

A complete general valence force field for secondary chlorides

W. H. MOORE and S. KRIMM

Harrison M. Randall Laboratory of Physics, University of Michigan,
Ann Arbor, Michigan 48104, U.S.A.

(Received 18 January 1973)

Abstract—A general valence force field for secondary chlorides has been refined which includes torsional force constants based on assignments of low frequency modes in model compounds. This force field also incorporates force constants related to observed intermolecular interactions. The good agreement between observed and calculated frequencies indicates that this force field will be useful in studying the conformation of secondary chlorides.

INTRODUCTION

IN AN effort to gain insight into the structure of stereo-specific poly(vinyl chloride), considerable attention has been given to the study of the vibrational frequencies of chlorine-substituted derivatives of the normal paraffins [1–6]. The well-established correlation in secondary chlorides between the frequency of the carbon–chlorine stretching vibration and the rotational isomer, and the availability of general valence force fields for hydrocarbons [7] and primary chlorides [8], formed the bases for the development of the original valence force field for secondary chlorides [1]. The lack of far infrared data, however, made it impossible to include force constants for the calculation of torsional modes in the refinement procedures used to develop these force fields. Relevant far infrared and Raman data for some model secondary chloride molecules are now available. We have already reported the assignment of these spectra, and have developed the force field necessary for the calculation of vibrations due to internal rotation [9]. We report here a complete general valence force field for secondary chlorides.

The spectral region of C–Cl stretching in secondary chlorides, 500–700 cm^{-1} , is highly diagnostic of local structure, because this vibration is relatively intense, is sensitive to the type of atoms trans to the chlorine atom across adjacent C–C bonds, is sensitive to the geometry of the carbon chain, and takes place in a spectral region which except for the C–Cl stretching vibrations themselves is relatively clear of other absorptions. The notation used here to describe molecular geometry relative

-
- [1] C. G. OPASKAR and S. KRIMM, *Spectrochim. Acta* **23A**, 2261 (1967).
 - [2] T. SHIMANOCHI and M. TASUMI, *Spectrochim. Acta* **17**, 755 (1961).
 - [3] P. KLABOE, *Spectrochim. Acta* **26A**, 87 (1970).
 - [4] M. TASUMI and T. SHIMANOCHI, *Polymer J.* **2**, 62 (1971).
 - [5] B. SCHNEIDER, J. ŠTOKR, D. DOSKOČILOVÁ, S. SÝKORA, J. JAKEŠ, and M. KOLÍNSKÝ, *J. Polymer Sci.* **22C**, 1073 (1969).
 - [6] D. DOSKOČILOVÁ, J. ŠTOKR, B. SCHNEIDER, H. PIVCOVÁ, M. KOLÍNSKÝ, J. PETRÁNEK and D. LÍM, *J. Polymer Sci.* **16C**, 215 (1967).
 - [7] R. G. SNYDER and J. H. SCHACHTSCHNEIDER, *Spectrochim. Acta* **21**, 169 (1965).
 - [8] R. G. SNYDER and J. H. SCHACHTSCHNEIDER, *J. Mol. Spectry* **30**, 290 (1969).
 - [9] W. H. MOORE, J. H. C. CHING, A. V. R. WARRIER and S. KRIMM, *Spectrochim. Acta* **29A**, 1847 (1974).

to the chlorine atom or atoms is that suggested by DOSKOČILOVA *et al.* [6]. This notation parallels that of SHIPMAN *et al.* [10]: an *S* for secondary chlorines with subscripts to designate the type of atom trans to the chlorine and primes on these subscripts to indicate rotation away from the planar zig-zag conformation. However, instead of the S_{HC} or S_{HH} notation, we now use ${}_{\text{H}}S_{\text{C}}$ or ${}_{\text{H}}S_{\text{H}}$. The left hand subscript is used to describe the geometry to the immediate left of the chlorine atom. Similarly, the right hand subscript describes the molecular geometry to the right of the chlorine atom. In the simpler secondary chlorides, e.g. 2-chloropropane, 2-chlorobutane, and 3-chloropentane, the old notation is certainly adequate. However, in the tri-substituted heptanes this new formalism can be compounded to designate unambiguously the molecular conformation with respect to all chlorine atoms present, e.g. ${}_{\text{H}}S_{\text{HH}}S_{\text{HC}}S_{\text{H}}$. When tetrahedral geometry is assumed, any rotation around a given carbon-carbon bond is meant to imply a rotation of $\pm 120^\circ$ from the planar zig-zag conformation. Using the notation described above, the empirically determined C—Cl stretching frequencies can be assigned as a function of molecular geometry in the neighborhood of the chlorine atom [10].

Recently, on the basis of a study of rotational isomeric structures of monohalide-substituted derivatives of *n*-pentanes and *n*-octanes, GATES *et al.* [11] stated that some of these assignments needed modification. Although an in-depth study of this work is only partially completed, from a comparison of these results with those reported by BENEDETTI and CECCHI [12] on 2-iodobutane and with our studies of secondary chlorides, two conclusions can be reached: (1) the characteristic frequency of the C—X stretching vibration (*X* = chlorine, bromine, or iodine) when the halogen is adjacent to a methyl group (as in 2-halogeno-butane, or 2,4 dihalogeno-pentane) does differ somewhat from the characteristic frequency of this stretching vibration in molecules like 3-chloropentane, 3-chlorooctane, etc. in which the halogen atom is between two methylene groups (see section on 3-chloropentane); (2) in going from chloro- to bromo- to iodo-substituted hydrocarbons, the region of C—X stretching moves from 500–700 cm^{-1} in the case of the chlorine-substituted derivatives to 480–580 cm^{-1} in the case of the iodine-substituted hydrocarbons. For 2-chlorobutane the C—Cl stretching modes contribute only relatively small amounts to the potential energy distribution of the C—C—C bending, C—C—Cl bending, and torsional modes. However, for 2-iodobutane this is not so. In ${}_{\text{H}}S_{\text{H}}$ 2-iodobutane, C—I stretching contributes 31 per cent to the potential energy distribution of an absorption due mainly to bending at 265 cm^{-1} . Moreover, in the ${}_{\text{H}}S_{\text{C}}$ rotational isomer of 2-iodobutane, the C—I stretching vibration contributes 57 per cent to the potential energy distribution of a similar bending mode at 270 cm^{-1} [12]. This indicates that the atomic motions differ considerably according to the particular halogen which is present. Therefore, the assignment of bands in this region through the correlation of frequency shifts for different halogenated paraffins is a risky business. We therefore still use the empirical data of SHIPMAN *et al.* [10] as a guide in the assignments of the fundamental vibrations of chlorinated hydrocarbons.

[10] J. J. SHIPMAN, V. L. FOLT and S. KRIMM, *Spectrochim. Acta* **18**, 1603 (1962).

[11] P. N. GATES, E. F. MOONEY and H. A. WILLIS, *Spectrochim. Acta* **23A**, 2043 (1967).

[12] E. BENEDETTI and P. CECCHI, *Spectrochim. Acta* **28A**, 1007 (1972).

DEVELOPMENT OF FORCE FIELD

OPASKAR and KRIMM [1] previously reported a force field for secondary chlorides which predicted well most of the normal modes of a group of model secondary chloride compounds and related polymers. However, their force field did not include any torsional force constants. In this study, our aim was to develop a force field which predicted torsional frequencies as well as those due to all other vibrational modes, and which reproduced the intermolecular interaction reported by WARRIER and KRIMM [13]. Initially, our force field was a composite of the most recent potential function for hydrocarbons reported by SNYDER [14] and the force field for secondary chlorides developed by OPASKAR and KRIMM [1], together with provisions for new torsional force constants and additional elements required to calculate vibrational frequencies of intermolecular normal modes. This force field was used to temporarily assign all new far infrared and Raman data on 2-chloropropane, 2-chlorobutane, and the two stereoisomers of 2,4-dichloropentane. The results of this study are reported in the previous paper [9].

In order to obtain agreement with the observed spectra, a small modification had to be made in the hydrocarbon part of the force field. In the vibrational spectrum of 2-chloropropane, there are two CH_3 bending modes, one symmetric and one antisymmetric. The portion of the potential function which was transferred from the n -paraffins determines the calculated frequencies of these bending vibrations. The initial normal coordinate calculations on 2-chloropropane predicted the antisymmetric umbrella vibration to be of higher frequency than the symmetric one. However, according to the data used by OPASKAR and KRIMM [1] and KLABOE [3], the higher frequency band, which was observed at 1385 cm^{-1} in liquid 2-chloropropane, has all of the characteristics of a symmetric, A' , vibration: (a) its infrared gas phase spectrum has a strong central maximum with a weaker peak on each side of the central one [15]; (b) it is the more intense band in the Raman spectrum (the 1374 cm^{-1} band not even being observed); (c) it is polarized in the Raman spectrum. In order to more accurately calculate the relative frequencies of the A' and A'' umbrella vibrations in the CH_3 groups, the diagonal force constant, H_β , for C—C—H bending, and the interaction force constant, f_β , between two such bendings in the same methyl group were allowed to vary. Although this violated the initial philosophy of our study, i.e. to maintain at a constant value all force constants which were transferred from the n -paraffin force field, we felt this to be justified because these constants were also found to predict inaccurately the relative values of the symmetric and antisymmetric umbrella modes in propane. GAYLES and KING [16] observed the infrared spectra of propane and its deuterium substituted derivatives and used the method of BADGER and ZUMWALT [15], and the GERHARD—DENNISON [17] analysis of the asymmetric rotor, to assign the observed fundamental frequencies. In this study the A_1 umbrella vibration of propane was found to occur at

[13] A. V. R. WARRIER and S. KRIMM, *J. Chem. Phys.* **52**, 4316 (1970).

[14] R. G. SNYDER, *J. Chem. Phys.* **47**, 1316 (1967).

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

[16] J. N. GAYLES and W. T. KING, *Spectrochim. Acta* **21**, 543 (1965).

[17] S. L. GERHARD and D. M. DENNISON, *Phys. Rev.* **43**, 197 (1933).

1391.9 cm^{-1} and the B_1 vibration at 1378 cm^{-1} . With H_β and f_β unchanged, the A_1 mode in propane is calculated at 1370 cm^{-1} and the B_1 mode at 1382 cm^{-1} [14]. The new refined values of H_β and f_β predict the A_1 umbrella vibration in propane at 1386 cm^{-1} and the B_1 mode at 1372 cm^{-1} . Similarly in 2-chloropropane with the new H_β and f_β , the symmetric umbrella vibration observed at 1385 cm^{-1} is now calculated at 1386 cm^{-1} , and the antisymmetric vibration, which is observed at 1374 cm^{-1} is now calculated at 1379 cm^{-1} .

The existence of a specific intermolecular vibration in secondary chlorides which involves the C—Cl bond, i.e. a C—Cl . . . H—C interaction, has been strongly suggested by experimental evidence [13, 18, 19]. The force field reported here includes stretching and bending force constants to describe such an intermolecular interaction.

Prior to this work, the 2,4-dichloropentanes have been studied extensively [1, 5, 20, 21] because they are excellent model compounds of the poly(vinyl chloride) polymers. Under the assumption of tetrahedral geometry and staggered molecular conformation, each of the two stereoisomers of 2,4-dichloropentane can assume six unique rotational conformations. Theoretically each stereoisomer exists as a mixture of all six of its own rotational isomers. By investigating the C—Cl stretching spectra of these molecules, SHIMANOUCI and TASUMI [2] concluded that the DL form of 2,4-dichloropentane existed mainly in the TT form and that the meso form was so dominated by the TG' conformation that infrared spectra contained no observable absorption due to other conformations. We have found this not to be true. Attempts to explain the infrared, Raman, and NMR spectra of the 2,4-dichloropentanes on the basis of only the most prevalent structures have failed [5, 21]. In this study, observed bands in the far infrared at 150 cm^{-1} in DL- and at 160 cm^{-1} in meso-2,4-dichloropentane could not be predicted by means of normal coordinate analyses of the preferred conformers. TASUMI *et al.* [4] were unable to predict bands in the vicinity of 180 cm^{-1} for PVC. These bands and their assignment to less prevalent conformations will be discussed in a subsequent publication.

The final force field was obtained by a refinement of 42 force constants to predict over 90 observed frequencies of chloropropane, ${}_H S_H$ and ${}_H S_C$ 2-chlorobutane, the ${}_H S_H$ ${}_H S_H$ form of DL-2,4-dichloropentane, and the ${}_H S_H$ ${}_C S_H$ form of meso-2,4-dichloropentane. The final refined force field is given in Table 1.

MODEL COMPOUNDS USED IN REFINEMENT PROCEDURE

2-Chloropropane

By using the theory of BADGER and ZUMWALT [15], OPASKAR and KRIMM [1] analyzed the symmetry of the absorption bands of the gas phase infrared spectrum of 2-chloropropane, and with the aid of normal coordinate analyses assigned these observed bands. The results of using the force field of Table 1 in a normal coordinate analysis of 2-chloropropane are given in Table 2. The assignments reported here agree with those of Ref [1]. The agreement between observed and calculated normal

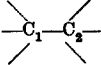
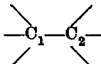
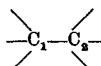
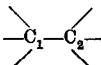
[18] A. V. R. WARRIER and S. KRIMM, *Macromolecules* **3**, 709 (1970).

[19] W. H. MOORE and S. KRIMM, *J. Am. Chem. Soc.*, in press.

[20] P. J. FLORY and A. D. WILLIAMS, *J. Am. Chem. Soc.* **91**, 3118 (1969).

[21] S. KRIMM, *Pure Appl. Chem.* **16**, 369 (1968).

Table 1. Force constants for secondary chlorides

Name	Value§	Environment	Coordinates coupled
* K_r	4.6990	C(H, H, H)	(C, H)
* K_d	4.5380	C(H, H)	(C, H)
† K_{dCl}	4.8460	C(H, Cl)	(C, H)
* K_E	4.532	C(H, H)—C(H, H)	(C, C)
K_{RCl}	4.7047	C(H, H)—C(H, Cl)	(C, C)
K_{Cl}	2.7844	C(H, Cl)	(C, Cl)
* H_α	0.5390	C(H ₁ , H ₂ , H ₃)	(H ₁ , C, H ₂)
H_β	0.6213	C(H ₁ , H ₂ , H ₃)—C	(C, C, H ₁)
* H_γ	0.663	C ₁ —C ₂ (H ₁ , H ₂)—C ₃	(C ₁ , C ₂ , H ₁)
H_ϕ	0.6567	C ₁ —C ₂ (H, Cl)	(C ₁ , C ₂ , H)
H_θ	0.8518	C(H, Cl)	(H, C, Cl)
H_E	1.1062	C ₁ —C ₂ (H, Cl)	(C ₁ , C ₂ , Cl)
$H_{1\omega}$	0.9792	C ₁ —C ₂ (H, Cl)—C ₃	(C ₁ , C ₂ , C ₃)
* $H_{2\omega}$	1.032	C ₁ —C ₂ (H, H)—C ₃	(C ₁ , C ₂ , C ₃)
* $H_{1\delta}$	0.533	C ₁ (H, H)—C ₂ (H ₁ , H ₂)—C ₃ (H, H)	(H ₁ , C ₂ , H ₂)
$H_{2\delta}$	0.5028	C ₁ (H, Cl)—C ₂ (H ₁ , H ₂)—C ₃ (H, Cl)	(H ₁ , C ₂ , H ₂)
$H_{3\delta}$	0.5198	C ₁ (H, H)—C ₂ (H ₁ , H ₂)—C ₃ (H, Cl)	(H ₁ , C ₂ , H ₂)
H_{1r}	0.1105	C ₁ (H, H, H)—C ₂ (H, Cl)—C	
H_{2r}	0.0775	C ₁ (H, H, H)—C ₂ (H, H)—C	
H_{3r}	0.1309	C ₁ (H, H, H)—C ₂ (H ₁ , Cl)—C(H, H, H)	
H_{4r}	0.0744	C—C ₁ (H, H)—C ₂ (H, Cl)—C	
* F_r	0.032	C(H ₁ , H ₂ , H ₃)	(C, H ₁)(C, H ₂)
* F_{2d}	0.019	C(H ₁ , H ₂)	(C, H ₁)(C, H ₂)
* F_{1R}	0.083	C ₁ (H, H)—C ₂ (H, H)—C ₃ (H, H)	(C ₁ , C ₂)(C ₂ , C ₃)
F_{2R}	0.177	C ₁ (H, Cl)—C ₂ (H, H)—C ₃ (H)	(C ₁ , C ₂)(C ₂ , C ₃)
F_{3R}	0.4058	C ₁ (H, H)—C ₂ (H, Cl)—C ₃ (H, H)	(C ₁ , C ₂)(C ₂ , C ₃)
F_{RCl}	0.6401	C ₁ —C ₂ (H, Cl)	(C ₁ , C ₂)(C ₂ , Cl)
* $F_{1R\gamma}$	0.174	C ₁ —C ₂ (H, H)	(C ₁ , C ₂)(C ₁ , C ₂ , H)
$F_{2R\gamma}$	0.1845	C ₁ (H ₁ , Cl)—C ₂ (H, H)	(C ₁ , C ₂)(C ₁ , C ₂ , H)
$F_{3R\gamma}$	0.1701	C ₁ (H ₁ , Cl)—C ₂ (H, H)	(C ₁ , C ₂)(C ₁ , C ₂ , H ₁)
$F_{1R\omega}$	0.349	C ₁ (H, Cl)—C ₂ —C ₃	(C ₁ , C ₂)(C ₁ , C ₂ , C ₃)†
* $F_{2R\omega}$	0.303	C ₁ —C ₂ —C ₃	(C ₁ , C ₂)(C ₁ , C ₂ , C ₃)
$F_{1R\gamma}$	—0.0218	C ₁ —C ₂ (H ₁ , H ₂)—C ₃ (H, Cl)	(C ₂ , C ₃)(C ₁ , C ₂ , H ₁) or (C ₁ , C ₂)(C ₃ , C ₂ , H ₁)
$F_{2R\gamma}$	—0.0868	C ₁ —C ₂ (H, Cl)—C ₃	(C ₁ , C ₂)(C ₃ , C ₂ , H)
* $F_{3R\gamma}$	—0.097	C ₁ —C ₂ (H, H)—C ₃	(C ₁ , C ₂)(C ₃ , C ₂ , H)
$F_{\omega Cl}$	—0.1117	C ₁ —C ₂ (H, Cl)—C ₃	(C ₂ , Cl)(C ₁ , C ₂ , C ₃)
F_{RE}	0.1003	C ₁ —C ₂ (H, Cl)	(C ₁ , C ₂)(C ₁ , C ₂ , Cl)
F_{ClE}	0.4005	C ₁ —C ₂ (H, Cl)	(C ₂ , Cl)(C ₁ , C ₂ , Cl)
$F_{\theta Cl}$	0.2399	C(H, Cl)	(C, Cl)(H, C, Cl)
* $F_{\beta\beta}$	—0.0272	C(H ₁ , H ₂ , H ₃)—C	(C, C, H ₁)(C, C, H ₂)
* $F_{\gamma\gamma}$	—0.0190	C(H ₁ , H ₂)—C	(C, C, H ₁)(C, C, H ₂)
* $F'_{\gamma\gamma}$	0.0210	C ₁ —C ₂ (H ₁ , H ₂)—C ₃	(C ₁ , C ₂ , H ₁)(C ₂ , C ₃ , H ₁)
* $F''_{\gamma\gamma}$	—0.022	C ₁ —C ₂ (H ₁ , H ₂)—C ₃	(C ₁ , C ₂ , C ₃)(C ₁ , C ₂ , H ₁)
$F_{2\gamma\omega}$	—0.0903	C ₁ —C ₂ (H, Cl)—C ₃	(C ₁ , C ₂ , C ₃)(C ₁ , C ₂ , H)

* Force constants transferred from Ref. [7].

† Force constant transferred from Ref. [1].

‡ A chlorine atom is attached to at least one of the carbon atoms involved.

§ Stretch constants are in units of mdyN/Å, stretch bend constants are in units of mdyN/rad, bend and torsion constants are in units of mdyN · Å/rad².|| Superscripts *t*, *g* imply that extreme atoms are *trans* and *gauche* to one another, respectively.¶ *Trans* implies that two angles are bisected by a common plane, *gauche* implies no such common bisector.** *op* implies out-of-plane bending, *ip* implies in-plane bending.

Table 1. (continued)

Name	Value§	Environment	Coordinates coupled
$F\varphi\theta$	0.1055	$C_1-C_2(H, Cl)$	$(C_1, C_2, H)(H, C_2, Cl)$
$*f_{1\gamma\gamma}^t$	0.073	$C_1(H_1, H_2)-C_3(H_3, H_4)$	$(H_1, C_1, C_2)(C_1, C_2, H_3) \parallel$
$*f_{1\gamma\gamma}^g$	-0.058	$C_1(H_1, H_2)-C_3(H_3, H_4)$	$(H_1, C_1, C_2)(C_1, C_2, H_3) \parallel$
$*f_{1\gamma\omega}^g$	-0.064	$C_1(H_1, H_2)-C_2-C_3$	$(H_1, C_1, C_2)(C_1, C_2, C_3)$
$*f_{1\gamma\omega}^t$	0.073	$C_1(H_1, H_2)-C_2-C_3$	$(H_1, C_1, C_2)(C_1, C_2, C_3)$
$*f_{1\omega\omega}^t$	0.097	$C_1-C_2-C_3-C_4$	$(C_1, C_2, C_3)(C_2, C_3, C_4)$
$*f_{1\omega\omega}^g$	-0.005	$C_1-C_2-C_3-C_4$	$(C_1, C_2, C_3)(C_2, C_3, C_4)$
$f_{2\omega\omega}^t$	0.095	$C_1-C_2(H, Cl)-C_3-C_4$	$(C_1, C_2, C_3)(C_2, C_3, C_4)$
$f_{2\omega\omega}^g$	0.0436	$C_1-C_2(H, Cl)-C_3-C_4$	$(C_1, C_2, C_3)(C_2, C_3, C_4)$
$f_{2\gamma\gamma}^t$	0.0803	$C_1(H_1, H_2)-C_2(H, Cl)$	$(H_1, C_1, C_2)(C_1, C_2, H)$
$f_{2\gamma\gamma}^g$	-0.0327	$C_1(H_1, H_2)-C_2(H, Cl)$	$(H_1, C_1, C_2)(C_1, C_2, H)$
$f_{2\gamma\omega}^t$	0.073	$C_1(H, Cl)-C_2-C_3$	$(H, C_1, C_2)(C_1, C_2, C_3)$
$f_{2\gamma\omega}^g$	-0.0077	$C_1(H, Cl)-C_2-C_3$	$(H, C_1, C_2)(C_1, C_2, C_3)$
$f_{\gamma\Xi}^g$	-0.1085	$C_1(H, Cl)-C_2(H_1, H_2)$	$(Cl, C_1, C_2)(C_1, C_2, H_1)$
$f_{\gamma\Xi}^t$	-0.1548	$C_1(H, Cl)-C_2(H_1, H_2)$	$(Cl, C_1, C_2)(C_1, C_2, H_1)$
$f_{\omega\Xi}^t$	-0.0774	$C_1(H, Cl)-C_2-C_3$	$(Cl, C_1, C_2)(C_1, C_2, C_3)$
$f_{\omega\Xi}^g$	-0.0193	$C_1(H, Cl)-C_2-C_3$	$(Cl, C_1, C_2)(C_1, C_2, C_3)$
$f_{\gamma\gamma}^t$	0.0136	$C_1-C_2(H_1)-C_3(H_2)$	$(C_1, C_2, H_1)(C_2, C_3, H_2) \parallel$
$f_{\gamma\gamma}^g$	0.0519	$C_1-C_2(H_1)-C_3(H_2)$	$(C_1, C_2, H_1)(C_2, C_3, H_2)$
$f_{\gamma\gamma}^t$	0.0034	$C_1-C_2(H_1)-C_3(H_2)-C_4$	$(C_1, C_2, H_1)(H_2, C_3, C_4) \parallel$
$f_{\gamma\gamma}^g$	0.0222	$C_1-C_2(H_1)-C_3(H_2)-C_4$	$(C_1, C_2, H_1)(H_2, C_3, C_4) \parallel$
$K_{Cl...H}$	0.07	$C-Cl...H-C$	$Cl...H$
$H_{\alpha p}^{**}$	0.01	$C-Cl...H-C$	$C-Cl...H$
$H_{\alpha' p}^{**}$	0.03	$C-Cl...H-C$	$C-Cl...H$
$H_{\beta p}^{**}$	0.01	$C-Cl...H-C$	$Cl...H-C$
$H_{\beta' p}^{**}$	0.25	$C-Cl...H-C$	$Cl...H-C$
$f_{\tau\tau}$	0.008	$C_1-C_2-C_3-C_4$	$\left(\begin{array}{c} \diagdown \\ -C_1- \\ \diagup \end{array} \right) \left(\begin{array}{c} \diagdown \\ -C_2- \\ \diagup \end{array} \right)$

frequencies are better (especially in the region below 600 cm^{-1}) than that previously obtained [1]. This improved agreement is due to the inclusion of torsional modes and to the actual refinement of the secondary chloride force field. For 2-chloropropane, as well as for the other secondary chlorides which were studied, the correlation between observed and calculated frequencies in the regions of methyl bending and rocking was inferior to that in other spectral regions. This suggests that the force constants which were transferred from the potential field for hydrocarbons could be refined to predict more accurately CH_3 bending and rocking modes in secondary chlorides.

2-Chlorobutane

The dependence of the $\text{C}-\text{Cl}$ stretching frequencies on structure, and the use of this relationship to identify the presence of various molecular conformations, is exemplified in the spectral assignments for 2-chlorobutane [1]. Observations of the infrared spectra of 2-chlorobutane at room and at low temperatures indicate that the 607 cm^{-1} carbon-chlorine stretching frequency increases in intensity at low temperatures. The behavior of this frequency, which is uniquely associated with the ${}_{\text{H}}S_{\text{H}}$ conformation of 2-chlorobutane, is assumed to be characteristic of all absorption bands associated with this rotational isomer. Therefore, following the logic for assignments used by Opaskar and Krimm, all observed bands whose intensities increase at low temperatures were assigned to the ${}_{\text{H}}S_{\text{H}}$ form of 2-chlorobutane. Table 3 gives the observed spectrum of 2-chlorobutane,

Table 2. Observed and calculated frequencies (in cm^{-1}), potential energy distributions and band assignments of 2-chloropropane

Observed		Calculated		Potential energy distribution §
Frequency* ‡	Symmetry †	Symmetry	Frequency	
256 vw	<i>S</i>	<i>A'</i>	256	$\tau_1(97)$
273 w	<i>A</i>	<i>A''</i>	273	$\tau_2(98)$
324 w	<i>A</i>	<i>A''</i>	327	$X_7(95)$
335 m	<i>S</i>	<i>A'</i>	337	$W_3(84)$
423 m	<i>S</i>	<i>A'</i>	421	$W_1(77), B_1(12)$
611 vs	<i>S</i>	<i>A'</i>	611	$X(83)$
(677 vw)		<i>A'</i>	$2 \times 335 = 670$	
(760 w)		<i>A'</i>	$423 + 335 = 758$	
885	<i>S</i>	<i>A'</i>	881	$R_1(73), B_1(19)$
933 mw	<i>A</i>	<i>A''</i>	924	$B_1(59), B_3(27)$
965?		<i>A''</i>	955	$B_3(52), B_4(25)$
(1025 sh)		<i>A'</i>	$611 + 423 = 1034$	
1061 vs	<i>S</i>	<i>A'</i>	1049	$B_2(63), B_1(11)$
1129 m	<i>A</i>	<i>A''</i>	1122	$R_2(53), H_\pi(12)$
1160 s	<i>S</i>	<i>A'</i>	1156	$B_1(45), R_1(21)$
(1223 vw)		<i>A'</i>	$2 \times 611 = 1222$	
1260 vs	<i>S</i>	<i>A'</i>	1256	$H_\sigma(88)$
(1308 vw)	<i>S</i>	<i>A'</i>	$885 + 423 = 1308$	
1328 w	<i>A</i>	<i>A''</i>	1327	$H_\pi(58), R_2(29)$
1374 s	<i>A</i>	<i>A''</i>	1379	$U_3(83), H_\pi(11)$
1385 s	<i>S</i>	<i>A'</i>	1386	$U_1(85), R_1(6)$
(1446s)		<i>A'</i>	1459	$A_1(69), A_3(21)$
		<i>A''</i>	1459	$A_4(66), A_3(26)$
to		<i>A''</i>	1460	$A_3(64), A_4(24)$
(1465 s)		<i>A'</i>	1461	$A_2(69), A_1(21)$

* Liquid phase frequencies.

† Symmetry from gas phase contours.

‡ Refs. [1] and [9].

§ For definitions of torsion coordinates see Ref. [9], for others see Ref. [1].

Frequencies in parentheses were not used in refinement procedure.

its behavior with respect to temperature, and the corresponding band assignments. The calculated potential energy distributions are reported in Table 4. The frequencies of the ${}_H S_H$ rotational isomer were not used in the refinement procedure.

Throughout this investigation, tetrahedral geometry and staggered conformations were assumed. These are popular, although arbitrary, assumptions. We know [22] that the C—C—C angle in secondary chlorides is closer to 112° than to the $109^\circ 28'$ associated with tetrahedral geometry. In the most recent refinement of the force field for *n*-paraffins [14], the value of the dihedral angle for gauche C—C bonds was set at $\pm 67^\circ$. The discrepancy between the observed frequency (627 cm^{-1}) of the C—Cl stretching vibration in ${}_H S_H$ 2-chlorobutane and the calculated value (642 cm^{-1}) reflects the inaccuracies in the staggered approximation and in the tetrahedral configuration. To demonstrate the sensitivity of the carbon—chlorine stretching frequency to torsion angle in the ${}_H S_H$ isomer of 2-chlorobutane, the C—Cl stretching frequency is plotted in Fig. 1 as a function of τ , the dihedral angle. This figure clearly shows that a 10° change in torsion angle changes the C—Cl stretching frequency in the ${}_H S_H$ isomer by approximately 17 cm^{-1} . At the same time the frequencies of C—Cl stretching vibrations in the ${}_H S_H$ and ${}_H S_C$ isomers are relatively insensitive to variations of $\pm 10^\circ$ in the dihedral angle.

Table 3. Assignments to observed frequencies (in cm^{-1}) of 2-chlorobutane

Observed liquid frequency §	Calculated frequency		
	$\text{H}^{\text{S}}\text{H} $	$\text{H}^{\text{S}}\text{C} $	$\text{H}^{\text{S}}\text{H}^{\text{¶}}$
77	77	83	72
	189	200	195
226*	223	(227)	215
244	245	(250)	243
290 w		(308)	
324 m	321		334
333 sh			341
374 m†		375	
386 m*	388		
418 mw†		423	
460 mw*	461		
522 m†			514
607 vs*	612		
627 m†			642
670 s†		671	
790 vs*	791	788	793
822 m†			840
843 s*	841	852	
950 ms†		947	944
958 ms*	957		
976 w†		970	
992 m*	996		991
1000 (?)†			997
1010 w†		1008	
1022 w*	1016		
1060 m†		1067	1064
1073 mw*	1071		
1108 w*	1106		
1118 m†			1115
1140 vw		(1135)	1145
1157 s†	1162	(1159)	
1238 vs‡	1231	(1245)	1236
1265 vw		(1255)	
1286 s*	1291		1280
1297 s*	1302		
1320 mw†		(1318)	1322
1347 vw			1351
1360 w*	1353	(1362)	
1382 vs‡	1384	(1381)	1381
	1395	1398	1393
1430 vw	(1426)	(1428)	1428
1447 vs‡	(1458)	(1458)	1458
	(1458)	(1458)	1459
	(1460)	(1460)	1460
1460 vs‡	(1462)	(1462)	1462

* Intensity increases at low temperatures.

† Intensity decreases at low temperatures.

‡ Intensity remains strong at low temperatures.

§ Ref. [1] and [9].

|| Frequencies in parentheses were not assigned before refinement.

¶ The $\text{H}^{\text{S}}\text{H}$ isomer was not used in refinement.

Besides the assignments of the far infrared absorption spectra of 2-chlorobutane, the assignments of the observed bands at 1297 and 1286 cm^{-1} differ from the assignments of OPASKAR and KRIMM [1]. These bands, which were both reported not to change in relative intensity upon cooling, were each assigned to both the $\text{H}^{\text{S}}\text{H}$ and $\text{H}^{\text{S}}\text{C}$ isomers. We have assigned the band at 1286 cm^{-1} to the $\text{H}^{\text{S}}\text{H}$ and $\text{H}^{\text{S}}\text{H}^{\text{¶}}$ isomers and the 1297 cm^{-1} band only to the $\text{H}^{\text{S}}\text{H}$ conformation. Our assignments were made

Table 4. Calculated frequencies (in cm^{-1}) and potential energy distributions for 2-chlorobutane

Frequency (a) $\text{H}^{\text{S}}\text{H}$ conformation	Potential energy distribution*
77	$\tau_2(92)$
189	$\tau_3(83)$
223	$\text{CCC}(30), W_2(24)$
245	$\tau_1(91)$
321	$W_2(49), X_{\pi}(41)$
388	$W_1(52), \text{CCC}(16)$
461	$\text{CCC}(27), W_1(24)$
612	$X(80), W_2(8)$
791	$r(55), B_{2i}(42)$
841	$R_2(39), B_{1i}(21)$
957	$B_{2r}(43), H_{\pi}(16)$
996	$B_{1r}(24), w(16)$
1016	$R_3(30), R_1(20)$
1071	$B_{2r}(17), r(15)$
1106	$R_1(43), R_2(10)$
1162	$R_2(23), B_{1r}(17)$
1231	$H_{\sigma}(53), t(19)$
1291	$H_{\sigma}(27), t(26)$
1302	$H_{\pi}(28), w(22)$
1353	$U_i(23), U_r(21)$
1384	$U_r(56), U_i(33)$
1395	$U_i(31), w(22)$
1426	$\delta(88)$
1458	$A_{1r}(51), A_{1i}(32)$
1458	$A_{2i}(88)$
1460	$A_{2r}(81), A_{1r}(8)$
1462	$A_{1i}(54), A_{1r}(29)$
(b) $\text{H}^{\text{S}}\text{C}$ conformation	
83	$\tau_2(80), \tau_3(18)$
200	$\tau_3(78)$
227	$W_2(31)$
250	$\tau_1(69), W_2(14)$
308	$X_{\pi}(79)$
375	$\text{CCC}(29), X(25)$
423	$W_1(67), W_2(14)$
671	$X(82), W_2(15)$
788	$r(53), B_{2i}(39)$
852	$R_2(39), B_{1i}(16)$
947	$B_{2r}(28), B_{1r}(17)$
970	$t(23), B_{2i}(22)$
1008	$R_3(27), B_{2r}(24)$
1067	$B_{1i}(27), R_3(21)$
1135	$R_1(27), R_2(14)$
1159	$B_{1r}(18), R_2(17)$
1245	$H_{\sigma}(70), t(7)$
1255	$t(34), H_{\sigma}(20)$
1318	$w(28), t(22)$
1362	$U_r(31), H_{\pi}(15)$
1381	$U_i(45), U_r(42)$
1398	$U_i(24), w(23)$
1428	$\delta(83)$
1458	$A_{2i}(34), A_{1r}(33)$
1458	$A_{2i}(57), A_{1r}(21)$
1460	$A_{2r}(86)$
1462	$A_{1i}(54), A_{1r}(29)$

* For definitions of torsion coordinates see Ref. [9], for others see Ref. [1].

† The $\text{H}^{\text{S}}\text{H}$ conformation was not used in the refinement procedures.

Table 4. (continued)

Frequency	Potential energy distribution*
(c) $\text{HSH}'\dagger$ conformation	
72	$\tau_2(93)$
195	$\tau_3(87)$
215	CCC(49), $W_1(31)$
243	$\tau_1(93)$
334	$X_{\pi}(52)$, $W_2(27)$
341	$W_2(52)$, $X_{\pi}(26)$
514	$X(33)$, CCC(25)
642	$X(71)$, $W_1(22)$
793	$r(53)$, $B_{2i}(44)$
840	$R_2(45)$, $R_3(16)$
944	$R_3(24)$, $R_1(22)$
991	$B_{2r}(30)$, $B_{1r}(21)$
997	$B_{1i}(19)$, $B_{1r}(17)$
1064	$B_{1i}(18)$, $B_{2r}(15)$
1115	$B_{1r}(19)$, $R_2(11)$
1145	$R_1(29)$, $r(14)$
1236	$H_{\sigma}(58)$, $i(17)$
1280	$i(39)$, $H_{\sigma}(23)$
1322	$H_{\sigma}(32)$, $R_2(23)$
1351	$U_i(30)$, $w(30)$
1381	$U_r(87)$
1393	$U_i(57)$, $w(24)$
1428	$\delta(92)$
1458	$A_{2i}(88)$
1459	$A_{1r}(60)$
1460	$A_{2r}(87)$
1462	$A_{1i}(60)$, $A_{1r}(26)$

solely on the basis of the results of the 2-chlorobutane normal coordinate analyses and the force field refinement. However, a very recent investigation by BENEDETTI and CECCHI [12] lends support to this assignment. Benedetti and Cecchi observed both the liquid and crystalline phase spectra of 2-chlorobutane. These spectra show that upon cooling the bands at 1297 and 1286 cm^{-1} increase in intensity. The intensity enhancement is greater at 1297 than at 1286 cm^{-1} . This temperature dependence suggests two things: (1) not all of the isomers present in liquid 2-chlorobutane contribute to the absorptions at 1286 and 1297 cm^{-1} ; (2) the combination of isomers

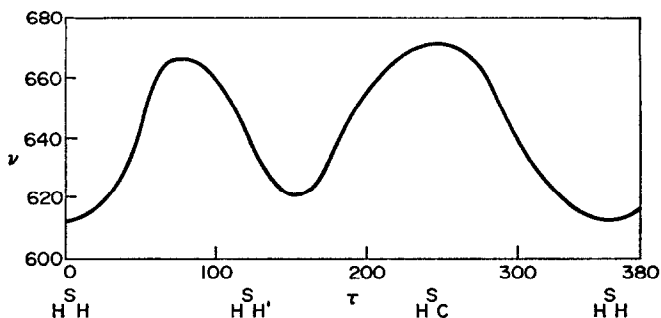


Fig. 1. Carbon-chlorine stretching frequency as a function of $\text{C}_2\text{—C}_3$ torsion angle in 2-chlorobutane.

which contribute to the band at 1286 cm^{-1} is different from that which contributes to the 1297 cm^{-1} band. With the assignment of the absorption at 1286 cm^{-1} to both the ${}_{\text{H}}\text{S}_{\text{H}}$ and ${}_{\text{H}}\text{S}_{\text{H}'}$ isomers, the intensity of this band would be expected to increase less at low temperatures than that of the 1297 cm^{-1} band, which at room temperatures has contributions only from the ${}_{\text{H}}\text{S}_{\text{H}}$ isomeric form.

2,4-Dichloropentane

The ${}_{\text{H}}\text{S}_{\text{H}}\text{H}\text{S}_{\text{H}}$ form of syndiotactic DL-2,4-dichloropentane and the ${}_{\text{H}}\text{S}_{\text{H}}\text{C}\text{S}_{\text{H}}$ form of isotactic meso-2,4-dichloropentane were also included in the least squares refinement. Results of normal coordinate calculations, and observed frequencies, are given in Tables 5 and 6.

Table 5. Observed and calculated frequencies (in cm^{-1}) and potential energy distributions of TT conformer of DL-2,4-dichloropentane

Observed frequency*	Calculated frequency	Potential energy distribution
	42 A	$\tau_{A2}(96)$
	58 B	$\tau_{B2}(90)$
120	120 A	CCC(52), $W_{A1}(29)$
	240 A	$\tau_{A1}(96)$
245 vw	241 B	$\tau_{B1}(91)$
273	267 A	$W_{A1}(43)$, $X_{\tau A}(39)$
310	312 B	$X_{\tau B}(44)$, $W_{B1}(33)$
343 m	342 B	$X_{\tau B}(42)$, $W_{B1}(39)$
368 m	371 A	$W_{A2}(65)$, $W_{A1}(10)$
460 m	458 B	$W_{B2}(74)$, $W_{B1}(12)$
(476 w)	472 A	$X_{\tau A}(28)$, CCC(26)
606 s	603 B	$X_B(84)$
627 s	625 A	$X_A(81)$
	{ 872 B	$r(59)$, $B_{B1}(23)$
(877 ms)	{ 884 A	$R_{A2}(40)$, $B_{A1}(29)$
938 s	939 B	$R_{B1}(25)$, $R_{B2}(23)$
978 m	985 A	$B_{A2}(35)$, $B_{A1}(33)$
1012 s	1023 B	$B_{B2}(61)$, $R_{B1}(10)$
1067 m	1068 B	$R_{B1}(44)$, $B_{B1}(30)$
1100 vw	1102 A	$R_{A1}(54)$, $t(10)$
1125 s	1119 A	$R_{A2}(21)$, $B_{A2}(19)$
1132 s	1139 B	$R_{B2}(42)$, $H_{\tau B}(10)$
1191 m	1188 A	$t(28)$, $H_{\sigma A}(23)$
1222 vvw	$2 \times 606 = 1212$	
1257 s	1252 B	$H_{\sigma B}(85)$
	1230 B	$w(44)$, $H_{\tau B}(36)$
(1288s)	1292 A	$H_{\sigma A}(51)$, $t(25)$
1325 mw	1325 A	$H_{\tau A}(56)$, $R_{A1}(15)$
	1361 B	$U_B(48)$, $w(23)$
1379 s	1381 A	$U_A(89)$
(1415 ms)	1397 B	$U_B(46)$, $H_{\tau B}(19)$
	1427 A	$\delta(95)$
	1459 A	$A_{A1}(72)$, $A_{A2}(18)$
(1443 s)	1459 B	$A_{B1}(78)$, $A_{B2}(20)$
(1450 m)	1459 B	$A_{B2}(80)$, $A_{B1}(10)$
	1460 A	$A_{A2}(72)$, $A_{A1}(18)$

* Ref. [1] and [9].

† For definitions of symmetry coordinates see Ref. [1] and [9].

Frequencies in parenthesis were not used in the refinement procedure.

Table 6. Observed and calculated frequencies (in cm^{-1}) and potential energy distributions of TG' conformer of *meso*-2,4-dichloropentane

Observed frequency	Calculated frequency	Potential energy distribution*
	49	$\tau_{B2}(82), \tau_{A2}(12)$
	56	$\tau_{A2}(75), \tau_{B2}(13)$
118	129	CCC(49), $W_{B1}(37)$
228	232	$X_{TA}(54), \tau_{B2}(22)$
	242	$\tau_{A1}(96)$
245 w	245	$\tau_{B1}(73)$
315 m	316	$W_{A1}(74)$
345 w	342	$X_{TB}(51), W_{B1}(23)$
392 w	393	$W_{A2}(64), X_{TB}(8)$
410 ms	405	$X_{TA}(18), \text{CCC}(15)$
460 w	466	$W_{B2}(63), W_{B1}(9)$
611 vs	615	$X_A(61), X_B(42)$
680 vs	674	$X_B(45), X_A(37)$
855 s	861	$r(42), R_{A1}(10)$
882 m	895	$R_{A2}(25), B_{A1}(21)$
926 s	921	$B_{B1}(26), R_{B2}(22)$
980 ms	989	$B_{B1}(31), B_{A2}(26)$
1006 s	1009	$B_{B2}(40), B_{A2}(16)$
1058 s	1059	$R_{A1}(32), t(13)$
1089 mw	1096	$R_{B1}(27), R_{A1}(15)$
1130 vs	1132	$R_{B1}(18), R_{A2}(16)$
	1145	$R_{B2}(22), B_{B2}(12)$
1199 m	1196	$t(31), H_{\sigma A}(26)$
1237 s	1246	$H_{\sigma B}(50), H_{\sigma A}(35)$
1272 s	1271	$H_{\sigma B}(30), H_{\sigma A}(28)$
1289 m	1291	$w(38), H_{\sigma A}(28)$
1337 mw	1335	$H_{TA}(40), t(22)$
1360	1365	$U_B(54), R_B(17)$
1378 vs	1382	$U_A(88)$
1415 vw	?1398	$U_B(39), H_{TB}(22)$
1427 w	1429	$\delta(91)$
1439 s	1459	$A_{A1}(73), A_{B2}(16)$
	1460	$A_{B1}(69), A_{B2}(16)$
1453 s	1460	$A_{A2}(59), A_{B2}(15)$
	1460	$A_{B2}(42), A_{A2}(29)$

* For definitions of symmetry coordinates see Ref. [1] and [9].

The force field for secondary chlorides predicts the observed spectra of the two dominant forms of DL- and *meso*-2,4-dichloropentane very well. In both isomers a band at 1415 cm^{-1} was observed. This absorption is strong in the spectrum of syndiotactic 2,4-dichloropentane and weak in the spectrum of the isotactic configuration. Absorption at 1415 cm^{-1} is also observed in the spectrum of isotactic 2,4,6-trichloroheptane [6]. The assignment of this band to a combined H—C—Cl bending and methyl bending is tentative. A Raman band at 1415 cm^{-1} in the spectrum of crystalline polyethylene has also caused assignment problems. This band was originally assigned to the B_{2g} methylene wagging mode [23]. More recently [14, 24] the wagging fundamental has been reassigned to an infrared band at 1382 cm^{-1} leaving

[23] J. H. SCHACHTSCHNEIDER and R. G. SNYDER, *Spectrochim. Acta* **19**, 117 (1963).[24] R. G. SNYDER, *J. Mol. Spectry* **23**, 224 (1967).

the Raman band at 1415 cm^{-1} unassigned. In 2,4-dichloropentane, 2,4,6-trichloroheptane, and in poly(vinyl chloride), bands appear at approximately 1427 cm^{-1} . Strong absorption between 1447 and 1460 cm^{-1} is present in the spectra of all secondary chlorides. We assign this strong unresolved absorption to asymmetric methyl bending modes which occur in the same general region in the *n*-paraffins. The bands in the region around 1430 cm^{-1} have been assigned to the HCH scissors fundamental of the methylene group. This assignment is verified by observing the spectra of poly(vinyl chloride), in which effects of methyl bending are not present [25].

MODEL COMPOUNDS NOT USED FOR FORCE FIELD REFINEMENT

To establish the validity of the force field, it was used to calculate the normal frequencies of 3-chloropentane, axial and equatorial monochlorocyclohexane, and several rotational isomers of each of the stereochemical forms of 2,4,6-trichloroheptane. Detailed assignments of the observed absorption spectra of the stereoisomers of 2,4,6-trichloroheptane will be discussed in a subsequent publication.

The results of normal coordinate calculations of equatorial and axial monochlorocyclohexane parallel those previously reported by OPASKAR and KRIMM [1]. The ${}_C S_C$ carbon-chlorine stretching frequency at 728 cm^{-1} in the equatorial form is calculated at 722 cm^{-1} . The two observed absorptions at 557 cm^{-1} and at 683 cm^{-1} in axial monochlorocyclohexane are both C—Cl stretching bands. This splitting of ${}_H S_{H'}$ C—Cl stretching was previously predicted [1]. Although we calculate a splitting, viz. 543 cm^{-1} and 705 cm^{-1} , the higher frequency does not agree well with the observed band at 683 cm^{-1} . The $\text{CH}_2\text{—CHCl—CH}_2$ environment was not present in any of the model compounds used in the refinement process. As a result, the force field was not refined to a ${}_H S_{H'}$ C—Cl stretching frequency. Moreover, in 2-chlorobutane, the frequency of the ${}_H S_{H'}$ C—Cl stretching vibration was found to be very sensitive to small variations in the dihedral angle around the *gauche* C—C bond. The discrepancy between the observed (683 cm^{-1}) and calculated (705 cm^{-1}) frequencies could presumably result from both of these factors.

3-Chloropentane

At room temperature, 3-chloropentane is considered to exist as a mixture of four rotational isomers, i.e. ${}_H S_H$, ${}_C S_H$, ${}_H S_{H'}$, and ${}_C S_{H'}$. The results of our calculations are given in Tables 7 and 8.

SHIPMAN *et al.* [10] and CARACULACU [26] independently studied the isomeric composition of 3-chloropentane by correlating the observed spectra in the region of the C—Cl stretching vibrations, $590\text{--}750\text{ cm}^{-1}$, with the rotational isomers believed to be characteristic of them. The study by Caraculacu included complete infrared and Raman spectra for liquid and solid phases of 3-chloropentane. In the region of the C—Cl stretching vibrations, a band observed at 606 cm^{-1} , which is assignable only to ${}_H S_H$ C—Cl stretching, persists in the solid state Raman and infrared spectra. As in 2-chlorobutane, the behavior of this band was assumed to be characteristic of

[25] S. KRIMM, V. L. FOLT, and J. J. SHIPMAN, *J. Polymer Sci.* **A1**, 2621 (1963).

[26] A. CARACULACU, J. ŠTOKR and B. SCHNEIDER, *Collection Czech. Chem. Commun.* **29**, 2783 (1964).

Table 7. Observed and calculated frequencies (in cm^{-1}) of 3-chloropentane

Observed frequency*				Calculated frequency			
Infrared		Raman		ν_{SH}	ν_{SH}	ν_{SH}	ν_{SH}
Liquid	Solid	Liquid	Solid				
		72	72	66	72	69	55
		80	80	82	78	74	91
		168	164	174	180	173	185
		194		197	201	194	193
		206	209	202		201	
		238	241	258	226		236
					243		241
		292	—			274	
						331	320
		362	—		348		
		374 ms	371 ms	362			
		398 s	—		397	408	381
400	—	426 s	427 s	430			
425 vw	425 w	457 w	—		464		
460 vw	—			474			
		533 ms	—			541	530
533 m	—	606 s	594 vs	615			
606 m	594 s	633 ms	—			641	
634 m	—	657 s	—		675		
657 sh	—	668 sh	—				694
667 sh	—	775 vw	762	774	777		785
776 m	768 vw	793 vw	—			783	800
795 m	—	812 ms	—		804	806	
811 s	—	824 ms	819 m	813			
826 s	820 m	849 ms	—			862	855
850 s	—	—	—		869		
870 s	—	875 ms	876 m	880			
876 s	878 s	916 w	—			909	906
915 m	—	927 w	927	929	925		
927 m	932 w			997	998	1006	987
		1016 ms	1015 vw	1023	1008	1015	1012
1019 w	1017 sh	1032 s	1035 sh				
1036 w	1036 m	1046 m	1043 w	1037	1033	1033	1032
1048 sh	1046 w				1065		1067
		1079 m	1078 w	1077		1071	
1080 m	1084 w	1107 m	1106 w	1106		1091	1110
1106 w	1110 vw	1123 m	—		1127		
1127	—	1145 m	1145 w	1146			
1145 sh	1148 w	1154 wsh	1154 w		1151	1155	1157
1154 m	1162	1229	1236	1225	1225	1223	1229
1231 s	1236 m	—	—	1254	1246		1243
1249 vwsh	1249 ^{sh} _{vw}					1269	
		1278 m	1278 m	1279		1273	1282
1278 m	1276 w	1307 w	1310 m		1290	1310	
1307 msh	—	—	—	1311	1314		1321
1316 s	1319 s	—	—	1353	1346	1348	1343
1333 w	—	1367 w	1368 vw	1367	1372	1366	1371
1342 w	1348 vw	1387 vw	—	1389	1389	1388	1387
—	1370 m	—	—	1393	1394	1393	1398
1386 s	1386 vw	1442 s	1442 s	1440	1440	1442	1444
		1455 s	1448 s	1444	1448	1446	1445
1442 m	1432	1458	1458	1458	1458	1458	1458
1457 s	1451 m	1461	1461	1461	1461	1461	1461
		1466 sh	1464 sh	1462	1462	1462	1462
1465 s	1467 m						

* Ref. [26].

Table 8. Calculated frequencies (in cm^{-1}) and potential energy distributions for 3-chloropentane

Calculated frequency	Potential energy distribution*	
(a) $\text{H}^{\text{S}}\text{H}$		
66	A'	$\tau_3(42), \tau_2(42)$
82	A''	$\tau_3(49), \tau_3(49)$
174	A'	$W_2(56), \text{CCC}_2(24), \text{CCC}_1(24)$
197	A''	$\tau_4(31), \tau_1(31), X_{\tau}(25)$
202	A'	$\tau_1(39), \tau_4(39), W_1(10)$
258	A''	$X_{\tau}(42), \tau_1(14), \tau_4(14)$
362	A'	$W_2(24), W_1(19), X(10)$
430	A'	$W_1(48)$
474	A''	$\text{CCC}_1(34), \text{CCC}_2(34), X_{\tau}(23)$
615	A'	$X_1(96)$
774	A''	$r_1(34), r_2(34)$
813	A'	$B_{21}(26), B_{22}(26), r_1(21), r_2(21)$
890	A'	$B_{11}(25), B_{12}(25), R_1(16), R_2(16)$
929	A''	$R_1(20), R_4(20), B_{11}(12), B_{12}(12)$
997	A''	$B_{21}(17), B_{22}(17), H_{\tau}(16)$
1023	A'	$R_4(19), R_1(19)$
1037	A''	$B_{11}(26), B_{12}(25), R_1(12), R_4(12)$
1077	A'	$r_1(9), r_2(9), R_1(7), R_2(7)$
1106	A''	$R_2(27), R_3(27)$
1146	A'	$R_2(12), R_3(12)$
1225	A'	$H_{\sigma}(53), t_2(9), t_1(9)$
1254	A''	$H_{\tau}(23), t_1(15), t_2(15)$
1279	A''	$H_{\tau}(25), t_1(15), t_2(15)$
1311	A'	$H_{\sigma}(32), t_1(26), t_2(26)$
1353	A'	$w_1(23), w_2(23)$
1367	A''	$U_1(22), U_2(22)$
1389	A'	$U_1(32), U_2(32)$
1393	A''	$U_1(23), U_2(23)$
1440	A'	$\delta_1(48), \delta_2(48)$
1444	A''	$\delta_1(46), \delta_2(46)$
1458	A'	$A_{21}(45), A_{22}(45)$
1458	A''	$A_{21}(45), A_{22}(45)$
1461	A'	$A_{11}(44), A_{12}(44)$
1462	A''	$A_{11}(43), A_{12}(43)$
(b) $\text{O}^{\text{S}}\text{H}$		
72		$\tau_2(88), \tau_3(13)$
78		$\tau_3(83)$
180		$W_2(39), \tau_4(26)$
201		$\tau_1(52), \tau_4(33)$
226		$X_{\tau}(42), \text{CCC}_2(21), \text{CCC}_1(14)$
243		$\tau_4(30), \tau_1(22), W_2(22)$
348		$\text{CCC}_2(34), X_{\tau}(23), \text{CCC}_1(12)$
397		$W_1(47), X(16)$
464		$\text{CCC}_1(24), W_1(19)$
675		$X(70), \text{CCC}_2(14)$
777		$r_2(52), B_{22}(31)$
804		$r_1(43), B_{21}(42)$
869		$B_{11}(24), R_2(22)$
925		$B_{12}(31), R_4(20)$
998		$t_2(17), B_{21}(15)$
1008		$R_1(29), B_{21}(10)$
1033		$R_4(29), B_{12}(18)$
1065		$R_1(17), B_{11}(17)$
1127		$R_3(38), B_{12}(14)$
1151		$R_2(19), r_2(16), B_{22}(11)$
1225		$H_{\sigma}(60), t_1(15)$

* The torsion coordinates (τ) are defined in Ref. [1]. Other symmetry coordinates are similar to those defined in Ref. [9].

Table 8. (continued)

Calculated frequency	Potential energy distribution*
1246	$t_2(29), H_\pi(24), B_{22}(13)$
1290	$t_1(47), H_\sigma(21)$
1314	$w_1(28), t_2(23), H_\pi(17)$
1346	$w_2(33), U_2(20)$
1372	$U_1(33), U_3(20)$
1389	$U_2(37), U_1(30), w_2(11), w_1(10)$
1394	$U_1(19), U_3(17), w_2(16), w_1(15)$
1440	$\delta_1(75), \delta_2(20)$
1448	$\delta_2(62), \delta_1(21)$
1458	$A_{22}(78), A_{21}(12)$
1458	$A_{21}(78), A_{22}(12)$
1461	$A_{12}(86)$
1462	$A_{11}(82)$
(c) HS_{H}	
69	$\tau_2(94)$
74	$\tau_3(92)$
173	$\text{CCC}_2(23), W_2(20), X_\pi(19), \text{CCC}_1(18)$
194	$\tau_1(47), \tau_4(17)$
201	$\tau_4(57), \tau_1(25)$
274	$\text{CCC}_1(25), \text{CCC}_2(19), \tau_4(15)$
331	$W_2(36), X_\pi(35)$
408	$\text{CCC}_2(37), X_\pi(16), W_1(14), X(10)$
541	$X(26), \text{CCC}_1(23), W_1(12)$
641	$X(70), W_1(19)$
783	$r_1(39), B_{21}(27), r_2(16), B_{22}(10)$
806	$B_{22}(34), r_2(33), B_{21}(14), r_1(12)$
862	$B_{12}(21), R_2(19), R_3(17), R_1(16)$
909	$R_1(24), B_{11}(18), R_3(12)$
1006	$R_4(21), B_{23}(13), t_2(11)$
1015	$B_{11}(36), w_1(14)$
1033	$B_{12}(28), R_4(16), B_{21}(12)$
1071	$r_2(14), B_{22}(11)$
1091	$R_2(15), B_{12}(13), w_1(11)$
1155	$R_3(30), r_1(11)$
1223	$H_\sigma(50), t_2(11)$
1269	$t_1(40), t_2(25)$
1273	$H_\pi(33), R_2(22)$
1310	$t_2(22), H_\sigma(20), t_1(19), w_2(15)$
1348	$w_1(33), R_1(19), R_2(12), w_2(13)$
1366	$U_2(26), H_\pi(21), U_1(16)$
1388	$U_1(37), U_3(33), w_1(11)$
1393	$U_1(24), U_3(23), w_2(16), w_1(14)$
1442	$\delta_2(84), \delta_1(10)$
1446	$\delta_1(78), \delta_2(10)$
1458	$A_{22}(63), A_{21}(28)$
1458	$A_{21}(62), A_{22}(28)$
1461	$A_{11}(59), A_{12}(28)$
1462	$A_{12}(56), A_{11}(26)$
(d) CS_{H}	
55	$\tau_2(59), \tau_3(40)$
91	$\tau_3(51), \tau_2(34)$
185	$\tau_4(38), \tau_1(20), W_2(20)$
193	$\tau_1(43), W_1(15), \text{CCC}_1(15)$
236	$\text{CCC}_1(22), W_1(20), \tau_1(20)$
241	$\tau_4(28), W_2(20), X_\pi(20), \text{CCC}_2(19)$
320	$X_\pi(55)$
381	$\text{CCC}_2(29), X(25), W_2(23)$
530	$\text{CCC}_1(31), W_1(26), X(12)$
694	$X(65), W_1(13)$
785	$r_2(41), B_{22}(31), R_2(13)$
800	$r_1(43), B_{21}(42)$

Table 8. (continued)

Calculated frequency	Potential energy distribution*
855	$R_2(25), B_{22}(18), R_1(16)$
908	$B_{13}(24), R_3(16), R_1(14), R_4(11)$
987	$R_4(20), R_1(13), w_2(11)$
1012	$B_{11}(37), R_1(16), H_\pi(12)$
1032	$R_4(27), B_{12}(18)$
1087	$B_{12}(18), r_1(13), B_{21}(12), t_1(12)$
1110	$r_2(11), H_\pi(11)$
1157	$R_3(29), r_1(10)$
1229	$H_\sigma(66), t_1(12)$
1243	$t_3(35), H_\pi(15), B_{33}(14)$
1282	$t_1(54), H_\sigma(17)$
1321	$w_2(27), t_2(23), H_\pi(22)$
1343	$w_1(37), R_1(18), R_3(16), U_1(16)$
1371	$U_2(44), U_1(16), H_\pi(15), R_4(13)$
1387	$U_1(50), U_2(23), w_1(11)$
1398	$w_2(23), U_2(19), w_1(14)$
1444	$\delta_2(82)$
1445	$\delta_1(82)$
1458	$A_{22}(64), A_{21}(27)$
1458	$A_{21}(64), A_{22}(27)$
1461	$A_{11}(54), A_{12}(34)$
1462	$A_{12}(50), A_{11}(31)$

all fundamental vibrational frequencies of the ${}_H S_H$ isomer. Therefore, at low temperatures an intensity enhancement of vibrations associated with the ${}_H S_H$ isomer is expected due to the presence of more molecules in the totally planar zig-zag configuration.

The other C—Cl stretching frequencies observed at 634 cm^{-1} , 657 cm^{-1} , and 667 cm^{-1} , respectively, are calculated at 641 cm^{-1} , 675 cm^{-1} , and 694 cm^{-1} for the ${}_H S_H$, ${}_C S_H$, and ${}_O S_H$ isomers, respectively (see Tables 7 and 8). The exact geometries assumed by the non-planar forms of 3-chloropentane are presently not known. The works of SCHNEIDER [5] and SÝKORA [27] indicate that, for non-trans conformations, the assumption of a staggered model is not valid. However, these authors have indicated that the staggered approximation is a good model for preferred conformations even when these conformations are non-planar. In light of this we have not addressed ourselves to resolving discrepancies between the observed and calculated frequencies for the ${}_C S_H$ and ${}_O S_H$ isomers of 3-chloropentane.

The region of the spectrum below the C—Cl stretching vibrations is due to torsional, skeletal, and C—C—Cl bending modes. In each isomer there are four torsional modes. The methyl torsions are predicted to occur at 202 and 197 cm^{-1} in the ${}_H S_H$ isomer, at 243 cm^{-1} and 201 cm^{-1} in the ${}_C S_H$ isomer, at 201 and 194 cm^{-1} in the ${}_H S_H$ isomer, and at 241 and 193 cm^{-1} in the ${}_O S_H$ isomer. The agreement between these torsional modes and the observed bands at 238 , 206 and 194 cm^{-1} supports the value of $0.0775\text{ m dyn-Å/rad}^2$ for this torsional force constant. The $\text{CH}_2\text{—CHCl}$ torsional force constant of $0.0744\text{ m dyn-Å/rad}^2$ and the interaction torsional force constant of $0.008\text{ m dyn-Å/rad}^2$ are almost totally responsible for predicting the torsional modes below 100 cm^{-1} . Raman bands are observed at

[27] S. SÝKORA, *Collection Czech. Chem. Commun.* **33**, 3514 (1968).

approximately 80 and 72 cm^{-1} for both liquid and solid phase samples of 3-chloropentane. These bands are assigned to the $\text{CH}_2\text{—CHCl}$ torsions of ${}_H S_H$ 3-chloropentane, which are calculated at 82 and 66 cm^{-1} . The excellent correlation which exists between the assignment of this torsion in 2-chlorobutane (observed at 77 cm^{-1} , calculated at 83 cm^{-1}) and the assignment in 3-chloropentane confirms the choice of the $\text{CH}_2\text{—CHCl}$ torsional force constant.

In the region of the spectrum between 990 cm^{-1} and 1070 cm^{-1} three separate bands are observed and either three or four frequencies are predicted for each isomer. Specific assignments in this region are not made. The band observed at 1019 cm^{-1} decreases in strength when observed in the solid state. Its assignment [26] to the ${}_H S_H$ isomer is considered questionable. Although three frequencies are predicted in this region for the ${}_H S_H$ conformation, none of the observed bands in this region displays the enhancement of infrared and Raman intensities which is assumed to be characteristic of the fundamental frequencies of the ${}_H S_H$ isomer. In the region of 1310–1350 cm^{-1} the same general features prevail. Any specific assignments would be pure conjecture.

CONCLUSIONS

We have refined a complete valence force field which effectively predicts the normal vibration frequencies of a group of secondary chlorides and related polymers. This force field, which includes elements relating to torsional and intermolecular vibrations, was obtained by using tetrahedral geometry and staggered conformations. The good agreement between observed and calculated frequencies encourages us to believe that this force field can be used in conjunction with energy calculations to give specific answers to questions concerning molecular configuration and conformation in secondary chlorides. The force field also satisfactorily predicts intermolecular frequencies which will be discussed in detail in a subsequent paper [19].

Acknowledgement—This research was supported by National Science Foundation Grant GP-27717.