A force field for secondary chlorides

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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 monochlorocyclohexane, 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 $S_{HH}$ frequency correlation is obtained from the spectrum of the unique structure of axial monochlorocyclohexane [4], interpreted in terms of our calculations (see below). The $S_{CH}$ frequencies are those observed for 2,2,4,4-tetramethyl-3-chloropentane, 758 cm$^{-1}$ [2], and for equatorial monochlorocyclohexane, 728 cm$^{-1}$ [4], both molecules being cases in which the conformation is unambiguously determinable.

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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 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

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A 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.](image)

[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

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, $r(Cl) = 1.795$ Å, all angles tetrahedral. They were found to be 62.33, 109.3 and 155.2 amu Å$^2$, 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 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

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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 \(B_3\) 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 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.

Table 1. Force constants for secondary chlorides

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
<th>Environment</th>
<th>Coordinates coupled</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_τ</td>
<td>4.699</td>
<td>(C(H_2, H_2, H_3))</td>
<td>(C, H_2)</td>
</tr>
<tr>
<td>F_τ</td>
<td>0.043</td>
<td>(C(H_2, H_2, H_3))</td>
<td>(C, H_2, C_2, H_3)</td>
</tr>
<tr>
<td>K_δ</td>
<td>4.554</td>
<td>(C_1, C_2(H_2))</td>
<td>(C_2, H_2)</td>
</tr>
<tr>
<td>F_δ</td>
<td>0.008</td>
<td>(C_1, C_2(H_2))</td>
<td>(C_2, H_2)</td>
</tr>
<tr>
<td>K_R</td>
<td>4.387</td>
<td>C_1, C_2(H_2)</td>
<td>(C_1, C_2)</td>
</tr>
<tr>
<td>F_R</td>
<td>0.101</td>
<td>C_1, C_2(H_2)</td>
<td>(C_1, C_2, C_3)</td>
</tr>
<tr>
<td>F_{R'y}</td>
<td>0.328</td>
<td>C_1, C_2(H)</td>
<td>(C_1, C_2, C_3)</td>
</tr>
<tr>
<td>F_{R'y'}</td>
<td>0.079</td>
<td>C_1, C_2(H)</td>
<td>(C_1, C_2, C_3)</td>
</tr>
<tr>
<td>F_{R'2o}</td>
<td>0.417</td>
<td>C_1, C_2(H)</td>
<td>(C_1, C_2, C_3)</td>
</tr>
<tr>
<td>H_α</td>
<td>0.540</td>
<td>(C(H_2, H_2, H_3))</td>
<td>(H_2, C, H_3)</td>
</tr>
<tr>
<td>H_δ</td>
<td>0.550</td>
<td>(C(H_2, H_2, H_3))</td>
<td>(H_2, C, H_3)</td>
</tr>
<tr>
<td>H_θ</td>
<td>0.045</td>
<td>(C(H_2, H_2, H_3))</td>
<td>(H_2, C, H_3)</td>
</tr>
<tr>
<td>F_α</td>
<td>-0.112</td>
<td>(C(H_2, H_2, H_3))</td>
<td>(C_2, C_4, H_4)</td>
</tr>
<tr>
<td>H_γ</td>
<td>0.656</td>
<td>(C(H_2, H_2, H_3))</td>
<td>(C_2, C_4, H_4)</td>
</tr>
<tr>
<td>F_γ</td>
<td>-0.021</td>
<td>(C(H_2, H_2, H_3))</td>
<td>(C_2, C_4, H_4)</td>
</tr>
<tr>
<td>F_γ'</td>
<td>0.013</td>
<td>(C(H_2, H_2, H_3))</td>
<td>(C_2, C_4, H_4)</td>
</tr>
<tr>
<td>H_∞</td>
<td>1.130</td>
<td>(C(H_2, H_2, H_3))</td>
<td>(C_2, C_4, C_6)</td>
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<tr>
<td>F_{Xα}</td>
<td>-0.031</td>
<td>(C(H_2, H_2, H_3))</td>
<td>(C_2, C_4, C_6)</td>
</tr>
<tr>
<td>f_{α'}</td>
<td>-0.011</td>
<td>(C(H_2, H_2, H_3))</td>
<td>(C_2, C_4, C_6)</td>
</tr>
<tr>
<td>f_{α'}</td>
<td>0.049</td>
<td>(C(H_2, H_2, H_3))</td>
<td>(C_2, C_4, C_6)</td>
</tr>
<tr>
<td>f_{α'}</td>
<td>-0.052</td>
<td>(C(H_2, H_2, H_3))</td>
<td>(C_2, C_4, C_6)</td>
</tr>
<tr>
<td>f_{γ}</td>
<td>0.137</td>
<td>(H_2, C, C_2)</td>
<td>(C_2, C_4, C_6)</td>
</tr>
<tr>
<td>f_{γ'}</td>
<td>-0.005</td>
<td>(H_2, C, C_2)</td>
<td>(C_2, C_4, C_6)</td>
</tr>
<tr>
<td>*K_X</td>
<td>3.338</td>
<td>C-X (X = chlorine)</td>
<td>(C, X)</td>
</tr>
<tr>
<td>*F_X</td>
<td>4.623</td>
<td>C_1(H_2, X)</td>
<td>(C_1, C_2)</td>
</tr>
<tr>
<td>F_{Xα}</td>
<td>0.730</td>
<td>C_1(H_2, X)</td>
<td>(C_1, C_2, C_3)</td>
</tr>
<tr>
<td>*F_{Xα}</td>
<td>-0.220</td>
<td>C_1(H_2, X)</td>
<td>(C_1, C_2, C_3)</td>
</tr>
<tr>
<td>f_{Xα}</td>
<td>-0.031</td>
<td>C_1(H_2, X)</td>
<td>(C_1, C_2, C_3)</td>
</tr>
<tr>
<td>K_X</td>
<td>4.846</td>
<td>C(H_2, X)</td>
<td>(C, H)</td>
</tr>
<tr>
<td>H_η</td>
<td>0.982</td>
<td>C_1(H_2, X)</td>
<td>(C_1, C_2)</td>
</tr>
<tr>
<td>F_{ηα}</td>
<td>0.076</td>
<td>C_1(H_2, X)</td>
<td>(C_1, C_2, C_3)</td>
</tr>
<tr>
<td>*F_{ηα}</td>
<td>0.300</td>
<td>C_1(H_2, X)</td>
<td>(C_1, C_2, C_3)</td>
</tr>
<tr>
<td>F_{η2}</td>
<td>0.550</td>
<td>C_1(H_2, X)</td>
<td>(C_1, C_2, C_3)</td>
</tr>
<tr>
<td>F_{η2}</td>
<td>0.060</td>
<td>C_1(H_2, X)</td>
<td>(C_1, C_2, C_3)</td>
</tr>
<tr>
<td>*H_δ</td>
<td>0.633</td>
<td>C_1(H_2, X)</td>
<td>(C_1, C_2)</td>
</tr>
<tr>
<td>F_{ηθ}</td>
<td>0.089</td>
<td>C_1(H_2, X)</td>
<td>(C_1, C_2, C_3)</td>
</tr>
<tr>
<td>F_{ηθ}</td>
<td>0.333</td>
<td>C_1(H_2, X)</td>
<td>(C_1, C_2, C_3)</td>
</tr>
<tr>
<td>f_{ηα}</td>
<td>-0.037</td>
<td>C_1(H_2, X)</td>
<td>(C_1, C_2, C_3)</td>
</tr>
<tr>
<td>f_{ηα}</td>
<td>0.070</td>
<td>C_1(H_2, X)</td>
<td>(C_1, C_2, C_3)</td>
</tr>
<tr>
<td>f_{ηα}</td>
<td>0.041</td>
<td>C_1(H_2, X)</td>
<td>(C_1, C_2, C_3)</td>
</tr>
<tr>
<td>f_{η2}</td>
<td>-0.024</td>
<td>C_1(H_2, X)</td>
<td>(C_1, C_2, C_3)</td>
</tr>
</tbody>
</table>

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

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—$K_r$

$$\text{Environment: } \text{C}(H_1, H_2, H_3); \text{ Coordinates coupled: } (C, H_1)$$

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

$$\text{Environment: } H_1-C_1-C_2-H_2; \text{ Coordinates coupled: } (H_1, C_2, C_3) (C_1, C_2, H_2)$$

(3) Interaction between two CC bonds when the middle carbon atom is connected to a chlorine atom—$F^X_R$

$$\text{Environment: } C_1-C_2(X)-C_3; \text{ Coordinates coupled: } (C_1, C_2) (C_2, C_3)$$

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] ($\omega$ 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 $K_{CX}$, $F_{X\phi}$, $F_{X\phi}$, $F_{X\omega}$ 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 $H_{\phi}$ 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 $F^X_R$ 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

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 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 conformations 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

Table 2. Symmetry coordinates for 2-chloropropane

<table>
<thead>
<tr>
<th>Class A' symmetry coordinates (symmetric with respect to the median plane)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1 = 2\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4 + \alpha_5 - \alpha_6$</td>
</tr>
<tr>
<td>$B_1 = 2\beta_3 - \beta_1 - \beta_2 + 2\beta_4 - \beta_5 - \beta_6$</td>
</tr>
<tr>
<td>$U_1 = \alpha_1 + \alpha_2 - \beta_1 - \beta_2 + \beta_4 + \alpha_5 + \alpha_6 - \beta_4 - \beta_5 - \beta_6$</td>
</tr>
<tr>
<td>$X_r = \text{C-Cl stretch}$</td>
</tr>
<tr>
<td>$H_\phi = 2\theta - \phi_1 - \phi_2$</td>
</tr>
<tr>
<td>$W' = W - \theta - \phi_1 + \phi_2 + \Xi_1 + \Xi_2$</td>
</tr>
<tr>
<td>$W_\alpha = W + \theta + \phi_1 + \phi_2 + \Xi_1 + \Xi_2$</td>
</tr>
<tr>
<td>$R_1 = R_1 + R_3$</td>
</tr>
<tr>
<td>$W_\beta = 2W - \Xi_1 - \Xi_2$</td>
</tr>
<tr>
<td>$A_2 = \alpha_1 - \alpha_2 + \alpha_3 - \alpha_6$</td>
</tr>
<tr>
<td>$B_2 = \beta_1 - \beta_2 + \beta_3 - \beta_4$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Class A&quot; symmetry coordinates (antisymmetric with respect to the median plane)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_3 = 2\alpha_1 - \alpha_2 - \alpha_3 - 2\alpha_4 + \alpha_5 + \alpha_6$</td>
</tr>
<tr>
<td>$B_3 = 2\beta_3 - \beta_1 - \beta_2 - 2\beta_4 + \beta_5 + \beta_6$</td>
</tr>
<tr>
<td>$U_2 = \alpha_1 + \alpha_2 - \beta_1 + \beta_2 - \beta_4 - \alpha_5 - \alpha_6 + \beta_4 + \beta_5 + \beta_6$</td>
</tr>
<tr>
<td>$X_r = \Xi_1 - \Xi_2$</td>
</tr>
<tr>
<td>$H_\phi = \phi_1 - \phi_2$</td>
</tr>
<tr>
<td>$R_2 = R_1 - R_3$</td>
</tr>
<tr>
<td>$A_4 = \alpha_1 - \alpha_2 - \alpha_3 + \alpha_6$</td>
</tr>
<tr>
<td>$B_4 = \beta_1 - \beta_2 - \beta_3 + \beta_4$</td>
</tr>
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</table>

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

<table>
<thead>
<tr>
<th>Observed</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency</td>
<td>Symmetry</td>
</tr>
<tr>
<td>324 w</td>
<td>A</td>
</tr>
<tr>
<td>335 m</td>
<td>S</td>
</tr>
<tr>
<td>423 m</td>
<td>S</td>
</tr>
<tr>
<td>611 vs</td>
<td>S</td>
</tr>
<tr>
<td>677 vW</td>
<td></td>
</tr>
<tr>
<td>760 w</td>
<td></td>
</tr>
<tr>
<td>884 s</td>
<td>S</td>
</tr>
<tr>
<td>933 mw</td>
<td>A</td>
</tr>
<tr>
<td>945 vW</td>
<td></td>
</tr>
<tr>
<td>965 t</td>
<td></td>
</tr>
<tr>
<td>1025 ch</td>
<td></td>
</tr>
<tr>
<td>1061 vs</td>
<td>S</td>
</tr>
<tr>
<td>1129 m</td>
<td>A</td>
</tr>
<tr>
<td>1160 s</td>
<td>S</td>
</tr>
<tr>
<td>1223 vW</td>
<td></td>
</tr>
<tr>
<td>1260 vs</td>
<td>S</td>
</tr>
<tr>
<td>1308 w</td>
<td>S</td>
</tr>
<tr>
<td>1229 w</td>
<td>A</td>
</tr>
<tr>
<td>1374 s</td>
<td>A</td>
</tr>
<tr>
<td>1385 s</td>
<td>S</td>
</tr>
<tr>
<td>1462</td>
<td></td>
</tr>
<tr>
<td>1464</td>
<td></td>
</tr>
<tr>
<td>1467</td>
<td></td>
</tr>
<tr>
<td>1468</td>
<td></td>
</tr>
</tbody>
</table>

* 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

Table 4. Coordinates for 2-chlorobutane

<table>
<thead>
<tr>
<th>( R_1 )</th>
<th>( R_2 )</th>
<th>( R_3 )</th>
<th>( R_4 )</th>
<th>( X )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( U_1 = \alpha_{12} + \alpha_{18} + \alpha_{19} - \beta_1 - \beta_2 - \beta_3 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A_{12} = 2\alpha_{12} - \alpha_{18} - \alpha_{19} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A_{18} = \alpha_{18} - \alpha_{19} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( B_{12} = 2\beta_1 - \beta_2 - \beta_3 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( B_{18} = \beta_2 - \beta_3 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \delta = 4\delta_3 - \gamma_1 - \gamma_2 - \gamma_3 - \gamma_4 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{CCC} = 5\omega_3 - \delta_3 - \gamma_1 - \gamma_2 - \gamma_3 - \gamma_4 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \iota = \gamma_1 - \gamma_3 - \gamma_4 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \tau = \gamma_1 - \gamma_3 - \gamma_4 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \omega = \gamma_1 + \gamma_3 - \gamma_4 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( H_\sigma = 2\theta - \delta_1 - \phi_3 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( W_4 = \omega_3 - \theta - \phi_3 + \varepsilon_1 + \varepsilon_2 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( W_5 = 2\omega_3 - \varepsilon_1 - \varepsilon_2 )</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>( X_\sigma = \varepsilon_1 - \varepsilon_2 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( H_\pi = \phi_1 - \phi_3 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( U_\pi = \phi_1 + \alpha_{98} + \alpha_{99} - \beta_7 - \beta_8 - \beta_9 )</td>
<td></td>
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<tr>
<td>( A_{1p} = 2\phi_8 - \alpha_{98} - \alpha_{99} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A_{3p} = \alpha_{98} - \alpha_{99} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( B_{1p} = 2\beta_7 - \beta_8 - \beta_9 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( B_{3p} = \beta_8 - \beta_9 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

(a) \( S_{HH} \) conformation

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Potential energy distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>213</td>
<td>( X_\pi(37) + \text{CCC}(38) - W_4(23) )</td>
</tr>
<tr>
<td>313</td>
<td>( W_5(45) + X_\sigma(23) )</td>
</tr>
<tr>
<td>376</td>
<td>( W_5(65) - \text{CCC}(12) )</td>
</tr>
<tr>
<td>454</td>
<td>( \text{CCC}(36) + W_1(12) )</td>
</tr>
<tr>
<td>611</td>
<td>( X(70) )</td>
</tr>
<tr>
<td>776</td>
<td>( r(44) + B_1(18) - B_4(14) )</td>
</tr>
<tr>
<td>842</td>
<td>( R_1(32) - B_4(18) )</td>
</tr>
<tr>
<td>950</td>
<td>( B_4(24) - B_1(20) + H_\sigma(19) )</td>
</tr>
<tr>
<td>1004</td>
<td>( B_{1p}(35) - B_4(18) + R_4(15) )</td>
</tr>
<tr>
<td>1022</td>
<td>( R_1(63) - R_4(15) )</td>
</tr>
<tr>
<td>1089</td>
<td>( D_2(27) + r(14) )</td>
</tr>
<tr>
<td>1109</td>
<td>( R_5(43) - B_4(12) )</td>
</tr>
<tr>
<td>1155</td>
<td>( R_1(31) + B_4(13) )</td>
</tr>
<tr>
<td>1232</td>
<td>( H_\sigma(43) + t(21) - B_1(14) )</td>
</tr>
<tr>
<td>1268</td>
<td>( H_\sigma(33) + \omega(29) + H_\sigma(13) )</td>
</tr>
<tr>
<td>1291</td>
<td>( t(48) - H_\sigma(29) )</td>
</tr>
<tr>
<td>1362</td>
<td>( U_1(65) - H_\sigma(11) )</td>
</tr>
<tr>
<td>1373</td>
<td>( U_1(87) )</td>
</tr>
<tr>
<td>1390</td>
<td>( \omega(30) - U_1(25) - H_\sigma(11) )</td>
</tr>
<tr>
<td>1450</td>
<td>( \bar{\delta}(90) )</td>
</tr>
<tr>
<td>1460</td>
<td>( A_{1p}(42) - A_{3p}(23) + A_{11}(22) )</td>
</tr>
<tr>
<td>1460</td>
<td>( A_{1p}(91) )</td>
</tr>
<tr>
<td>1461</td>
<td>( A_{1p}(44) + A_{1p}(38) )</td>
</tr>
<tr>
<td>1485</td>
<td>( A_{1p}(63) + A_{1p}(20) )</td>
</tr>
</tbody>
</table>
Table 5 (cont.)

(b) \(S_{HH'}\) conformation

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Potential energy distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>208</td>
<td>(\text{CCC}(37) + W_o(34) + X_w(15))</td>
</tr>
<tr>
<td>317</td>
<td>(X_w(68) - W_o(15))</td>
</tr>
<tr>
<td>328</td>
<td>(W_o(76))</td>
</tr>
<tr>
<td>340</td>
<td>(\text{CCC}(27) - X(26) - W_o(21))</td>
</tr>
<tr>
<td>631</td>
<td>(X(59))</td>
</tr>
<tr>
<td>779</td>
<td>(r(40) + B_{11}(29))</td>
</tr>
<tr>
<td>840</td>
<td>(R_o(44) + R_o(18) + R_o(11) - B_{11}(11))</td>
</tr>
<tr>
<td>946</td>
<td>(R_o(28) - R_o(22) + B_{11}(17) + H_w(11))</td>
</tr>
<tr>
<td>953</td>
<td>(B_{11}(19) + B_{11}(10) + R_o(17))</td>
</tr>
<tr>
<td>1039</td>
<td>(B_{11}(37) + \omega(16) - B_{11}(13) - B_{11}(11))</td>
</tr>
<tr>
<td>1084</td>
<td>(B_{11}(22) + R_o(16))</td>
</tr>
<tr>
<td>1121</td>
<td>(R_o(15) + R_o(13) - R_o(13))</td>
</tr>
<tr>
<td>1147</td>
<td>(R_o(30) - r(13))</td>
</tr>
<tr>
<td>1231</td>
<td>(H_{11}(60))</td>
</tr>
<tr>
<td>1264</td>
<td>(t(64))</td>
</tr>
<tr>
<td>1320</td>
<td>(H_w(50) + t(11))</td>
</tr>
<tr>
<td>1332</td>
<td>(\omega(41) + U_{11}(24) + R_o(12))</td>
</tr>
<tr>
<td>1372</td>
<td>(U_{11}(63))</td>
</tr>
<tr>
<td>1386</td>
<td>(U_{11}(62) - \omega(16))</td>
</tr>
<tr>
<td>1452</td>
<td>(\delta(84))</td>
</tr>
<tr>
<td>1460</td>
<td>(A_{11}(73) + A_{11}(14))</td>
</tr>
<tr>
<td>1460</td>
<td>(A_{11}(11))</td>
</tr>
<tr>
<td>1462</td>
<td>(A_{11}(60) + \delta(11))</td>
</tr>
<tr>
<td>1464</td>
<td>(A_{11}(62) + A_{11}(13))</td>
</tr>
</tbody>
</table>

(c) \(S_{OH}\) conformation

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Potential energy distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>218</td>
<td>(W_o(40) + \text{CCC}(28))</td>
</tr>
<tr>
<td>225</td>
<td>(X_w(70))</td>
</tr>
<tr>
<td>330</td>
<td>(W_o(54) + \text{CCC}(14))</td>
</tr>
<tr>
<td>418</td>
<td>(W_o(27) + W_o(24) - \text{CCC}(18))</td>
</tr>
<tr>
<td>670</td>
<td>(X(92))</td>
</tr>
<tr>
<td>762</td>
<td>(r(55) + B_{11}(27))</td>
</tr>
<tr>
<td>857</td>
<td>(R_o(35) - B_{11}(17) - B_{11}(16) + R_o(13))</td>
</tr>
<tr>
<td>951</td>
<td>(B_{11}(23) - B_{11}(21) - H_w(14))</td>
</tr>
<tr>
<td>975</td>
<td>(R_o(25) + B_{11}(22) + t(19))</td>
</tr>
<tr>
<td>1021</td>
<td>(B_{11}(61) + B_{11}(25))</td>
</tr>
<tr>
<td>1073</td>
<td>(B_{11}(30) - R_o(17) - B_{11}(13))</td>
</tr>
<tr>
<td>1138</td>
<td>(R_o(28) - B_{11}(13))</td>
</tr>
<tr>
<td>1155</td>
<td>(R_o(29))</td>
</tr>
<tr>
<td>1235</td>
<td>(H_o(30) - t(20) - H_o(11))</td>
</tr>
<tr>
<td>1287</td>
<td>(B_o(48) + t(21))</td>
</tr>
<tr>
<td>1296</td>
<td>(\omega(42) - t(19))</td>
</tr>
<tr>
<td>1351</td>
<td>(U_{11}(27) - H_o(23) + U_{11}(12))</td>
</tr>
<tr>
<td>1373</td>
<td>(U_{11}(76) - U_{11}(13))</td>
</tr>
<tr>
<td>1383</td>
<td>(U_{11}(46) - \omega(16))</td>
</tr>
<tr>
<td>1451</td>
<td>(\delta(88))</td>
</tr>
<tr>
<td>1460</td>
<td>(A_{11}(39) + A_{11}(32) - A_{11}(18))</td>
</tr>
<tr>
<td>1460</td>
<td>(A_{11}(90))</td>
</tr>
<tr>
<td>1461</td>
<td>(A_{11}(55) - A_{11}(17))</td>
</tr>
<tr>
<td>1464</td>
<td>(A_{11}(54) + A_{11}(30))</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Observed liquid frequency (cm$^{-1}$)</th>
<th>$S_{HH}$</th>
<th>$S_{HH'}$</th>
<th>$S_{CH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sim 290$ w</td>
<td>313</td>
<td>317</td>
<td>295</td>
</tr>
<tr>
<td>324 m</td>
<td>325 sh</td>
<td>328</td>
<td></td>
</tr>
<tr>
<td>374 m†</td>
<td>376</td>
<td></td>
<td>390</td>
</tr>
<tr>
<td>386 m*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>418 mw†</td>
<td>454</td>
<td></td>
<td>418</td>
</tr>
<tr>
<td>450 mw*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>522 mw†</td>
<td>611</td>
<td></td>
<td>540</td>
</tr>
<tr>
<td>627 mw†</td>
<td></td>
<td></td>
<td>631</td>
</tr>
<tr>
<td>670 mw†</td>
<td>776</td>
<td></td>
<td>676</td>
</tr>
<tr>
<td>790 mw*</td>
<td>779</td>
<td></td>
<td>752</td>
</tr>
<tr>
<td>822 mw†</td>
<td>840</td>
<td></td>
<td>857</td>
</tr>
<tr>
<td>845 mw*</td>
<td>843</td>
<td></td>
<td>951</td>
</tr>
<tr>
<td>950 mw*</td>
<td>956</td>
<td></td>
<td>975</td>
</tr>
<tr>
<td>970 mw†</td>
<td>1004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sim 1000$ (1)†</td>
<td></td>
<td>993</td>
<td></td>
</tr>
<tr>
<td>1010 mw†</td>
<td></td>
<td>1009</td>
<td></td>
</tr>
<tr>
<td>1022 mw*</td>
<td>1022</td>
<td></td>
<td>1021</td>
</tr>
<tr>
<td>1060 mw†</td>
<td>1084</td>
<td></td>
<td>1073</td>
</tr>
<tr>
<td>1073 mw*</td>
<td>1059</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1106 mw*</td>
<td>1109</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1118 mw†</td>
<td></td>
<td>1121</td>
<td></td>
</tr>
<tr>
<td>1140 mw§</td>
<td></td>
<td>1138</td>
<td></td>
</tr>
<tr>
<td>1157 mw§</td>
<td>1155</td>
<td>1147</td>
<td>1155</td>
</tr>
<tr>
<td>1238 mw‡</td>
<td>1232</td>
<td>1231</td>
<td>1235</td>
</tr>
<tr>
<td>1265 mw‡</td>
<td></td>
<td>1264</td>
<td></td>
</tr>
<tr>
<td>1286 m‡</td>
<td>1283</td>
<td></td>
<td>1267</td>
</tr>
<tr>
<td>1297 m‡</td>
<td>1291</td>
<td></td>
<td>1296</td>
</tr>
<tr>
<td>1320 mw‡</td>
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<td></td>
</tr>
<tr>
<td>1347 mw‡</td>
<td></td>
<td>1332</td>
<td>1351</td>
</tr>
<tr>
<td>1360 mw*</td>
<td>1362</td>
<td>1372</td>
<td>1378</td>
</tr>
<tr>
<td>1382 mw‡</td>
<td>1373</td>
<td>1380</td>
<td>1388</td>
</tr>
<tr>
<td>1447 mw‡</td>
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<td>1451</td>
</tr>
<tr>
<td>1460 mw‡</td>
<td></td>
<td>1464</td>
<td>1464</td>
</tr>
</tbody>
</table>

* 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 monochlorocyclohexane were calculated. In the axial form of this molecule the chlorine conformation is $S_{CC}$, 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 $S_{HH}$ 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 $C_3$ symmetry, are given in Table 8.

Table 7. Observed and calculated frequencies of monochlorocyclohexane, with potential energy distributions and possible assignments

<table>
<thead>
<tr>
<th>Observed bands†</th>
<th>Calculated frequency</th>
<th>Potential energy distribution‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$(cm$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$I$</td>
<td>Equatorial</td>
</tr>
<tr>
<td></td>
<td></td>
<td>99 $A'$</td>
</tr>
<tr>
<td>199*</td>
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</tr>
<tr>
<td></td>
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</tr>
<tr>
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<td>255 $A'$</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>447 $A''$</td>
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<tr>
<td></td>
<td></td>
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<td>511 $A'$</td>
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<tr>
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<td>5</td>
<td>557 $A'$</td>
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<td>684 $A'$</td>
</tr>
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<td>736 $A'$</td>
</tr>
<tr>
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<td>770 $A''$</td>
</tr>
<tr>
<td>773 (a)</td>
<td>0</td>
<td>804 $A'$</td>
</tr>
<tr>
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<td>833 $A'$</td>
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<tr>
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<td>843 $A'$</td>
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<tr>
<td>918 (a)</td>
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<td>870 $A''$</td>
</tr>
<tr>
<td>867 (a)</td>
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<td>873 $A''$</td>
</tr>
<tr>
<td>852 (a)</td>
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<td>882 $A'$</td>
</tr>
<tr>
<td>888 (a, e)</td>
<td>8</td>
<td>900 $A'$</td>
</tr>
<tr>
<td>888 (a, e)</td>
<td>8</td>
<td>920 $A'$</td>
</tr>
<tr>
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<td>1</td>
<td>924 $A'$</td>
</tr>
<tr>
<td>993 (a, e)</td>
<td>8</td>
<td>988 $A'$</td>
</tr>
<tr>
<td>1014 (a)</td>
<td>4</td>
<td>994 $A'$</td>
</tr>
<tr>
<td>1030 (a)</td>
<td>2</td>
<td>340 + 683 = 1023 (?)</td>
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<tr>
<td>1050 (e)</td>
<td>0</td>
<td>1067 $A'$</td>
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<td>1067 $A''$</td>
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<tr>
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<td>1096 $A'$</td>
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<tr>
<td>1098 (e)</td>
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<td>1106 $A'$</td>
</tr>
<tr>
<td>~1110 (e)</td>
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<td>1111 $A'$</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
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<tr>
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<td>1216 $A'$</td>
</tr>
<tr>
<td>1217 (c, a1)</td>
<td>8</td>
<td>1216 $A'$</td>
</tr>
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<td>1284 $A'$</td>
</tr>
<tr>
<td>1262 (a1)</td>
<td>10</td>
<td>1324 $A''$</td>
</tr>
<tr>
<td>1262 (c)</td>
<td>10</td>
<td>1324 $A''$</td>
</tr>
<tr>
<td>1267 (a)</td>
<td>10</td>
<td>1239 $A''$</td>
</tr>
<tr>
<td>1270 (c)</td>
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<td>1278 $A'$</td>
</tr>
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</tr>
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<td>1321 $A''$</td>
</tr>
<tr>
<td>1339 (a, e)</td>
<td>4</td>
<td>1331 $A'$</td>
</tr>
<tr>
<td>1352 (a, e)</td>
<td>4</td>
<td>1354 $A'$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1358 $A''$</td>
</tr>
</tbody>
</table>
Table 7 (cont.)

<table>
<thead>
<tr>
<th>Observed bands (cm⁻¹)</th>
<th>I</th>
<th>Calculated frequency</th>
<th>Potential energy distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Equatorial</td>
<td>Axial</td>
</tr>
<tr>
<td>1434 (a, e)</td>
<td>1</td>
<td>1460 A&quot;</td>
<td>1451 A'</td>
</tr>
<tr>
<td>1450 (a, e)</td>
<td>10</td>
<td>1452 A&quot;</td>
<td></td>
</tr>
<tr>
<td>1462 (a, e)</td>
<td>1</td>
<td>1453 A'</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1454 A&quot;</td>
<td>1455 A'</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1458 A'</td>
<td>1459 A'</td>
</tr>
</tbody>
</table>

* 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

\[
\begin{align*}
R_{A1} &= R_1 + R_4 \\
R_{A2} &= R_2 + R_5 \\
X_{A1} &= X_1 + X_4 \\
U_{A1} &= \alpha_{11} + \alpha_{12} + \alpha_{22} - \beta_1 - \beta_2 - \beta_3 + \alpha_{60} + \alpha_{90} + \alpha_{90} - \beta_6 - \beta_6 - \beta_{10} \\
A_{A1} &= 2\alpha_{11} - \alpha_{12} - \alpha_{22} + 2\alpha_{60} - \alpha_{90} - \alpha_{90} \\
A_{A2} &= \alpha_{11} - \alpha_{12} + \alpha_{22} - \alpha_{90} + \alpha_{90} \\
B_{A1} &= 2\beta_1 - \beta_2 - \beta_3 + 2\beta_6 - \beta_6 - \beta_{10} \\
B_{A2} &= \beta_1 - \beta_2 + \beta_3 - \beta_{10} \\
H_{A1} &= \phi_1 - \phi_2 + \phi_3 + \phi_4 \\
X_{A1} &= \Xi_1 + \Xi_4 - \Xi_2 + \Xi_3 \\
W_{A1} &= 2\omega_1 - \omega_2 + \omega_4 - \omega_3 - \omega_3 - \omega_4 \\
W_{A2} &= \omega_1 - \omega_2 - \omega_3 + \omega_4 - \omega_4 + \omega_3 - \omega_3 + \omega_4 - \omega_3 - \omega_4 \\
H_{A2} &= 2\phi_1 - \phi_2 + \phi_3 - \phi_4 \\
C_{A1} &= 5\omega_1 - \delta - \gamma_1 - \gamma_8 - \gamma_8 - \gamma_8 \\
\delta &= 4\phi_1 - \gamma_1 - \gamma_8 - \gamma_8 - \gamma_8 \\
\gamma &= \gamma_1 - \gamma_8 - \gamma_8 - \gamma_8 \\
&= \gamma_1 - \gamma_8 - \gamma_8 - \gamma_8 \\
\end{align*}
\]

Class B coordinates

\[
\begin{align*}
R_{B1} &= R_1 - R_4 \\
R_{B2} &= R_2 - R_5 \\
X_{B1} &= X_1 - X_4 \\
U_{B1} &= \alpha_{11} + \alpha_{12} + \alpha_{22} - \beta_1 - \beta_2 - \beta_3 + \alpha_{60} - \alpha_{90} + \beta_6 + \beta_6 + \beta_{10} \\
A_{B1} &= 2\alpha_{11} - \alpha_{12} - \alpha_{22} - 2\alpha_{60} + \alpha_{90} + \alpha_{90} \\
A_{B2} &= \alpha_{11} - \alpha_{12} + \alpha_{22} + \alpha_{90} - \alpha_{90} \\
B_{B1} &= 2\beta_1 - \beta_2 - \beta_3 - 2\beta_6 + \beta_6 + \beta_{10} \\
B_{B2} &= \beta_1 + \beta_2 + \beta_3 - \beta_{10} \\
H_{B1} &= \phi_1 - \phi_2 + \phi_3 - \phi_4 \\
X_{B1} &= \Xi_1 - \Xi_4 + \Xi_2 - \Xi_3 \\
W_{B1} &= 2\omega_1 - \omega_2 + \omega_4 - \omega_3 + \omega_3 - \omega_4 \\
W_{B2} &= \omega_1 - \omega_2 - \omega_3 + \omega_4 + \omega_4 - \omega_3 + \omega_3 - \omega_4 \\
H_{B2} &= 2\phi_1 + \phi_2 - \phi_3 + \phi_4 \\
\omega &= \gamma_1 + \gamma_8 + \gamma_8 - \gamma_8 \\
\rho &= \gamma_1 + \gamma_8 + \gamma_8 - \gamma_8 \\
\end{align*}
\]
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

<table>
<thead>
<tr>
<th>Observed frequency (cm⁻¹)</th>
<th>Frequency (cm⁻¹)</th>
<th>Potential energy distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>255 vw</td>
<td>122 A</td>
<td>CCC(39) - Xₚ₆₁(32)</td>
</tr>
<tr>
<td>260 A</td>
<td></td>
<td>Wₐ₄₂(51) - Xₚ₆₁(30)</td>
</tr>
<tr>
<td>283 B</td>
<td></td>
<td>Xₚ₆₁(30) + W₉₄₁(37)</td>
</tr>
<tr>
<td>343 m</td>
<td>325 B</td>
<td>W₉₄₁(55) - Xₚ₆₁(30) - W₉₄₁(17)</td>
</tr>
<tr>
<td>368 m</td>
<td>354 A</td>
<td>Wₐ₄₁(57) - Wₐ₄₁(14)</td>
</tr>
<tr>
<td></td>
<td>446 B</td>
<td>W₉₄₁(55) + W₉₄₁(16)</td>
</tr>
<tr>
<td>460 mw</td>
<td>466 A</td>
<td>CCC(30) + Xₚ₆₁(26) + Rₙ₆₁(18)</td>
</tr>
<tr>
<td>606 s</td>
<td>605 B</td>
<td>X₉₉₁(78)</td>
</tr>
<tr>
<td>627 s</td>
<td>624 A</td>
<td>Xₐ₄₁(74)</td>
</tr>
<tr>
<td>877 ms</td>
<td>872 A</td>
<td>R₉₆₁(33) - B₉₆₁(27) - B₉₆₁(11)</td>
</tr>
<tr>
<td></td>
<td>877 B</td>
<td>t(48) - B₉₆₁(22) + H₉₆₁(16)</td>
</tr>
<tr>
<td>938 s</td>
<td>943 B</td>
<td>R₉₆₁(32) + R₉₆₁(26) - B₉₆₁(19)</td>
</tr>
<tr>
<td>978 m</td>
<td>994 A</td>
<td>B₉₆₁(31) - B₉₆₁(20) + R₉₆₁(13) + H₉₆₁(11)</td>
</tr>
<tr>
<td>1012 s</td>
<td>1017 B</td>
<td>B₉₆₁(45) + R₉₆₁(32)</td>
</tr>
<tr>
<td>1057 m</td>
<td>1086 B</td>
<td>B₉₆₁(47) + B₉₆₁(25) + H₉₆₁(14)</td>
</tr>
<tr>
<td>1100 vw</td>
<td>1110 A</td>
<td>R₉₆₁(47) + Rₙ₆₁(18)</td>
</tr>
<tr>
<td>1125 s</td>
<td>1121 A</td>
<td>B₉₆₁(27) + R₉₆₁(26) - H₉₆₁(13)</td>
</tr>
<tr>
<td>1132 s?</td>
<td>1145 B</td>
<td>R₉₆₁(44) + B₉₆₁(14) - H₉₆₁(14)</td>
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<tr>
<td>1191 m</td>
<td>1176 A</td>
<td>Hₐ₄₁(43) + t(35)</td>
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<tr>
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<td>1239 B</td>
<td>Hₐ₄₁(38) + t(39)</td>
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<td>1255 B</td>
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<td>1285 A</td>
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<tr>
<td>1325 mw</td>
<td>1327 A</td>
<td>Hₐ₄₁(49) - t(19)</td>
</tr>
<tr>
<td>1379 s</td>
<td>1373 B</td>
<td>U₉₆₁(92)</td>
</tr>
<tr>
<td>1415 ms</td>
<td>1374 A</td>
<td>U₉₆₁(86)</td>
</tr>
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<td>1405 B</td>
<td>c(36) - R₉₆₁(26) - H₉₆₁(22)</td>
</tr>
<tr>
<td>1443 s )</td>
<td>1452 A</td>
<td>δ(95)</td>
</tr>
<tr>
<td>1450 m)</td>
<td>1461 A</td>
<td>A₉₆₁(84)</td>
</tr>
<tr>
<td></td>
<td>1461 A</td>
<td>A₉₆₁(83)</td>
</tr>
<tr>
<td></td>
<td>1461 B</td>
<td>A₉₆₁(84)</td>
</tr>
<tr>
<td></td>
<td>1464 B</td>
<td>A₉₆₁(78)</td>
</tr>
</tbody>
</table>
A force field for secondary chlorides

The \( TT \) conformation of \textit{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 \textit{meso} 2,4-dichloropentane is the \( TG \) form \[16\] (\( \text{G = gauche} \)), and our calculations were done for this structure.

The comparisons between observed \[15, 16\] and calculated frequencies for these 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 \textit{dL} compound and about 0.8 per cent for the \textit{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 \( \text{CHCl} \) groups by the intervening \( \text{CH}_2 \) 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 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.

**Acknowledgments**—We are indebted to R. G. Snyder and J. H. Schachtschneider of the Shell Development Co., Emeryville, California, for permitting us to use their force field for primary chlorides prior to publication. We are deeply grateful to J. J. Shipman of the B. F. Goodrich Co., Brecksville, Ohio, for the spectral data on 2-chloropropane and 2-chlorobutane, and for the low frequency bands of the 2,4-dichloropentanes. This research was supported by a grant from the National Science Foundation.