Structure III in Table VI. Second moments were also computed for (a) $CH_3CHCl^{37}CH_3$ using the same parameters except with the CCl distance shortened by 0.00005 Å; (b) $C^{13}H_3CHCl^{35}CH_3$ with the C^{13}–C distance shortened by 0.00005 Å; and (c) $CH_3C^{13}HCl^{35}CH_3$ with the C^{13}Cl distance and the two C^{13}–C distances shortened by 0.00005 Å. These computed second moments were then used with Eq. (1) to compute the coordinates and the bond distances and bond angles given in Table IX. Comparison of the values in Table IX with the originally assumed structure shows that the differences of 0.00005 Å give rise to discrepancies of several thousandths of an angstrom unit, particularly in the coordinates of the central carbon atom. Since possible angle changes were not considered, and since 0.00005 Å is only a rough estimate of the bond shortening, no great weight should be given to the differences shown in Table IX other than as an estimate of the uncertainties in the various parameters.

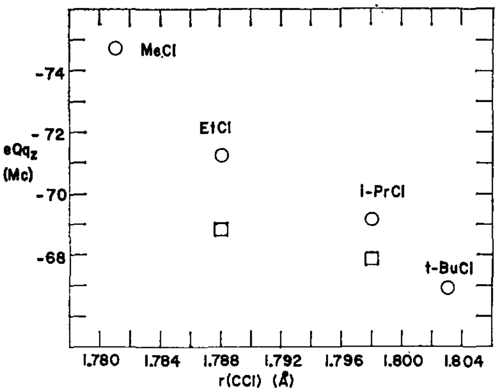

FIG. 3. Plot of chlorine quadrupole coupling constant vs carbon-chlorine distance in methyl, ethyl, isopropyl, and t-butyl chlorides. Circles are values based on assumed cylindrical charge distribution near chlorine nucleus; squares are values based on assumed coincidence of z axis of quadrupole tensor and CCl internuclear line.

The difference between a second moment of a substituted species computed assuming no bond shortening and the corresponding value computed assuming that the bond is shortened may be used to estimate the change in inertial defect upon isotopic substitution. The factors in parentheses for the heavy atoms in Table VII were selected on this basis.

QUADRUPOLE COUPLING CONSTANTS

Selected differences in the frequencies of the hyperfine components of the transitions in $CH_3CHCl^{35}CH_3$ listed in Table II were expressed as linear functions of the quadrupole coupling parameters $\chi_{aa}=eQ(\partial^2V/\partial a^2)=eQq_m$ and $(\chi_{bb}-\chi_{cc})=eQq_m\eta$. The experimental splittings were then used in a least-squares treatment to obtain the quadrupole parameters. The determined values together with the relation $\chi_{aa}+\chi_{bb}+\chi_{cc}=0$, gave the values of χ_{aa}, χ_{bb} and χ_{cc} in Table X.

Since the measured spectra are insensitive to $\chi_{ac}(\chi_{ab}=\chi_{bc}=0)$ an assumption must be made in order to determine the quadrupole coupling constants in the principal axis system of the coupling constant tensor. We have made the usual two assumptions: (I) a principal axis (the z axis) coincides with the CCl internuclear line and the angle (θ_z) between this line and the a principal inertial axis may be deter-

TABLE XII. Comparison of the molecular parameters of 2-chloropropane with those of similar molecules.

Molecule	r(CC)	r(CCl)	∠CCC	∠CCCl or ∠CCH
$(CH_3)_3CCl$[a]	1.530 Å	1.803 Å	110.9°	108.0°
$(CH_3)_2CHCl$[b]	1.522	1.798	112.7	109.4
CH_3CH_2Cl[c]	1.520	1.788		111.0
CH_3Cl[d]		1.781		
$(CH_3)_3CH$[e]	1.525		111.1	107.9
$(CH_3)_2CH_2$[f]	1.526		112.4	109.5

[a] Reference 16.

[b] This work.

[c] Reference 1.

[d] Reference 2.

[e] Reference 18.

[f] Reference 17.

mined from the structure; and (II), the charge distribution in the vicinity of the chlorine nucleus is cylindrically symmetric, in which case

$$\chi_{zz}=-2\chi_{xx}=-2\chi_{yy}=-2\chi_{bb}.$$

The results of the two assumptions are shown in Table X. It may be seen that the two values of χ_{zz} differ by 2.5% and that the values of θ_z differ by 1.8° which is greater than the uncertainty in the angle between the CCl line and the *a* axis obtained from the structure. Equivalent differences have been found for other molecules and it is still not clear which of the assumptions gives a better value of χ_{zz} and η_z.

The value of I, the ionic character of the carbon–chlorine bond shown in Table X, was determined from the equation[14]

$$I=(1-s^2+d^2-II)-(q_{zz}/q_{at}).$$

Here s^2 and d^2 are the *s* and *d* character of the chlorine orbital involved in the carbon-chlorine bond, II is related to the double-bond character of the CCl bond, $eQq_{zz}=\chi_{zz}$, and $eQq_{at}=-109.74$ Mc/sec is the quadrupole coupling constant of atomic chlorine. The values of I have been computed assuming that $s^2=0.15$ and that d^2 and II are negligible.

INTERNAL ROTATION

Rotational transitions in the first excited torsional state of $(CH_3)_2CHCl^{35}$ and in the first excited CH_3 torsional state (0,1) and the first excited CD_3 torsional state (1,0) of $CD_3CDCl^{35}CH_3$ were examined in a search for further hyperfine structure due to internal rotation of the methyl groups. The rotational constants and moments of inertia of the ground state, and (0,1) and (1,0) excited states of $CD_3CDCl^{35}CH_3$ are listed in Table XI. The assignments were based on the relative intensity of the rotational transitions and on the quadrupole hyperfine structure. No splittings ascribable to internal rotation were observed. The 12_{49}–12_{48} transition in the (0,1) torsional state was calculated[15] to be the most sensitive of the observed lines to internal rotation effects. Assuming that a 0.5 Mc/sec splitting would have been observed, the absence of splitting sets a lower limit to the potential barrier hindering internal rotation of 3450 cal/mole.

DISCUSSION

The systematic increase in CCl bond length and the corresponding decrease in quadrupole coupling constants from methyl to ethyl to isopropyl to *t*-butyl chloride has already been pointed out by Lide.[16] We have plotted the relationship in Fig. 3 in order to point out more clearly the importance of determining which of the assumptions used to fix the quadrupole coupling constants is more reliable.

The CC bond distance in 2-chloropropane is close to that found for ethyl chloride[1] and propane,[17] and the CCC angle is approximately the same as in propane. The CCl angle is 1.6° smaller than in ethyl chloride and 1.4° larger than in *t*-butyl chloride[16] indicating a fairly severe rearrangement in angles upon substitution of a methyl group for a hydrogen atom. In contrast, substitution of chlorine for hydrogen in propane and tertiary butane[18] has very little effect on the angular arrangement. The CC and CCl bond lengths and the CCC and CCCl bond angles for 2-chloropropane are compared with values for similar compounds in Table XII.

The CH bonds of the methyl groups are staggered with respect to the bonds on the central carbon. However, examination of the methyl group parameters shows an unsymmetrical methyl group. The CH bond distances are the same, but the CCH_α angle appears to be approximately one degree larger than the CCH_β or CCH_γ angles, which are equal. A complete analysis of the unsymmetrical nature was not attempted since the *c* coordinates of the hydrogen atoms are small and because of the relatively large vibrational effects upon deuterium substitution.

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