A force field for secondary chlorides

C. G. Opaskar* and S. Krimm

Harrison M. Randall Laboratory of Physics, University of Michigan, Ann Arbor
Michigan

Abstract—A force field has been derived for monochloro- and 2,4-dichloro-hydrocarbons. The Snyder–Schachtschneider force field for hydrocarbons was used as a starting point, the constants associated with the secondary chlorine being determined from an assignment of the gas phase spectrum of 2-chloropropane and the carbon–chlorine stretching frequencies of the three isomers of 2-chlorobutane. The force field was tested on 3-chloropentane, axial and equatorial monochloro*cyclo*hexane, and the most stable conformations of *dl* and *meso* 2,4-dichloropentane, giving good agreement in all of these cases. The conformation dependence of the carbon–chlorine stretching frequency is thus shown to derive primarily from structural differences between conformers.

INTRODUCTION

THE experimental correlation of vibrational frequencies with rotational isomeric structure in secondary chlorides is now well established [1, 2]. In particular, a detailed study of model compounds [2] has shown that the absorption bands arising from the stretching of the carbon–chlorine bond have frequencies which are sensitive both to the two atoms *trans* to the chlorine atom across the neighboring carbon–carbon bonds as well as to the local conformation of the carbon chain. This dependence is summarized in Fig. 1, which shows the six conformations possible near a chlorine atom and the observed carbon–chlorine stretching frequencies associated with each. The conformations are labelled S (for secondary chlorine), with subscripts designating the atoms *trans* to the chlorine and primes to distinguish conformations in which, for *trans* hydrogens, the next-nearest-neighbor carbon atoms have been rotated away from the planar zig-zag position [2]. These rotations about carbon–carbon bonds are taken to have values of $+120°$ and $-120°$ from the *trans* planar zig-zag conformation, an assumption which may not be exactly correct in all cases since non-bonded interactions in linear molecules may lead to stabilization of structures with slightly different values of this torsion angle [3]. The correlation ranges for S_{HH}, $S_{HH'}$, and S_{CH} are derived from a detailed study of model compounds in which, in some instances, the conformational structure is unambiguous [2]. The $S_{H'H'}$ frequency correlation is obtained from the spectrum of the unique structure of axial monochloro*cyclo*hexane [4], interpreted in terms of our calculations (see below). The S_{CC} frequencies are those observed for 2,2,4,4-tetramethyl-3-chloropentane, 758 cm^{-1} [2], and for equatorial monochloro*cyclo*hexane, 728 cm^{-1} [4], both molecules being cases in which the conformation is unambiguously determinable.

---

* Present address: Shell Development Co., Houston, Texas.

[1] S. MIZUSHIMA, T. SHIMANOUCHI, K. NAKAMURA, M. HAYASHI and S. TSUCHIYA, *J. Chem. Phys.* **26,** 970 (1957).
[2] J. J. SHIPMAN, V. L. FOLT and S. KRIMM, *Spectrochim. Acta* **18,** 1603 (1962).
[3] R. A. SCOTT and H. A. SCHERAGA, *J. Chem. Phys.* **44,** 3054 (1966).
[4] P. KLAEBOE, J. J. LOTHE and K. LUNDE, *Acta Chem. Scand.* **10,** 1465 (1956).

No comparable molecule has been found for the $S_{CH'}$ conformation, so that the carbon–chlorine stretching frequency for this structure is as yet not known with certainty, although it has been claimed to be located at 667 cm^{-1} in 3-chloropentane [5].

The origin of this dependence of carbon–chlorine stretching frequency on conformation has not as yet been elucidated in any detail. It could arise from either of two essentially different factors: the dependence of frequency on structural differences between conformations, or the dependence on potential energy terms
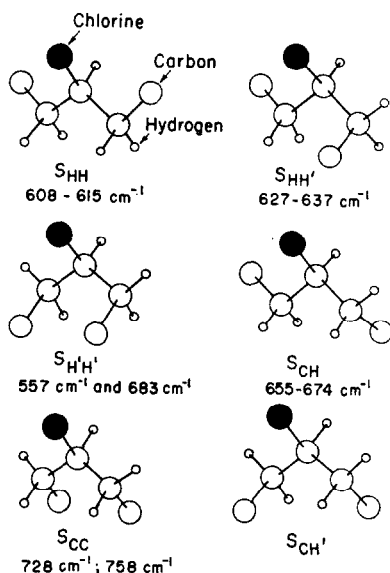

Fig. 1. Conformations of secondary chlorides and empirically determined carbon–chlorine stretching frequencies.

which are specific to each conformation. Or it might result from a combination of these factors. We have examined the first of these possibilities, attempting to derive a force field which contains no dominant conformation-dependent potential energy terms. It appears that this is possible to a good approximation for monochloro- and 2,4-dichloro-hydrocarbons, which are the systems which we have investigated.

DERIVATION OF THE FORCE FIELD

Our approach to the derivation of a force field for secondary chlorides was the following. A very satisfactory valence force field has been determined for saturated hydrocarbons [6], based on the refinement of 308 observed frequencies in 17 molecules. The force constants in this potential function were transferred, where applicable, to the chlorinated hydrocarbons, some minor interaction constants being dropped. Another set of force constants for primary chlorides was available [7], which required only a few additional constants to make it suitable for secondary chlorides. This

[5] A. Caraculacu, J. Štokr and B. Schneider, *Coll. Czech. Chem. Commun.* **29**, 2783 (1964).
[6] R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta* **21**, 169 (1965).
[7] J. H. Schachtschneider, private communication.

combined set of force constants was used to fit all of the frequencies of 2-chloropropane and the carbon–chlorine stretching frequencies of the three conformations of 2-chlorobutane, adjustments being made only in some of the chlorine constants. The force field was then tested on various monochloro- and dichloro-hydrocarbons to determine if it was transferable and therefore acceptable as a satisfactory potential function for secondary chlorides. Torsion coordinates were not included in these calculations primarily because no experimental data are available on such frequencies in secondary chlorides. A model calculation using a torsion constant which gave calculated torsion frequencies of about 200 cm^{-1}, approximately the value in propane
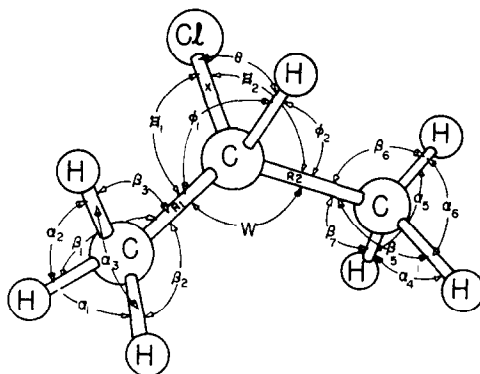

Fig. 2. Molecule of 2-chloropropane with internal coordinates.

[8], showed that the torsion coordinates interact only very weakly with the carbon–chlorine stretching coordinate: the carbon–chlorine stretching frequency is shifted by only 2 cm^{-1}. We felt, therefore, that the conclusions concerning the conformation dependence of the carbon–chlorine stretching frequency would not be significantly affected by the exclusion of torsion angles.

1. *Assignments for 2-chloropropane*

In order to use 2-chloropropane in the refinement procedure for the force constants involving the chlorine atom, it was necessary to have correct assignments for the vibrational bands. This was done by comparison of the spectrum with that of propane, and by study of the gas phase band contours.

The molecule of 2-chloropropane is illustrated in Fig. 2. Its gas phase spectrum is shown in Fig. 3. The shape of an absorption band in the gas phase spectrum of an asymmetric top molecule depends upon the orientation of the corresponding vibrational dipole moment with respect to the axes of the principal moments of inertia of the molecule [9]. If the changing dipole moment is parallel to the axis of least moment of inertia then the absorption band will have a strong central maximum with two weaker maxima on either side. This is also true if the changing dipole moment is parallel to the axis of greatest moment of inertia, so long as the molecule is not close to being a symmetric top. On the other hand, if the changing dipole moment is parallel to the axis of intermediate moment of

[8] J. H. SCHACHTSCHNEIDER and R. G. SNYDER, *Spectrochim. Acta* **19**, 117 (1963).

[9] G. HERZBERG, *Infrared and Raman Spectra*. Van Nostrand (1945).

inertia the central maximum will be absent from the absorption band. The moments of inertia of 2-chloropropane were calculated using the following constants: $m_H = 1$ amu, $m_C = 12$ amu, $m_{Cl} = 35$ amu, $r(CH) = 1.09$ Å, $r(CC) = 1.54$ Å, $r(CCl) = 1.795$ Å, all angles tetrahedral. They were found to be 62.33, 109.3 and 155.2 amu-Å², the principal axes corresponding to the greatest and least moments of inertia being located in the symmetry plane of the molecule while the axis corresponding to the intermediate moment is perpendicular to this plane. This fortunate circumstance thus permits the band shape to be used to identify the symmetry type of the corresponding vibrational mode.

A quantitative characterization of the expected band shape is also possible by determining the separation of the outer maxima in the two band types considered
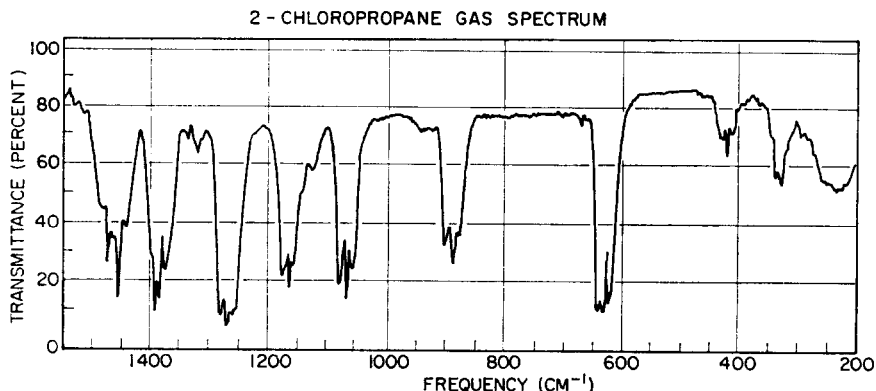

Fig. 3. Infrared spectrum of 2-chloropropane, gas phase, room temperature.

above [10]. Such calculations lead to the prediction that bands with a central maximum will have outer maxima separated by about 20 cm^{-1}, while bands without a central maximum will have the outer maxima separated by about 10 cm^{-1}.

Absorption bands with the above characteristics are indeed identifiable in the spectrum. Thus, bands in the gas phase spectrum centered at 421, 630, 887, 1065, 1163, and 1269 cm^{-1} can be assigned unambiguously to modes which are symmetric with respect to the symmetry plane (the plane of the CHCl group), while bands at 930 and 1130 cm^{-1} can be assigned to antisymmetric modes. In several other cases band overlap occurs, but a sorting out based on the predicted separation of the maxima, as well as on the location of the liquid phase peaks (see Table 3), seems feasible. Thus, in the low frequency region the observed band contour can be accounted for by a symmetric band centered at 335 cm^{-1} plus an antisymmetric band centered at 324 cm^{-1}. The group of bands near 1325 cm^{-1} is best fitted by a symmetric band centered near 1315 cm^{-1} and an antisymmetric band centered at 1330 cm^{-1}. The band contour near 1375 cm^{-1} is very satisfactorily accounted for by a symmetric band centered at 1392 cm^{-1} and an antisymmetric band centered at 1378 cm^{-1}.

The general nature of the mode associated with a given band is determinable on

[10] R. M. BADGER and L. R. ZUMWALT, J. Chem. Phys. 6, 711 (1938).

the basis of the assignments for propane [8]. Thus the 2-chloropropane band at 421 cm^{-1} can be correlated with the CCC bending mode of propane observed at 375 cm^{-1}. The 630 cm^{-1} band is obviously the carbon–chlorine stretching mode [2]. The symmetric CC stretching mode occurs in propane at 868 cm^{-1}, and the 887 cm^{-1} band of 2-chloropropane is therefore most reasonably associated with this vibration. In propane a band at 921 cm^{-1} is assigned to the antisymmetric CCH bending mode of the two methyl groups; a comparable assignment to the antisymmetric band in 2-chloropropane at 930 cm^{-1} is indicated. The totally symmetric methyl CCH bending mode in propane is located at 1157 cm^{-1}, which suggests such an assignment for the 1163 cm^{-1} band of 2-chloropropane. Two major modes for which the frequency correspondence is not so close are: (a) the B_2 methyl CCH bending vibration of propane at 1187 cm^{-1}, which would be a symmetric vibration in 2-chloropropane, and (b) the B_1 antisymmetric CC stretching mode of propane at 1052 cm^{-1}, which would also be antisymmetric in 2-chloropropane. On the basis of band symmetries we assign these modes to the 2-chloropropane bands at 1065 and 1130 cm^{-1} respectively. The very large difference in frequency in the first case may not be unexpected, since in propane this vibration has a large contribution from CH$_2$ rocking [8], which disappears in 2-chloropropane. A similar disparity in contributions from various internal coordinates could account for the difference in the antisymmetric CC stretching frequencies (see Table 3). The internal symmetric methyl bending modes of propane at 1389 cm^{-1} (A_1) and 1370 cm^{-1} (B_1) have their counterparts (with appropriate symmetry) in the 2-chloropropane bands at 1392 and 1378 cm^{-1} respectively. The assignment of the strong symmetric band of 2-chloropropane at 1269 cm^{-1} to a movement of the H atom of the CHCl group in the symmetry plane is now indicated, as is the assignment of the 1330 cm^{-1} band to the motion of this H atom perpendicular to the symmetry plane (the analogous CH$_2$ wagging mode of propane occurs at 1331 cm^{-1}).

Since the hydrocarbon portion of our potential function was transferred without modification from the earlier work [6], we expect the corresponding calculated normal modes of 2-chloropropane to fit in with the assignments arrived at above from the experimental data. As we shall see this is indeed the case. The assignments of the remaining bands to motions within the carbon–chlorine portion of the molecule should then provide guidelines for refining those additional force constants associated with this group.

2. *Assignments for 2-chlorobutane*

Since 2-chlorobutane exists as a mixture of three conformational isomers, S_{HH}, $S_{HH'}$ and S_{CH} [2], an analysis of its spectrum comparable to that done above for 2-chloropropane was not feasible. However, the three carbon–chlorine stretching vibrations are convincingly known [2], and could be used in the refinement procedure. They are, for the liquid: S_{HH}– 607 cm^{-1}, $S_{HH'}$– 627 cm^{-1}, S_{CH}– 670 cm^{-1}. It might be remarked here that these frequencies vary somewhat with the phase of the specimen, probably mainly as a result of differential environmental effects, although in some cases possibly due to small changes in internal geometry. We have chosen the liquid state frequencies as our standard ones, primarily because most molecules were studied in this state.

3. *Refinement of the force field*

The force field was determined through normal coordinate calculations on 2-chloropropane and 2-chlorobutane combined with a study of possibly pertinent elements of the Jacobian matrix. This is a matrix whose elements are the derivatives of the frequencies with respect to the force constants [11]. Using the elements of

Table 1. Force constants for secondary chlorides

Name	Value	Environment	Coordinates coupled	
K_r	4.699	$C(H_1, H_2, H_3)$	(C, H_1)	
F_r	0.043	$C(H_1, H_2, H_3)$	$(C, H_1) (C, H_2)$	
K_d	4.554	$C_1—C_2(H_1)—C_3$	(C_2, H_1)	
F_d	0.006	$C_1—C_2(H_1, H_2)—C_3$	$(C_2, H_1) (C_2, H_2)$	
K_R	4.387	$C_1—C_2$	(C_1, C_2)	
F_R	0.101	$C_1—C_2—C_3$	$(C_1, C_2) (C_2, C_3)$	
$F_{R\gamma}$	0.328	$C_1—C_2(H)$	$(C_1, C_2) (C_1, C_2, H)$	
$F_{R\gamma'}$	0.079	$C_1—C_2(H)—C_3$	$(C_1, C_2) (H, C_2, C_3)$	
$F_{R\omega}$	0.417	$C_1—C_2—C_3$	$(C_1, C_2) (C_1, C_2, C_3)$	
$H\alpha$	0.540	$C(H_1, H_2, H_3)$	(H_1, C, H_2)	
$H\delta$	0.550	$C_1—C_2(H_1, H_2)—C_3$	(H_1, C_2, H_2)	
$H\beta$	0.645	$C_1—C_2(H_1, H_2, H_3)$	(C_1, C_2, H_1)	
$F\beta$	−0.012	$C_1—C_2(H_1, H_2, H_3)$	$(C_1, C_2, H_1) (C_1, C_2, H_2)$	
$H\gamma$	0.656	$C_1—C_2(H_1, H_2)—C_3$	(C_1, C_2, H_1)	
$F\gamma$	−0.021	$C_1—C_2(H_1, H_2)—C_3$	$(C_1, C_2, H_1) (C_1, C_2, H_2)$	
$F\gamma'$	0.013	$C_1—C_2(H_1, H_2)—C_3$	$(C_1, C_2, H_1) (H_1, C_2, C_3)$	
$H\omega$	1.130	$C_1—C_2—C_3$	(C_1, C_2, C_3)	
$F\gamma\omega$	−0.031	$C_1—C_2(H)—C_3$	$(C_1, C_2, C_3) (C_1, C_2, H)$	
$f\omega^t$	−0.011	$C_1—C_2—C_3—C_4$	$(C_1, C_2, C_3) (C_2, C_3, C_4)$	180
$f\gamma\omega^t$	0.049	$C_1—C_2—C_3—H$	$(C_1, C_2, C_3) (C_2, C_3, H)$	180
$f\gamma\omega^g$	−0.052	$C_1—C_2—C_3—H$	$(C_1, C_2, C_3) (C_2, C_3, H)$	60
$f\gamma^t$	0.127	$H_1—C_1—C_2—H_2$	$(H_1, C_1, C_2) (C_1, C_2, H_2)$	180
$f\gamma^g$	−0.005	$H_1—C_1—C_2—H_2$	$(H_1, C_1, C_2) (C_1, C_2, H_2)$	60
*K_X	3.338	C—X (X = chlorine)	(C, X)	
*K_R^X	4.623	$C_1(H, X)—C_2$	(C_1, C_2)	
F_{RX}	0.730	$C_1—C_2—X$	$(C_1, C_2) (C_2, X)$	
*$F_{X\omega}$	−0.220	$C_1—C_2(X)—C_3$	$(C_2, X) (C_1, C_2, C_3)$	
$f\gamma\omega^X$	−0.031	$C_1—C_2(X, H)—C_3$	$(C_1, C_2, C_3) (C_1, C_2, H)$	
K_d^X	4.846	C(H, X)	(C, H)	
$H\Xi$	0.982	$C_1—C_2—X$	(C_1, C_2, X)	
$F_{R\Xi}$	0.075	$C_1—C_2—X$	$(C_1, C_2) (C_1, C_2, X)$	
*F_R^X	0.300	$C_1—C_2(X)—C_3$	$(C_1, C_2) (C_2, C_3)$	
$F_{X\Xi}$	0.550	$C_1—C_2—X$	$(C_2, X) (C_1, C_2, X)$	
$H\theta$	0.860	C(X, H)	(X, C, H)	
*$H\phi$	0.633	$C_1—C_2(H, X)$	(C_1, C_2, H)	
$F\gamma\theta$	0.089	$C_1—C_2(H, X)$	$(C_1, C_2, H) (H, C_2, X)$	
$F_{X\theta}$	0.333	C(H, X)	$(C, X) (H, C, X)$	
$f\gamma\Xi^g$	−0.037	$C_1(H)—C_2(X)$	$(H, C_1, C_2) (C_1, C_2, X)$	60
$f\gamma\Xi^t$	0.070	$C_1(H)—C_2(X)$	$(H, C_1, C_2) (C_1, C_2, X)$	180
$f\omega\Xi^t$	0.041	$C_1—C_2—C_3(X)$	$(C_1, C_2, C_3) (C_2, C_3, X)$	180
$f\omega\Xi^g$	−0.024	$C_1—C_2—C_3(X)$	$(C_1, C_2, C_3) (C_2, C_3, X)$	60

* Modified or added force constant.
Bond stretching constants in mdyn/Å.
Angle bending constants in mdyn·Å.

the Jacobian as a guide, five force constants were either added or modified in the set based on the hydrocarbon [6] and primary chloride [7] constants. These modifications, although implying a choice of force field, were straightforward enough so that use of a least squares procedure did not seem warranted.
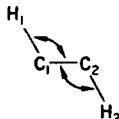
[11] D. A. Long, R. B. Gravenor and M. Woodger, *Spectrochim. Acta* 19, 937 (1963).

The final set of force constants is shown in Table 1. The notation is explained by the following examples:

(1) CH stretching constant for a primary carbon—K_r
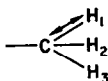
Environment: $C(H_1, H_2, H_3)$; Coordinates coupled: (C, H_1)

(2) Interaction between two CCH angles for H atoms in the *trans* position—$f_\gamma{}^t$

Environment: H_1—C_1—C_2—H_2; Coordinates coupled: (H_1, C_1, C_2) (C_1, C_2, H_2) 180

(3) Interaction between two CC bonds when the middle carbon atom is connected to a chlorine atom—$F_R{}^X$.

Environment: C_1—$C_2(X)$—C_3; Coordinates coupled: (C_1, C_2) (C_2, C_3)

The other constants are defined in a similar manner.

The first 23 constants in Table 1 were transferred unaltered from the set for saturated hydrocarbons [6]; the remainder, other than $F_{X\omega}$, were transferred from the set for the primary chlorides [7] (ω corresponds to the coordinate W in Fig. 2). Jacobian elements were computed for the carbon–chlorine stretching frequencies for about 25 force constants. The force constants which most influenced the splittings between the S_{HH}, $S_{HH'}$ and S_{CH} frequencies were K_{CX}, $F_{X\Xi}$, $F_{X\theta}$, $F_{X\phi}$, $F_{X\omega}$ and F_{RX} ($F_{X\phi}$ and $F_{X\omega}$ are zero for primary chlorides). It was found that $F_{X\omega}$ and $F_{X\phi}$ were most effective in this regard, $F_{X\omega}$ being much more influential than $F_{X\phi}$. Since using the latter to fit the carbon–chlorine stretching frequencies was found to mar somewhat the agreement at higher frequencies, it was decided to leave this constant at zero and use only $F_{X\omega}$. The optimum value of -0.220 found for $F_{X\omega}$ necessitated slight modifications in K_X (raising it by 0.2) and in $K_R{}^X$ (raising it by 0.3). The constant H_ϕ was decreased from its value of 0.676 in the primary chlorides in order to give agreement with the assignments of the $C(X)$—H bending modes of 2-chloropropane, and $F_R{}^X$ was modified from its value of 0.101 for hydrocarbons in order to obtain better agreement for the CC stretching modes of 2-chloropropane.

4. *Results for 2-chloropropane and 2-chlorobutane*

The normal coordinate calculations were done using the Wilson **GF** matrix method [12] and the Taylor symmetrization procedure [13], and were performed on an

[12] E. B. WILSON, J. C. DECIUS and P. C. CROSS, *Molecular Vibrations*. McGraw-Hill (1955).
[13] W. J. TAYLOR, *J. Chem. Phys.* **18**, 1301 (1950).

IBM 7090 computer. The calculation of atomic motions followed the method of
Hunziker [14].

The 2-chloropropane molecule with its internal coordinates has been given in
Fig. 2. The symmetry coordinates used in the calculations are given in Table 2.
The calculated frequencies, symmetries and potential energy distributions are
given in Table 3, and compared with observed liquid phase frequencies and gas
phase band symmetries. Only contributions to the potential energy which are

Table 2. Symmetry coordinates for 2-chloropropane

Class A' symmetry coordinates (symmetric with respect to the median plane)

$A_1 = 2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6$
$B_1 = 2\beta_3 - \beta_1 - \beta_2 + 2\beta_6 - \beta_4 - \beta_5$
$U_1 = \alpha_1 + \alpha_2 + \alpha_3 - \beta_1 - \beta_2 - \beta_3 + \alpha_4 + \alpha_5 + \alpha_6 - \beta_4 - \beta_5 - \beta_6$
$X = $ C—Cl stretch
$H_\sigma = 2\theta - \phi_1 - \phi_2$
$W_1 = W - \theta - \phi_1 - \phi_2 + \Xi_1 + \Xi_2$
$W_2 = W + \theta + \phi_1 + \phi_2 + \Xi_1 + \Xi_2$
$R_1 = R_1 + R_2$
$W_3 = 2W - \Xi_1 - \Xi_2$
$A_2 = \alpha_2 - \alpha_3 + \alpha_5 - \alpha_6$
$B_2 = \beta_2 - \beta_1 + \beta_5 - \beta_4$

Class A'' symmetry coordinates (antisymmetric with respect to the median plane)

$A_3 = 2\alpha_1 - \alpha_2 - \alpha_3 - 2\alpha_4 + \alpha_5 + \alpha_6$
$B_3 = 2\beta_3 - \beta_1 - \beta_2 - 2\beta_6 + \beta_4 + \beta_5$
$U_2 = \alpha_1 + \alpha_2 + \alpha_3 - \beta_1 - \beta_2 - \beta_3 - \alpha_4 - \alpha_5 - \alpha_6 + \beta_4 + \beta_5 + \beta_6$
$X_\pi = \Xi_1 - \Xi_2$
$H_\pi = \phi_1 - \phi_2$
$R_2 = R_1 - R_2$
$A_4 = \alpha_2 - \alpha_3 - \alpha_5 + \alpha_6$
$B_4 = \beta_2 - \beta_1 - \beta_5 + \beta_4$

greater than 10 per cent have been included. The CH stretching frequencies, although
calculated and giving good agreement, have been omitted from this and subsequent
tables since they were not used in the analyses. It will be seen that the agreement
between observed and calculated frequencies is reasonably good, the average deviation
between observed and calculated frequencies in the range of 600–1500 cm^{-1} being
about 0.5 per cent (frequencies below 600 cm^{-1} might be expected to deviate more
because of the exclusion of the torsion coordinates in the calculation).

The 2-chlorobutane molecule with its internal coordinates is shown in Fig. 4.
The coordinates used in the calculations are listed in Table 4. In Table 5 are given
the calculated frequencies and potential energy distributions for the three con-
formations of this molecule. A detailed comparison of observed and calculated
frequencies is difficult because of the presence of the three isomers in the liquid.
However, it can be readily seen that the carbon–chlorine stretching frequencies
are satisfactorily accounted for in the three structures by our force field. A possible
correlation with observed bands may be feasible by examining the effect of decreasing
temperature on the spectrum, since this would be expected to favor the concentration

[14] H. Hunziker, *Spectrochim. Acta* 17, 131 (1961).

Table 3. Observed and calculated frequencies and assignments for 2-chloropropane

Observed		Calculated		
Frequency*	Symmetry†	Frequency	Symmetry	Potential energy distribution‡
324 w	A	310	A''	$X_\pi(89)$
335 m	S	329	A'	$W_3(66) - W_1(16)$
423 m	S	419	A'	$W_1(62) + W_3(15)$
611 vs	S	611	A'	$X(76)$
677 vw		$2 \times 335 = 670$	A'	
760 w		$335 + 423 = 758$	A'	
885 s	S	884	A'	$R_1(76) + B_1(15)$
933 mw	A	923	A''	$B_3(36) + B_4(36) + H_\pi(21)$
945 vw		$335 + 611 = 946$	A'	
965 ?		965	A''	$B_3(35) - B_4(33) - R_2(24)$
1025 sh		$423 + 611 = 1034$	A'	
1061 vs	S	1078	A'	$B_2(51) - B_1(14) - H\sigma(13)$
1129 m	A	1133	A''	$R_2(53) - B_4(15) + H_\pi(14)$
1160 s	S	1144	A'	$B_1(44) - R_1(23)$
1223 vw		$2 \times 611 = 1222$	A'	
1260 vs	S	1260	A'	$H\sigma(80) + B_2(11)$
1308 w	S	$423 + 885 = 1308$	A'	
1328 w	A	1323	A''	$H_\pi(55) - R_2(17)$
1374 s	A	1375	A''	$U_2(84)$
1385 s	S	1378	A'	$U_1(95)$
1446 s⎱ 1465 s⎰		1462	A''	$A_4(86)$
		1464	A'	$A_1(83)$
		1467	A'	$A_2(81)$
		1467	A''	$A_3(82)$

* Liquid phase frequencies.
† From gas phase band contours.
‡ In per cent with only coordinates contributing > 10 per cent included. See Table 2 for definition of coordinates.
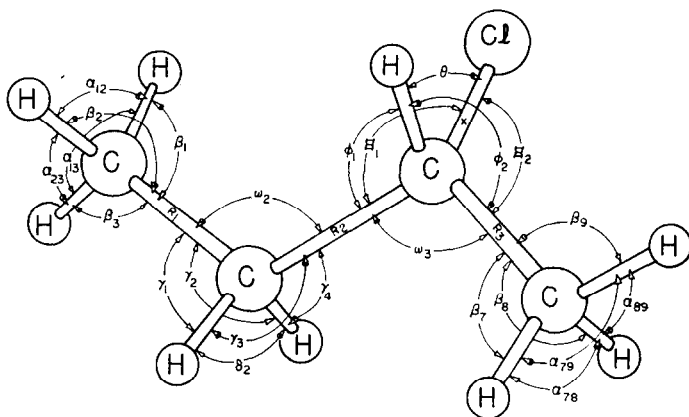
Fig. 4. Molecule of 2-chlorobutane with internal coordinates.

of one isomer. In Table 6 are listed the observed frequencies of liquid 2-chlorobutane [2], together with the effect of decreasing temperature on the relative intensities of the bands [15] (in this case after cooling for several hours with liquid nitrogen, without freezing of the sample). It will be seen that, judging from the carbon–chlorine stretching frequencies, the S_{HH} conformation is favored at lower temperature. We have therefore tried to assign those bands which remain intense at low temperature

[15] J. J. SHIPMAN, private communication.

Table 4. Coordinates for 2-chlorobutane

$$R_1 = R_1$$
$$R_2 = R_2$$
$$R_3 = R_3$$
$$X = X$$
$$U_l = \alpha_{12} + \alpha_{13} + \alpha_{23} - \beta_1 - \beta_2 - \beta_3$$
$$A_{1l} = 2\alpha_{12} - \alpha_{13} - \alpha_{23}$$
$$A_{2l} = \alpha_{13} - \alpha_{23}$$
$$B_{1l} = 2\beta_1 - \beta_2 - \beta_3$$
$$B_{2l} = \beta_2 - \beta_3$$
$$\delta = 4\delta_2 - \gamma_1 - \gamma_2 - \gamma_3 - \gamma_4$$
$$CCC = 5\omega_2 - \delta_2 - \gamma_1 - \gamma_2 - \gamma_3 - \gamma_4$$
$$t = \gamma_1 - \gamma_2 - \gamma_3 + \gamma_4$$
$$r = \gamma_1 - \gamma_2 + \gamma_3 - \gamma_4$$
$$\omega = \gamma_1 + \gamma_2 - \gamma_3 - \gamma_4$$
$$H_\sigma = 2\theta - \phi_1 - \phi_2$$
$$W_1 = \omega_3 - \theta - \phi_1 - \phi_2 + \Xi_1 + \Xi_2$$
$$W_2 = 2\omega_3 - \Xi_1 - \Xi_2$$
$$X_\pi = \Xi_1 - \Xi_2$$
$$H_\pi = \phi_1 - \phi_2$$
$$U_r = \alpha_{78} + \alpha_{79} + \alpha_{89} - \beta_7 - \beta_8 - \beta_9$$
$$A_{1r} = 2\alpha_{78} - \alpha_{79} - \alpha_{89}$$
$$A_{2r} = \alpha_{79} - \alpha_{89}$$
$$B_{1r} = 2\beta_7 - \beta_8 - \beta_9$$
$$B_{2r} = \beta_8 - \beta_9$$

Table 5. Calculated frequencies and potential energy distributions for 2-chlorobutane

(a) S_{HH} conformation

Frequency (cm^{-1})	Potential energy distribution
213	$X_\pi(37) + CCC(28) - W_2(23)$
313	$W_2(55) + X_\pi(23)$
376	$W_1(59) - CCC(12)$
454	$CCC(36) + W_1(12)$
611	$X(75)$
776	$r(44) + B_{1l}(18) - B_{2l}(14)$
843	$R_2(32) - B_{2r}(18)$
956	$B_{2r}(24) - B_{1l}(20) + H_\pi(19)$
1004	$B_{1r}(35) - B_{2l}(16) + R_3(15)$
1022	$R_1(63) - R_3(15)$
1089	$B_{2l}(27) + r(14)$
1109	$R_3(43) - B_{1r}(12)$
1155	$R_2(31) + B_{2r}(13)$
1232	$H_\sigma(43) + t(21) - B_{1l}(14)$
1263	$H_\pi(33) + \omega(25) + H_\sigma(13)$
1291	$t(48) - H_\sigma(26)$
1362	$U_l(65) - H_\pi(11)$
1373	$U_r(87)$
1390	$\omega(30) - U_l(25) - H_\pi(11)$
1450	$\delta(90)$
1460	$A_{2r}(42) - A_{1r}(23) + A_{1l}(22)$
1460	$A_{2l}(91)$
1461	$A_{2r}(44) + A_{1r}(38)$
1465	$A_{1l}(52) + A_{1r}(25)$

Table 5 (*cont.*)

(b) $S_{HH'}$ conformation

Frequency (cm^{-1})	Potential energy distribution
208	CCC(37) + W_1(34) + X_π(15)
317	X_π(58) — W_1(15)
328	W_2(75)
540	CCC(27) — X(26) — W_1(21)
631	X(59)
779	r(46) + B_{1l}(29)
840	R_2(44) + R_1(18) + R_3(11) — B_{2r}(11)
946	R_1(28) — R_3(22) + B_{2r}(17) + H_π(11)
993	B_{2l}(19) + B_{2r}(19) + R_2(17)
1009	B_{1r}(37) + ω(16) — B_{2l}(13) — B_{1l}(11)
1084	B_{1l}(22) + R_1(16)
1121	R_{1r}(15) + R_2(13) — R_1(13)
1147	R_3(30) — r(13)
1231	$H\sigma$(69)
1264	t(54)
1320	H_π(50) + t(11)
1332	ω(41) + U_l(24) + R_2(12)
1372	U_r(83)
1380	U_l(62) — ω(15)
1452	δ(84)
1460	A_{2r}(73) + A_{1l}(14)
1460	A_{2l}(91)
1462	A_{1r}(66) + δ(11)
1464	A_{1l}(62) + A_{1r}(13)

(c) S_{OH} conformation

Frequency (cm^{-1})	Potential energy distribution
218	W_2(40) + CCC(26)
295	X_π(70)
390	W_1(54) + CCC(14)
418	W_2(27) + W_1(24) — CCC(18)
676	X(62)
762	r(53) + B_{1l}(27)
857	R_2(35) — B_{2l}(17) — B_{2r}(16) + R_3(13)
951	B_{2l}(23) — B_{2r}(21) — H_π(14)
975	R_3(25) + B_{1l}(22) + t(19)
1021	R_1(51) + B_{1r}(25)
1073	B_{1r}(30) — R_1(17) — B_{2l}(13)
1138	R_3(28) — B_{1l}(13)
1155	R_2(29)
1235	$H\sigma$(30) — t(20) — H_π(11)
1267	$H\sigma$(48) + t(21)
1296	ω(42) — t(19)
1351	U_l(27) — H_π(23) + U_r(12)
1373	U_r(76) — U_l(13)
1383	U_l(46) — ω(16)
1451	δ(88)
1460	A_{1r}(39) + A_{2r}(32) — A_{1l}(18)
1460	A_{2l}(90)
1461	A_{2r}(55) — A_{1r}(17)
1464	A_{1l}(54) + A_{1r}(30)

to the S_{HH} conformation, and to determine if the remaining bands can be assigned reasonably to vibrations of the $S_{HH'}$ and S_{CH} structures. Study of Table 6 indicates that this is quite satisfactorily achieved. Using the assignments for the S_{HH} conformation, the average deviation between observed and calculated frequencies in the range of 600–1500 cm^{-1} is found to be about 0.5 per cent.

Table 6. Assignments to observed frequencies of 2-chlorobutane

Observed liquid frequency (cm^{-1})	Calculated frequency		
	S_{HH}	$S_{HH'}$	S_{CH}
~290 w			295
324 m	313	317	
333 sh		328	
374 m†			390
386 m*	376		
418 mw†			418
460 mw*	454		
522 m†		540	
607 vs*	611		
627 m†		631	
670 s†			676
790 vs*	776	779	762
822 m†		840	
843 s*	843		857
950 ms†		946	951
958 ms*	956		
976 w†			975
992 m*	1004		
~1000 (?)†		993	
1010 w†		1009	
1022 w*	1022		1021
1060 m†		1084	1073
1073 mw*	1089		
1108 w*	1109		
1118 m†		1121	
1140 vw			1138
1157 s‡	1155	1147	1155
1238 vs‡	1232	1231	1235
1265vw		1264	
1286 s‡	1263		1267
1297 s‡	1291		1296
1320 mw†		1320	
1347 vw		1332	1351
1360 w*	1362	1372	1373
1382 vs‡	1373	1380	1383
	1390		
1447 vs‡	1450	1452	1451
	⎧1460	1460	1460
1460 vs‡	⎪1460	1460	1460
	⎪1461	1462	1461
	⎩1465	1464	1464

* Relative intensity increases on cooling.
† Relative intensity decreases on cooling.
‡ Remains strong at low temperature.

TESTS OF THE FORCE FIELD

The results on 2-chloropropane and 2-chlorobutane encouraged us to think that a satisfactory force field had been derived for secondary chlorides. In order to evaluate this conclusion we applied the force field to the calculation of the frequencies of other chlorinated hydrocarbons, containing either a single chlorine atom or two

chlorine atoms in a 2,4 position. Particular attention was given to molecules whose conformation was unambiguous, and to the ability of the force field to predict the carbon–chlorine stretching frequencies.

1. *Monochlorohydrocarbons*

Application of the force field to linear monochlorohydrocarbons of known structure gave satisfactory results. Thus, for the S_{HH} conformation of 3-chloropentane, whose spectrum can be identified since only this isomer is present in the solid state [5], the calculated carbon–chlorine stretching frequency was 610 cm^{-1} while the observed band is found at 606 cm^{-1} [5]. Good agreement is also obtained for the other modes of this molecule. (Detailed assignments for 3-chloropentane will be discussed in a subsequent paper.)

In order to examine the predictive ability of the force field for conformations other than those from which it was derived, the normal modes of the two conformational isomers of monochloro*cyclo*hexane were calculated. In the axial form of this molecule the chlorine conformation is $S_{H'H'}$, whereas in the equatorial form the conformation is S_{CC}. Experimental studies of the spectrum of this molecule [4] permit the isolation of the equatorial form in the solid state and, by difference from the liquid state spectrum, the identification of some of the bands of the axial form. A comparison between observed and calculated frequencies is given in Table 7, which incorporates the above information as well as some intensity and Raman polarization data in order to make assignments. It will be seen that, other than in the 1300–1500 cm^{-1} region where much overlap occurs and detailed comparisons are therefore difficult, the observed bands are well accounted for. This is not only true for the carbon–chlorine stretching vibrations, but selective agreement is evident elsewhere in the spectrum. For the suggested assignments the average deviation in the range of 500–1300 cm^{-1} is about 0.8 per cent for both conformations. We might note incidentally that although the carbon–chlorine stretching mode of the axial form was assigned to the band at 683 cm^{-1} [4], the 557 cm^{-1} band is more justifiably given this designation on the basis of the potential energy distributions in these modes. The larger intensity of the latter band supports this conclusion. In fact, of course, the calculations indicate that the $S_{H'H'}$ conformation should really be considered to have two characteristic "carbon–chlorine stretching frequencies" associated with it, in distinction to the single frequencies associated with the other conformations.

2. *2,4-dichlorohydrocarbons*

The force field was also applied to hydrocarbons with chlorine atoms in a 2,4 position, i.e., separated by a CH$_2$ group. The aim here was to see if the interactions which lead to frequency splittings would be satisfactorily reproduced. The molecules chosen for this test were the *dl* and *meso* 2,4-dichloropentanes, since the liquid form of each contains essentially one stable conformation [15, 16].

The *dl* form of 2,4-dichloropentane is shown in Fig. 5, with its internal coordinates. This is the most stable conformation in the liquid [16]. It is designated TT, for the *trans* arrangement of carbon–carbon bonds across both $R2$ and $R3$. The symmetry coordinates for this structure, which has C_2 symmetry, are given in Table 8.

[16] T. SHIMANOUCHI and M. TASUMI, *Spectrochim. Acta* **17**, 755 (1961).

Table 7. Observed and calculated frequencies of monochloro*cyclo*hexane, with potential energy distributions and possible assignments

ν(cm⁻¹)	I	Equatorial	Axial	Potential energy distribution‡
			86 A'	CCC(49), ϕ(15), Ξ(13)
		99 A'		Ξ(25), CCC(24), W(21)
			145 A''	CCC(67), Ξ(15)
199*	0	175 A''		CCC(87)
			234 A'	CCC(49), Ξ(21)
		254 A''		Ξ(78), CCC(11)
258*	1	255 A'		CCC(55)
298	2		296 A''	Ξ(64), CCC(21)
339*⎫	10		331 A'	W(35), Ξ(21), CCC(11), r(11)
340 ⎭	6	357 A'		X(22), Ξ(20), CCC(15)
382*	0	403 A'		W(40), ϕ(18), r(16), CCC(11)
434	2	447 A''		CCC(76)
			465 A''	CCC(73)
471	3		477 A'	CCC(60), r(11)
512	5	511 A'		CCC(42), r(32)
557	7		566 A'	X(60)
683 (a)	5		684 A'	X(36), r(12), CCC(11), R(11)
728 (e)	9	736 A'		X(53)
790 (e)	1	779 A''		r(75), R(11)
773 (a)	0		780 A''	r(75), R(12)
		804 A'		R(60), r(13)
806 (a)	3		804 A'	R(85)
816 (e)	8	833 A'		r(39), R(31)
858 (a)	5		843 A'	r(56)
867 (a)	4		870 A''	R(60)
852 (e)	2	873 A''		r(66)
888 (a, e)⎫	8		882 A'	R(72)
888 (a, e)⎭	8	900 A'		R(48), t(23)
920 (a, e)⎫	1		920 A''	r(53)
920 (a, e)⎭	1	924 A''		R(51)
993 (a, e)⎫	8	988 A'		CCC(19), r(30)
993 (a. e)⎭	8		994 A'	r(38), CCC(31)
1014 (a)	4	340 + 683 = 1023 (?)		
1030 (e)	2	340 + 728 = 1068 (?)		
1050 (e)	0	1057 A'		R(49), ω(13)
			1063 A'	R(51), ω(28)
			1065 A''	R(41), ϕ(14), ω(11)
1074 (e) (dp)	0	1067 A''		t(46), ϕ(18)
1098 (a)	3		1094 A''	t(40), R(17)
1088 (e)	0	1096 A''		R(69), ω(12)
1098 (a)	3		1106 A'	r(41)
~1110 (e)	0	1111 A''		R(32), t(15), ω(14)
1132 (e)	1	1131 A'		θ(22), r(32), R(14)
1148 (a)⎫	2		1156 A''	t(31), ω(26)
1148 (a)⎭	2		1159 A''	R(18), ϕ(16), t(31), ω(12)
1186 (e) (dp)	0	1201 A''		t(25), ω(16), R(15)
1217 (e, a?)	8		1206 A'	θ(43), ϕ(14)
1217 (e, a?)	8	1216 A'		ϕ(29), t(15)
1238 (e)	0	1240 A'		t(66), R(12)
1262 (a)⎫	10		1243 A'	t(69), R(11)
1262 (a)⎭	10		1248 A''	t(66)
1259 (e)	10	1248 A''		t(58), ϕ(11)
1267 (a)	10		1258 A'	t(41), θ(26)
1270 (e)	10	1278 A'		θ(31), ϕ(19), t(28)
1301 (e) (dp?)	0	1284 A''		ω(47), ϕ(15), t(15)
			1314 A''	ϕ(39), t(15), ω(12)
			1320 A''	ω(42), t(11)
		1321 A''		ω(70)
		1326 A'		ω(65)
1325 (a, e) ⎫	1⎫		1331 A'	ω(69), R(13)
1339 (a, e) ⎬	4⎬		1331 A''	ω(67)
1352 (a, e) ⎭	4⎭	1354 A'		ω(53), R(16)
		1358 A''		ω(20), R(19), ϕ(16)
			1367 A'	ω(50), R(20)
			1388 A''	ω(31), R(27), t(14)

Table 7 *(cont.)*

Observed bands		Calculated frequency		
ν(cm^{-1})	I	Equatorial	Axial	Potential energy distribution
		1400 A''		$R(23)$, $\phi(12)$, $\omega(11)$, $t(11)$
		1450 A'		$\delta(97)$
			1451 A'	$\delta(97)$
		1452 A''		$\delta(98)$
1434 (a, e)	1	1453 A'		$\delta(97)$
1450 (a, e)	10		1453 A''	$\delta(92)$
1462 (a, e)	1		1454 A'	$\delta(91)$
		1454 A''		$\delta(98)$
			1455 A''	$\delta(92)$
		1458 A'		$\delta(97)$
			1459 A'	$\delta(97)$

* Raman band.
† Liquid phase frequencies from Ref. [4] (I = intensity).
‡ Coordinates have general physical character similar to those of 2-chlorobutane (see Fig. 4 and Table 4).
(a) = Band present only in axial isomer.
(e) = Band present in equatorial isomer (solid state spectrum).
(a, e) = Bands common to both isomers.
dp = Depolarized Raman band.

Table 8. Symmetry coordinates for *dl* 2,4-dichloropentane

Class *A* coordinates

$R_{A1} = R_1 + R_4$
$R_{A2} = R_2 + R_3$
$X_A = X_1 + X_2$
$U_A = \alpha_{12} + \alpha_{13} + \alpha_{23} - \beta_1 - \beta_2 - \beta_3 + \alpha_{89} + \alpha_{80} + \alpha_{90} - \beta_8 - \beta_9 - \beta_{10}$
$A_{A1} = 2\alpha_{12} - \alpha_{13} - \alpha_{23} + 2\alpha_{89} - \alpha_{80} - \alpha_{90}$
$A_{A2} = \alpha_{13} - \alpha_{23} + \alpha_{90} - \alpha_{80}$
$B_{A1} = 2\beta_1 - \beta_2 - \beta_3 + 2\beta_9 - \beta_8 - \beta_{10}$
$B_{A2} = \beta_2 - \beta_3 + \beta_8 - \beta_{10}$
$H_{\pi A} = \phi_1 - \phi_2 - \phi_3 + \phi_4$
$X_{\pi A} = \Xi_1 - \Xi_2 - \Xi_3 + \Xi_4$
$W_{A1} = 2\omega_2 - \Xi_1 - \Xi_2 + 2\omega_4 - \Xi_3 - \Xi_4$
$W_{A2} = \omega_2 - \theta_1 - \phi_1 - \phi_3 + \Xi_1 + \Xi_2 + \omega_4 - \theta_2 - \phi_3 - \phi_4 + \Xi_3 + \Xi_4$
$H_{\sigma A} = 2\theta_1 - \phi_1 - \phi_2 + 2\theta_2 - \phi_3 - \phi_4$
$CCC = 5\omega_3 - \delta_3 - \gamma_1 - \gamma_2 - \gamma_3 - \gamma_4$
$\delta = 4\delta_3 - \gamma_1 - \gamma_2 - \gamma_3 - \gamma_4$
$t = \gamma_1 - \gamma_2 - \gamma_3 + \gamma_4$

Class *B* coordinates

$R_{B1} = R_1 - R_4$
$R_{B2} = R_2 - R_3$
$X_B = X_1 - X_2$
$U_B = \alpha_{12} + \alpha_{13} + \alpha_{23} - \beta_1 - \beta_2 - \beta_3 - \alpha_{89} - \alpha_{80} - \alpha_{90} + \beta_8 + \beta_9 + \beta_{10}$
$A_{B1} = 2\alpha_{12} - \alpha_{13} - \alpha_{23} - 2\alpha_{89} + \alpha_{80} + \alpha_{90}$
$A_{B2} = \alpha_{13} - \alpha_{23} - \alpha_{90} + \alpha_{80}$
$B_{B1} = 2\beta_1 - \beta_2 - \beta_3 - 2\beta_9 + \beta_8 + \beta_{10}$
$B_{B2} = \beta_2 - \beta_3 - \beta_8 + \beta_{10}$
$H_{\pi B} = \phi_1 - \phi_2 + \phi_3 - \phi_4$
$X_{\pi B} = \Xi_1 - \Xi_2 + \Xi_3 - \Xi_4$
$W_{B1} = 2\omega_2 - \Xi_1 - \Xi_2 - 2\omega_4 + \Xi_3 + \Xi_4$
$W_{B2} = \omega_2 - \theta_1 - \phi_1 - \phi_2 + \Xi_1 + \Xi_2 - \omega_4 + \theta_2 + \phi_3 + \phi_4 - \Xi_3 - \Xi_4$
$H_{\sigma B} = 2\theta_1 - \phi_1 - \phi_2 - 2\theta_2 + \phi_3 + \phi_4$
$\omega = \gamma_1 + \gamma_2 - \gamma_3 - \gamma_4$
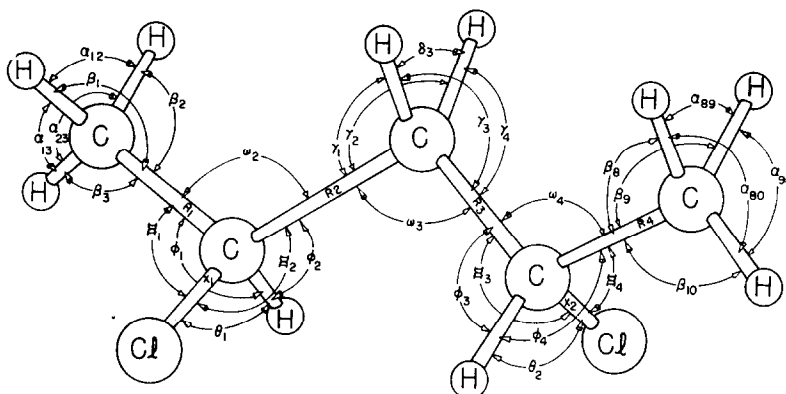$r = \gamma_1 - \gamma_2 + \gamma_3 - \gamma_4$

Fig. 5. Molecule of *dl* 2,4-dichloropentane (*TT* conformation) with
internal coordinates.

Table 9. Observed and calculated frequencies and potential energy distributions of *TT*
conformation of *dl* 2,4-dichloropentane

Observed frequency (cm^{-1})	Calculated	
	Frequency (cm^{-1})	Potential energy distribution
	122 A	$CCC(39) - X_{\pi A}(32) - W_{A1}(21)$
255 vw	266 A	$W_{A1}(51) - X_{\pi A}(30)$
	283 B	$X_{\pi B}(39) + W_{B1}(37)$
343 m	325 B	$W_{B1}(35) - X_{\pi B}(30) - W_{B2}(17)$
368 m	354 A	$W_{A2}(67) - W_{A1}(14)$
	446 B	$W_{B2}(55) + W_{B1}(16)$
460 mw	466 A	$CCC(30) + X_{\pi A}(26) + R_{A1}(18)$
606 s	605 B	$X_B(78)$
627 s	624 A	$X_A(74)$
877 ms	$\begin{cases} 872\ A \\ 877\ B \end{cases}$	$R_{A2}(33) - B_{A1}(27) - B_{A2}(11)$ $r(48) - B_{B1}(22) + H_{\pi B}(16)$
938 s	943 B	$R_{B1}(32) + R_{B2}(26) - B_{B1}(19)$
978 m	994 B	$B_{A2}(31) - B_{A1}(20) + R_{A1}(13) + H_{\pi A}(11)$
1012 s	1017 B	$B_{B2}(45) + R_{B1}(32)$
1067 m	1086 B	$B_{B1}(27) + R_{B1}(23) + H_{\sigma B}(14)$
1100 vw	1110 A	$R_{A1}(47) + B_{A1}(18)$
1125 s	1121 A	$B_{A2}(27) + R_{A2}(26) - H_{\pi A}(13)$
1132 s?	1145 B	$R_{B2}(44) + B_{B2}(14) - H_{\pi B}(14)$
1191 m	1176 A	$H_{\sigma A}(43) + t(35)$
1222 vw	1239 B	$H_{\pi B}(38) + \omega(38)$
1257 s	1255 B	$H_{\sigma B}(81)$
1288 s	1285 A	$H_{\sigma A}(43) - t(22) - H_{\pi A}(12)$
1325 mw	1327 A	$H_{\pi A}(49) - t(19)$
1379 s	$\begin{cases} 1373\ B \\ 1374\ A \end{cases}$	$U_B(92)$ $U_A(86)$
1415 ms	1405 B	$\omega(36) - R_{B2}(26) - H_{\pi B}(22)$
1443 s ⎱ 1450 m⎰	$\begin{cases} 1452\ A \\ 1461\ A \\ 1461\ A \\ 1461\ B \\ 1464\ B \end{cases}$	$\delta(95)$ $A_{A2}(84)$ $A_{A1}(83)$ $A_{B2}(84)$ $A_{B1}(78)$

The TT conformation of *meso* 2,4-dichloropentane has C_s symmetry, so that the coordinates of Table 8 can be used in this case with the A' coordinates corresponding to the A and the A'' coordinates to the B, except that the r and t coordinates exchange places. The stable conformation of *meso* 2,4-dichloropentane is the TG form [16] ($G = gauche$), and our calculations were done for this structure.

The comparisons between observed [15, 16] and calculated frequencies for these

Table 10. Observed and calculated frequencies and potential energy distributions of TG conformation of *meso* 2,4-dichloropentane

Observed frequency (cm^{-1})	Calculated	
	Frequency (cm^{-1})	Potential energy distribution
	125	$CCC(33) - W_{B1}(31) - X_{\pi B}(11)$
	223	$X_{\pi A}(70) - R_{A2}(12)$
315 w	305	$W_{A1}(64) + X_{\pi B}(11)$
345 m	325	$X_{\pi B}(33) - W_{B1}(26) + W_{B2}(14)$
392 w	385	$W_{A2}(58) + X_{\pi A}(11)$
410 ms	419	$W_{B2}(29) - X_{\pi B}(16) - CCC(12)$
460 w	449	$W_{B2}(35) + W_{B1}(15)$
611 vs	614	$X_A(52) + X_B(23)$
680 vs	675	$X_B(40) - X_A(21)$
855 s	855	$r(48) + H_{\pi B}(11)$
882 m	889	$B_{A1}(27) - R_{A2}(24)$
926 s	922	$B_{B1}(28) - R_{B1}(23) - R_{B2}(21)$
980 ms	999	$B_{B2}(20) - B_{A1}(16) + R_{B1}(12) + B_{A2}(12)$
1006 s	1023	$B_{A2}(29) + R_{A1}(26) - B_{B2}(14)$
1058 s	1070	$R_{A1}(19) + B_{B2}(15) + B_{A1}(13)$
1089 mw	1104	$R_{B1}(24) + B_{B1}(15)$
1130 vs	$\begin{cases}1137\\1147\end{cases}$	$R_{A2}(28) + B_{A2}(11) + R_{B1}(11)$ $R_{B2}(39) + B_{B2}(16) - H_{\pi B}(13)$
1199 m	1186	$H_{\sigma A}(34) + t(33)$
1237 s	1232	$H_{\sigma B}(30) + \omega(27) + H_{\pi B}(13)$
1272 s	1265	$H_{\sigma B}(51) - \omega(14)$
1289 m	1276	$H_{\sigma A}(49)$
1337 mw	1332	$H_{\pi A}(41) - t(27)$
1378 vs	$\begin{cases}1372\\1374\end{cases}$	$U_B(84)$ $U_A(77)$
1415 vw	1390	$\omega(28) - H_{\pi B}(27) - R_{B2}(24)$
1427 w 1439 s 1453 s	$\begin{cases}1451\\1461\\1461\\1462\\1463\end{cases}$	$\delta(91)$ $A_{B2}(75)$ $A_{A2}(88)$ $A_{A1}(79)$ $A_{B1}(78)$

two structures are given in Tables 9 and 10. For the assignments proposed in these tables the average deviation between observed and calculated frequencies in the range of 600–1400 cm^{-1} is about 0.6 per cent for the *dl* compound and about 0.8 per cent for the *meso* compound. As will be seen, the carbon–chlorine frequencies are predicted quite well.

It may be worth remarking on the interaction splittings of the carbon–chlorine stretching frequencies in the two isomers of the 2,4-dichloropentanes. This splitting may seem large in view of the separation of the two CHCl groups by the intervening CH$_2$ group. However, we must recognize that the so-called carbon–chlorine stretching mode is far from a pure "group frequency". We have calculated the atomic motions corresponding to this mode in the three conformations of 2-chlorobutane, and these are shown schematically in Fig. 6. It will be seen from these figures that the carbon

atom attached to the chlorine and the two carbon atoms on either side of this carbon atom all partake significantly in the motion during this vibration. We should really designate the four-atom group C—C(Cl)—C as the "group" involved in this frequency. It should therefore not be surprising that when two such "groups" are joined together, as they are in 2,4-dichloropentane, the characteristic frequency is significantly affected by their mechanical coupling. Furthermore, this coupling
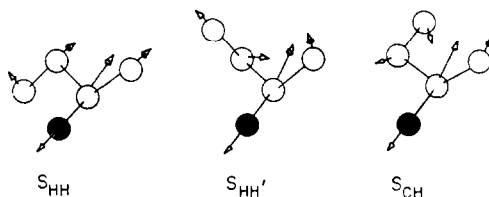

S_{HH} $S_{HH'}$ S_{CH}

Fig. 6. Atomic motions of chlorine and carbon atoms in the carbon–chlorine stretching vibration of the three conformations of 2-chlorobutane.

will be a function of geometry (i.e., conformation) since the detailed atomic motions reflect the location of the next-nearest-neighbor carbon atoms (see Fig. 6).

CONCLUSIONS

We have developed a force field for secondary chlorides based on the extension of existing force fields for hydrocarbons and primary chlorides and based on the premise that the empirically observed conformation dependence of the carbon–chlorine stretching frequencies arises predominantly through changes in the G matrix. The results of testing this force field on several independent molecules lead us to believe that the latter assumption is a valid one. We of course recognize that this force field may not be the last word on the subject: Questions of uniqueness always exist, torsion coordinates must be included, and refinement to tetrahedral geometry may present problems [17]. However, the generally good agreement between observed and calculated frequencies for the molecules considered indicates to us that the proposed force field is a good one, that eventual refinement will probably be minor, and that it is presently useful and reliable in investigating conformational questions involving secondary chlorides not containing 1,2-dichloro structures. We have applied it successfully to the analysis of the spectrum of poly(vinyl chloride), which will be reported on later.

[17] C. G. OPASKAR and S. KRIMM, *Spectrochim. Acta* **21**, 1165 (1965).