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Assignment of torsion and low frequency bending vibrations of secondary chlorides

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Abstract—Far infrared and Raman spectra of 2-chloropropane, 2-chlorobutane and *dl*- and meso-2,4-dichloropentane have been analyzed in order to assign the torsional force constants in the valence force field for secondary chlorides. Band assignments have been based on experimental data as well as preliminary normal vibration calculations. With incorporation of torsional force constants, and a global refinement of the force field, the observed low frequency bands of the above molecules, as well as those of 3-chloropentane, are very well accounted for.

Introduction

During the last decade normal coordinate analysis has been used effectively as a spectroscopic tool in the study of molecular and polymer structure [1–9]. In addition to work on hydrocarbon polymers, some effort has been devoted to the use of such analyses of the characteristics of vibrational spectra to study the conformational structure of secondary chlorides and related polymers [10–13]. In most of these studies the bending and torsional modes which occur at frequencies below 300 cm^{-1} have been inadequately treated. In many cases this region of the spectrum has been completely neglected. This neglect has been justified on the basis that torsional modes have a relatively small effect on other infrared vibrations, i.e., internal rotations are isolated and uncoupled to other intramolecular vibrations. As early as 1965, however, Miyazawa and Fukushima [14] warned that, for significant refined treatments of the methylene (CH_2) rocking and C—C—Cl bending vibrations, the modes due to internal rotation could not be ignored. However, the lack of experimental data on these far infrared bands made it impossible to include force constants for the prediction of internal rotation vibrations in force field refinement procedures. The single exception is ethane. The general valence force field for ethane [1] contains

[1] R. G. Snyder, *J. Chem. Phys.* **47**, 1316 (1967).
[2] C. G. Opaskar and S. Krimm, *Spectrochim. Acta* **23A**, 2261 (1967).
[3] C. G. Opaskar and S. Krimm, *J. Polymer Sci.* (*A2*) **7**, 57 (1969).
[4] E. Benedetti and P. Cecchi, *Spectrochim. Acta* **28A**, 1007 (1972).
[5] R. G. Snyder, *J. Mol. Spectry.* **28**, 273 (1968).
[6] R. G. Snyder and J. H. Schachtschneider, *J. Mol. Spectry* **30**, 290 (1969).
[7] B. L. Crawford and S. R. Brinkley, *J. Chem. Phys.* **9**, 69 (1941).
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[11] J. H. Schachtschneider and R. G. Snyder, *J. Polymer Sci.* **C7**, 99 (1964).
[12] M. Tasumi, T. Shimaouchi and T. Miyazawa, *J. Mol. Spectry* **11**, 422 (1963).
[13] J. Jakeš and S. Krimm, *Spectrochim. Acta* **27A**, 35 (1971).
[14] T. Miyazawa and K. Fukushima, *J. Mol. Spectry* **15**, 308 (1965).

a diagonal torsion force constant, $H_\tau = 0{\cdot}072$ mdyn-Å/rad.[2] which was taken to fit the torsional frequency of ethane at 280 cm^{-1} [15].

This force constant for internal rotation in ethane has been transferred without change to the force fields of the normal paraffins and polyethylene [1], neo-pentane [16], primary chlorides [6], secondary and primary bromides [5] and very recently to secondary iodides [4]. In our study of secondary chlorides, which incorporates far infrared and Raman data, we have found that this torsional force constant is not transferable. The force constants which are required in order to predict the frequencies of hindered rotations in ethane, 1-chloroethane, 2-chloropropane and 2-chlorobutane are determined not simply by the presence of a methyl rotor but also by the other constituents attached to the carbon–carbon bond around which the torsional vibrations occur. Moreover, for 2-chloropropane the two torsional modes interact and the frequencies are split. Unlike propane, in order to reproduce the splitting in a normal coordinate calculation of 2-chloropropane an interaction torsional force constant is needed.

The problem is made more evident by a specific consideration of ethane and its 1-chloro derivative. The ethane molecule (staggered model) possesses D_{3d} symmetry and its torsional mode, which belongs to the A_{1u} symmetry species, is both infrared and Raman inactive. The value of 280 cm^{-1} for the frequency of the internal rotation vibration in ethane was originally determined from specific heat data by KISTIAKOWSKY *et al.* [17]. More recently, GETTY and LEROI [18] reported the frequency of ethane's torsional mode to be 289 cm^{-1}, 310 cm^{-1} and 304 cm^{-1} in the vapor, liquid and solid states, respectively. If these more recent values are correct, and if the torsional force constant for ethane is transferable to a general valence force field for all liquid normal paraffins, the earlier value of $H_\tau = 0{\cdot}072$ mdyn-Å/rad [2] should be adjusted to fit the frequency of the liquid phase torsional mode at 310 cm^{-1} In spite of this apparent inapplicability of a torsional force constant of $H_\tau = 0{\cdot}072$, it does predict well the observed torsional frequencies in propane: the internal rotations in propane are observed at 223 cm^{-1} and 208 cm^{-1} [19], and are predicted by normal coordinate analysis at 220 cm^{-1} and 200 cm^{-1} [1]. With respect to other normal paraffins, no far infrared bands have been reported. As a result, although torsional frequencies have been calculated, no criteria are available for ascertaining their validity.

When the original torsional force constant of SNYDER [1] was used in normal coordinate analyses of primary chlorides and bromides, the correlation between observed and predicted internal rotation frequencies was inferior to that obtained for other frequencies. The torsional vibration at 253 cm^{-1} is predicted at 207 cm^{-1}. A test calculation on 1-chloroethane indicated that a torsional force constant of 0·1174 was required in order to predict the torsional frequency at 253 cm^{-1} as observed. Likewise, the CH_2—CH_2Cl internal rotation in 1-chloropropane is

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[16] R. G. SNYDER and J. H. SCHACHTSCHNEIDER, *Spectrochim. Acta* **21**, 169 (1965).
[17] G. B. KISTIAKOWSKY, J. R. LACHER and F. STETT, *J. Chem. Phys.* **7**, 289 (1939).
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[19] J. N. GAYLES, JR. and W. T. KING, *Spectrochim. Acta* **21**, 543 (1965).

calculated at 94 cm^{-1} [6] when the old value of 0·072 is used for the torsional force constant. It is probable, however, that the band observed at 140 cm^{-1} [23] should be assigned to this CH_2—CH_2Cl internal rotation in 1-chloropropane. Again a torsional force constant which is larger than 0·072 is needed in order to predict the observed frequency of the torsional vibration.

The present work addresses itself to reporting new infrared and Raman spectra below 300 cm^{-1} for 2-chloropropane, 2-chlorobutane and for *dl*- and meso-2,4-dichloropentane, to assigning these and previously observed far infrared and Raman bands, and to the development of torsional force constants for secondary chlorides. The far infrared and Raman spectra of 3-chloropentane, which were recorded by CARACULACU [20], are also assigned.

The WILSON GF method [21] is used to calculate the normal modes of all molecules analyzed. The *s* vectors for atomic motions associated with torsional coordinates are constructed from the sum of three trans-torsional rotations, i.e., the motion of eight atoms. Our approach to the assignment of these modes and the development of the associated torsional force constants for secondary chlorides parallels the method used by OPASKAR and KRIMM [2] to obtain the secondary chloride potential field. Initially the force constant $H_\tau = 0{\cdot}072$ was added to the general valence force field for the 2- and 2,4-chlorine-substituted hydrocarbons. Using this force field, model calculations were done on 2-chloropropane, 2-chlorobutane and on *dl*- and meso-2,4-dichloropentane. From these model calculations the torsional and far infrared bending modes were assigned to observed data. Finally, the entire force field was subjected to a series of least squares refinement procedures. In this paper all of the torsional and bending modes below 360 cm^{-1} are reported with their respective assignments.

EXPERIMENTAL

Low frequency infrared spectra were recorded on a Perkin–Elmer Model 301 spectrometer. Double beam operation was employed, the frequencies being reliable to ± 3 cm^{-1}. For liquid phase spectra, high density polyethylene cells were used. In the low temperature studies, temperatures of 77°K were obtained. CsI and polyethylene windows were used for spectra down to and below 200 cm^{-1}, respectively. The infrared spectra for 2-chloropropane are given in Fig. 1, for 2-chlorobutane in Fig. 2, and for meso-2,4-dichloropentane in Fig. 3. The Raman spectra from 360–100 cm^{-1} of meso- and *dl*-2,4-dichloropentane were recorded on a Spex Ramalog Spectrometer, Model 1401, and are given in Figs. 4 and 5.

ASSIGNMENTS

2-Chloropropane

OPASKAR and KRIMM correctly assigned all of the stretching and bending vibrations of 2-chloropropane by a comparison of its spectrum with that of propane and an analysis of its gas phase infrared band contours [2]. Subsequently,

[20] A. CARACULACU, J. STOKR and B. SCHNEIDER, *Collect. Czech. Chem. Commun.* **29**, 2783 (1964).
[21] E. B. WILSON, JR., J. C. DECIUS and P. C. CROSS, *Molecular Vibrations*, McGraw-Hill, New York (1955).

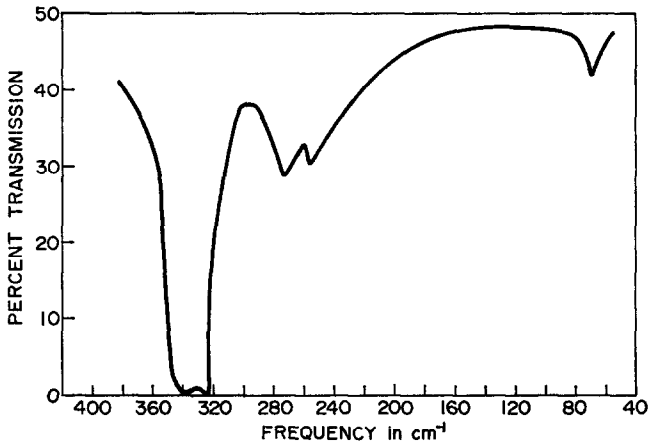

Fig. 1. Low temperature infrared spectrum of 2-chloropropane.

KLABOE [22] recorded the Raman spectrum of 2-chloropropane, verified the assignments of Opaskar and Krimm, and reported two new Raman (and far infrared) bands at 276 cm^{-1} and at 253 cm^{-1}. These modes were assigned by Klaboe to the A'' and A' torsional modes. The absorption band near 276 cm^{-1} has been independently observed by us and others [22, 23]. Although McDevitt *et al.* failed to observe any liquid phase 2-chloropropane absorption near 253 cm^{-1}, they did report a band at 247 cm^{-1} in the solid state spectrum of 2-chloropropane.

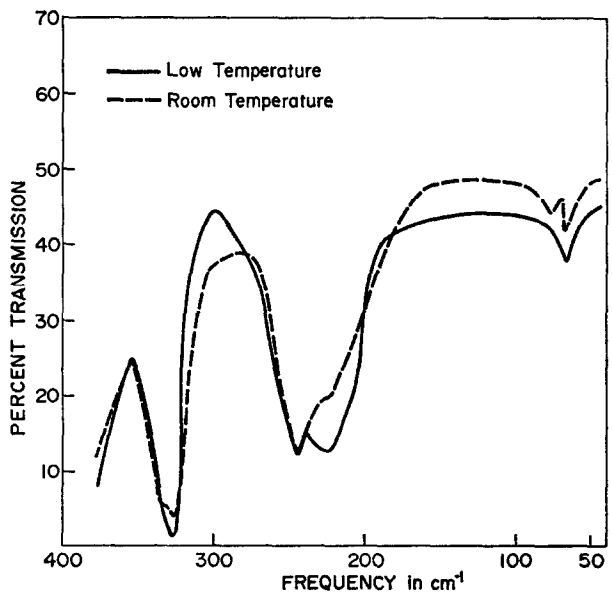

Fig. 2. Infrared spectra of 2-chlorobutane.

[22] P. KLABOE, *Spectrochim. Acta* **26A**, 87 (1970).
[23] N. T. MCDEVITT, A. L. ROZEK, F. BENTLEY and A. D. DAVIDSON, *J. Chem. Phys.* **42**, 1173 (1965).

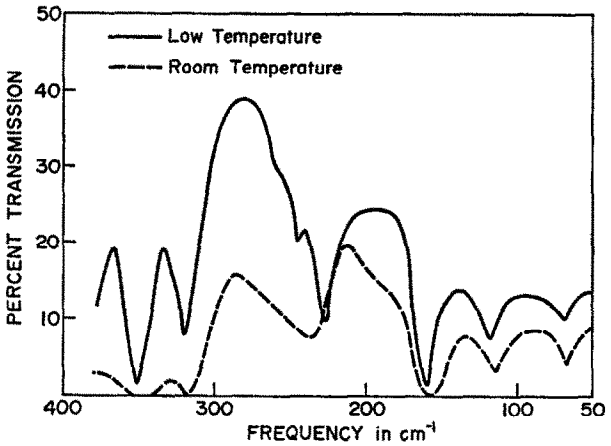

Fig. 3. Infrared spectra of meso-2,4-dichloropentane.

A model normal coordinate calculation which used the earlier force field for secondary chlorides [2] plus $H_\tau = 0{\cdot}072$ was done on 2-chloropropane. This calculation predicted torsional frequencies at 200 cm^{-1} and 198 cm^{-1}. (Recall that the force field which contained this same diagonal force constant, when used in a normal coordinate analysis of propane, predicted a 20 cm^{-1} separation between the frequencies of the symmetric and antisymmetric internal rotations [1].) Our inability to predict any significant splitting in 2-chloropropane caused some concern until another 2-halopropane was considered. In 2-bromopropane, KLABOE [22] observed the two internal rotation frequencies at 267 cm^{-1} and 249 cm^{-1}. MCDEVITT [23] also observed these two frequencies at 265 cm^{-1} and 244 cm^{-1}. However, a force field whose only torsional element is $H_\tau = 0{\cdot}072$ predicts these torsional frequencies at 199 cm^{-1} and 198 cm^{-1} [5].

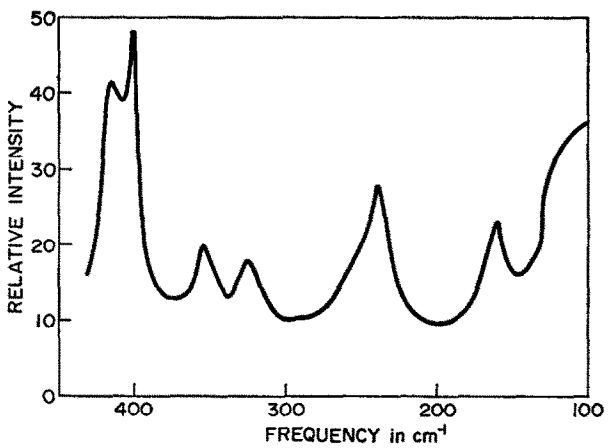

Fig. 4. Raman spectrum of meso-2,4-dichloropentane, at room temperature.

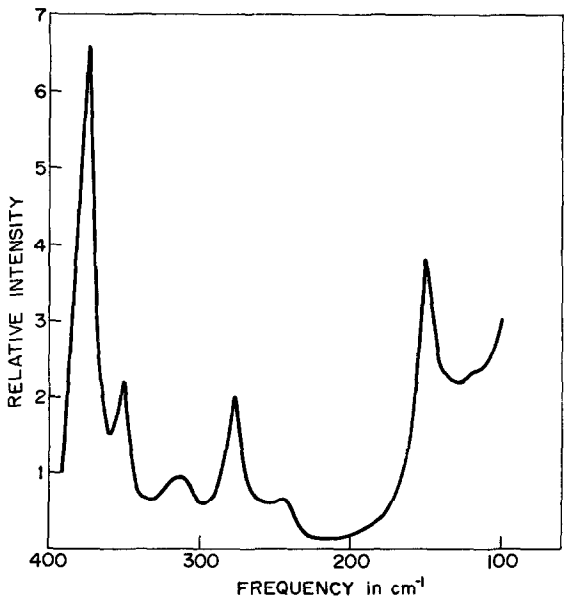

Fig. 5. Raman spectrum of *dl*-2,4-dichloropentane, at room temperature.

The above results emphasize what was indicated by studies of 1-chloroethane and 1-chloropropane, i.e., in halide substituted hydrocarbons larger torsional force constants are required than in the normal paraffins. In addition they show that for the 2-halopropanes an interaction element must be introduced into the force field in order to predict correctly the observed splitting between the two torsional frequencies.

In the torsional portion of our potential field, such an interaction force constant between two CH_3—CHCl torsions was used. By increasing the diagonal force constant from 0·072 to 0·13 mdyn-Å/rad.^{2}, and by introducing an interaction force constant $f_{\tau\tau} = 8{\cdot}0 \times 10^{-3}$, we were able to predict in a normal coordinate analysis of 2-chloropropane two internal rotation frequencies at 273 cm^{-1} and 256 cm^{-1}, as observed. The effect of an interaction force constant is also to improve the frequencies calculated for propane. For example, for $H_\tau = 0{\cdot}0775$ and $f_{\tau\tau} = 0{\cdot}0025$, the torsional frequencies are calculated at 222 cm^{-1} and 208 cm^{-1}, compared to observed values of 223 cm^{-1} and 208 cm^{-1} [19].

2-Chlorobutane

Excluding a very weak shoulder at 290 cm^{-1} which disappears at low temperatures, only three far infrared bands were observed for 2-chlorobutane, at 244 cm^{-1}, 226 cm^{-1} and 77 cm^{-1} (Fig. 2). At low temperatures the band at 226 cm^{-1} shifted to 228 cm^{-1} and increased in intensity relative to the 244 cm^{-1} band. The 77 cm^{-1} band was observed only at room temperature. McDevitt *et al.* [23] also observed the higher two of these three frequencies.

At room temperature 2-chlorobutane exists as a mixture of three rotational isomers, ${}_{H}S_{H}$, ${}_{H}S_{C}$ and ${}_{H}S_{H'}$. (In this notation, the subscripts give the atoms trans

to the Cl atom across the C—C bonds which join at the secondary chlorine C atom.) Since the carbon–chlorine stretching frequencies were known for each of these isomeric forms, OPASKAR and KRIMM [2] assigned the vibrational spectrum of ${}_{H}S_{H}$ 2-chlorobutane by noting that the intensity of the bands associated with this rotational isomer usually increased with decreasing temperature. Their logic leads us to assign the band at 228 cm^{-1} to the ${}_{H}S_{H}$ isomer, the 244 cm^{-1} band to both the ${}_{H}S_{H}$ and ${}_{H}S_{C}$ isomers, and the 77 cm^{-1} band to the ${}_{H}S_{C}$ isomer. Four ${}_{H}S_{H}$ 2-chlorobutane vibrational modes were not assigned by Opaskar and Krimm, a CH_3—CHCl torsion, a CHCl—CH_2 torsion, a CH_2—CH_3 torsion, and a combined C—C—Cl, C—C—C bending mode. Model calculations on the ${}_{H}S_{H}$ and ${}_{H}S_{C}$ isomers predicted the CH_3—CHCl torsion at about 260 cm^{-1}, the CH_2—CHCl at 77 cm^{-1}, the CH_3—CH_2 at 189 cm^{-1}, and the bending mode at approximately 225 cm^{-1}. The potential field used in this calculation contained diagonal torsional force constants of 0·13 mdyn-Å/rad^2 for the CH_3—CHCl torsion and 0·072 mdyn-Å/rad^2 for the other two torsions. As a result of these calculations the band at 244 cm^{-1} was assigned to the CH_3—CHCl internal rotation, the 77 cm^{-1} to the CH_2—CHCl torsion, and the 226 cm^{-1} band to a combined C—C—C and C—C—Cl bending vibration. The CH_3—CH_2 torsional mode was assumed not to be observed. It was necessary in the final refinement procedure to assign slightly different torsional force constants to the CH_3—CHCl internal rotation in 2-chloropropane and in 2-chlorobutane. This initially led us to question these assignments for 2-chlorobutane. However, results for *dl*- and meso-2,4-dichloropentane confirmed the assignments of the 244 cm^{-1} and 228 cm^{-1} bands in 2-chlorobutane. The correctness of the 77 cm^{-1} assignment is verified by our normal coordinate calculations on 3-chloropentane.

2,4-*Dichloropentane*

For the preferred TT conformation of the *dl* stereoisomer of 2,4-dichloropentane, several previously unreported Raman bands were observed, at 315 cm^{-1}, 273 cm^{-1}, 150 cm^{-1} and very weak absorptions at approximately 245 cm^{-1} and 120 cm^{-1}. For the meso conformer of 2,4-dichloropentane, new infrared and Raman data were observed at 245 cm^{-1}, 228 cm^{-1}, 160 cm^{-1} and 118 cm^{-1} (Figs. 3 and 4). Using the same force field which was used to assign the previously unassigned bands of 2-chlorobutane, model calculations were done for the two stereoisomers of 2,4-dichloropentane. The results suggested that the force field could be satisfactorily transferred to 2,4-dichloropentane. The 245 cm^{-1} band was assigned to the CH_3—CHCl torsions in the meso form. The band at 275 cm^{-1} in *dl*-2,4-dichloropentane was identified as a bending mode which shifted to 228 cm^{-1} in the meso isomer. The 120 cm^{-1} and 118 cm^{-1} bands are also bending modes in the *dl*- and meso-forms, respectively.

FORCE FIELD

With the above assignments, the complete force field for secondary chlorides was subjected to a least squares refinement procedure. The method used was the one introduced by KING [24]. Although the final complete secondary chloride force field is reported elsewhere [25], we will describe in a general way the procedure followed.

[24] W. T. KING, I. M. MILLS and B. L. CRAWFORD, *J. Chem. Phys.* **27**, 455 (1957).
[25] W. H. MOORE and S. KRIMM, following paper.

OPASKAR and KRIMM [2] reported a force field for secondary chlorides which was composed of the valence force field for saturated hydrocarbons determined by SNYDER [16] and a force field for primary chlorides which had been adjusted to render it applicable to secondary chlorides [6]. The force field for saturated hydrocarbons has since been adjusted to render it more effective for both planar and nonplanar conformations, i.e., liquid *n*-paraffins [1]. This new force field, combined with the force field for secondary chlorides, made up the initial potential field used in this work. After the assignments described above had been made, all force constants which had been transferred from Ref. [2] and all torsional force constants were refined. The observed frequencies of 2-chloropropane, ${}_{H}S_{H}$ and ${}_{H}S_{C}$ 2-chlorobutane, and of *dl*- and meso-2,4-dichloropentane were used in the refinement procedure. The resulting refined force field was then used in normal coordinate analyses on four isomers of 3-chloropentane. Subsequent calculations on isomers of 2,4,6-trichloroheptane [26], and on poly(vinyl chloride) and its deuterated derivatives [27], support the validity of this force field.

RESULTS

The observed and calculated normal frequencies of 2-chloropropane below 500 cm^{-1}, with associated potential energy distributions, are given in Table 1. The agreement between observed and calculated frequencies is very good. The torsional mode with A' symmetry is assigned to the lower of the two observed values for internal rotation. This assignment is consistent with polarization data reported by KLABOE [22] for 2-iodopropane. No polarization data were observed for either of the torsional modes in 2-chloropropane.

Although the 2-chlorobutane molecule has no symmetry, our analyses were done in terms of a group of coordinates which characterize the normal modes in terms of special group frequencies. Table 2 gives the results of normal coordinate analyses on the three isomers of 2-chlorobutane. The ${}_{H}S_{H'}$ isomer was not included in the refinement procedure. The correlation between the observed and calculated frequencies

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

Observed		Calculated		Potential energy distribution‡
frequency*	symmetry†	symmetry	frequency	
256 vw (253 [22])	S	A'	256	$\tau_1(97)$
273 w (276 [22])	A	A''	273	$\tau_2(98)$
324 w	A	A''	327	$X_\pi(95)$
335 m	S	A'	337	$W_2(84)$
423 m [2]	S	A'	421	$W_1(77)$, $B_1(12)$

* Liquid phase frequencies, this work.

† Symmetry from gas phase contours.

‡ τ_1, τ_2 = CH_3—CHCl torsions, X_π = C—C—Cl bending, B = methyl rocking, W = combined C—C—Cl, C—C—C, C—C—H, H—C—Cl bending (see Ref. [2] for details).

[26] W. H. MOORE and S. KRIMM, to be published.

[27] W. H. MOORE and S. KRIMM, to be published.

Table 2. Observed and calculated frequencies (cm^{-1}) and potential energy distributions for 2-chlorobutane

Observed frequency	Calculated frequency	Potential energy distribution§
	(a) $_{H}S_{H}$ Conformation	
77†	77	$\tau_2(92)$
	189	$\tau_3(83)$
226*	223	CCC(39), $W_2(24)$
244‡	245	$\tau_1(91)$
324 m	321	$W_3(49)$, $X_\pi(41)$
386 m*‖	388	$W_1(52)$, CCC(16)
460 mw*‖	461	CCC(27), $W_1(24)$
	(b) $_{H}S_{C}$ Conformation	
77†	83	$\tau_2(80)$, $\tau_3(18)$
	200	$\tau_3(78)$
(226)*¶	227	$W_3(31)$
(244)‡	250	$\tau_1(69)$, $W_2(14)$
(290) vw‖	308	$X_\pi(79)$
374 m†‖	375	CCC(29), $X(25)$
418 mw†‖	423	$W_1(67)$, $W_2(14)$
	(c) $_{H}S_{H'}$ Conformation	
(77)†	72	$\tau_2(93)$
	195	$\tau_3(87)$
	215	CCC(49), $W_1(31)$
(244)‡	243	$\tau_1(93)$
(335)	334	$X_\pi(52)$, $W_2(27)$
	341	$W_3(52)$, $X_\pi(26)$
(522)‖	514	$X(33)$, CCC(25)

* Relative intensity increases on cooling.
† Relative intensity decreases on cooling.
‡ Remains strong at low temperatures.
§ $\tau_1 = CH_3—CHCl$ torsion, $\tau_2 = CHCl—CH_2$ torsion, $\tau_3 = CH_2—CH_3$ torsion, $X_\pi = C—C—Cl$ bending, $X = C—Cl$ stretching W—see Ref. [2] for details of this coordinate.
¶ Frequencies in parentheses were not used in refinement.
‖ Ref. [2].

for 2-chlorobutane is remarkable. Some spectroscopists who have observed the 244 cm^{-1} and the 226 cm^{-1} bands in 2-chlorobutane have assigned these bands either both to methyl torsions [23] or the 244 cm^{-1} band to C—C—Cl bending and the 226 cm^{-1} band to a methyl torsion [4]. In the refinement procedure all observed frequencies for 2-chlorobutane are listed in numerical order. Often when serious assignment errors have been made, frequencies either do not converge to assigned values, or a tendency is observed of misassigned modes to approach their correct values by exchanging places in the numerical ordering. This did not happen. However, although we call the band at 226 cm^{-1} a bending mode, the elements of the Jacobian matrix and the potential energy distribution for this mode show considerable contributions from the $CH_3—CH_2$ internal rotation.

For 2,4-dichloropentane only the TT conformation of the *dl* stereoisomer and the TG' conformation of the meso stereoisomer were considered. The results for the 2,4-dichloropentanes are given in Tables 3 and 4. The excellent agreement between observed and calculated frequencies for this molecule supports the validity of our potential function for secondary chlorides.

Two observed features of the far infrared spectra of the model compounds considered here have not been discussed: a band at approximately 67 cm^{-1}, which

Table 3. Observed and calculated frequencies (cm^{-1}) and potential energy distributions of *TT* conformer of *dl*-2,4-dichloropentane

Observed frequency	Calculated frequency	Potential energy distribution*
	42	$\tau_{A2}(96)$
	58	$\tau_{B2}(90)$
120 (R)†	120	CCC(52), $W_{A1}(29)$
	240	$\tau_{A1}(96)$
245 vw (R)	241	$\tau_{B1}(91)$
273 (R)	267	$W_{A1}(43)$, $X_{\pi A}(39)$
310 (i.r.)	312	$X_{\pi B}(44)$, $W_{B1}(33)$
343 m (i.r.)	342	$X_{\pi B}(42)$, $W_{B1}(39)$
368 m (i.r.)	371	$W_{A2}(65)$, $W_{A1}(10)$
460 m (i.r.)	458	$W_{B2}(74)$, $W_{B1}(12)$
476 w (i.r.)	472	$X_{\pi A}(28)$, CCC(26)

* τ_{A2}, τ_{B2} = CHCl—CH_2 torsions, τ_{A1}, τ_{B1} = CH_3—CHCl torsions, X_π = C—C—Cl bending, W = combined bending of C—C—C, C—C—Cl, H—C—Cl and C—C—H (see Ref. [2] for details).

† i.e. = infrared, R = Raman.

appears in the spectra of 2-chloropropane, 2-chlorobutane, 2,4-dichloropentane and 3-chlorohexane; and two bands at 150 cm^{-1} and 160 cm^{-1} in *dl*- and meso-2,4-dichloropentane respectively. The 67 cm^{-1} absorption is due to an intermolecular interaction [28] and the 150 and 160 cm^{-1} bands are assigned to non-dominant conformers of 2,4-dichloropentane. These bands and their assignments are discussed in detail elsewhere [25, 29].

Table 4. Observed and calculated frequencies (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	$X_{\pi A}(54)$, $\tau_{B2}(22)$
	242	$\tau_{A1}(96)$
245 w	245	$\tau_{B1}(73)$
315 m‡	316	$W_{A1}(74)$
345‡	342	$X_{\pi B}(51)$, $W_{B1}(23)$
392 w‡	393	$W_{A2}(64)$, $X_{\pi B}(8)$
410 ms‡	405	$X_{\pi A}(18)$, CCC(15)
460 w‡	466	$W_{B2}(63)$, $W_{B1}(9)$

* Infrared.

† See Table 3 for explanation.

‡ Ref. [2].

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

[29] W. H. MOORE and S. KRIMM, to be published.

Table 5. Observed and calculated frequencies (cm^{-1}), potential energy distribution, and band assignments of 3-chloropentane

Observed frequency* Infrared		Raman		Calculated frequency	PED†
		(a) $_HS_H$			
Liquid	Solid	Liquid	Solid		
		72	72	66	$\tau_3(42)$, $\tau_2(42)$
		80	80	82	$\tau_2(49)$, $\tau_3(49)$
		168	164	174	$W_2(56)$, CCC(48)
		194		197	$\tau_1(31)$, $\tau_4(31)$, $X_\pi(25)$
		206	209	202	$\tau_1(39)$, $\tau_4(39)$, $W_1(10)$
		238	241	258	$X_\pi(42)$, $\tau_4(14)$, $\tau_1(14)$
		374 ms	371 ms	362	$W_2(24)$, $W_1(19)$, $X(10)$
425 vw	425 w	426 s	427 s	430	$W_1(48)$
				474	CCC(68), $X_\pi(23)$
		(b) $_cS_H$			
				72	$\tau_2(88)$, $\tau_3(13)$
				78	$\tau_3(83)$
				180	$W_2(39)$, $\tau_4(26)$, $\tau_2(15)$
		194		201	$\tau_1(52)$, $\tau_4(33)$
				226	$X_\pi(42)$, CCC(35)
		238	241	243	$\tau_4(30)$, $\tau_1(22)$, $W_2(22)$
		362		348	CCC(46), $X_\pi(23)$, $X(12)$
400		398 s		397	$W_1(47)$, $X(16)$
460 vw		457 w		464	CCC(24), $W_1(19)$
		(c) $_HS_{H'}$			
				69	$\tau_2(94)$
				74	$\tau_3(92)$
		168		173	CCC(41), $W_2(20)$, $X_\pi(19)$
		194		194	$\tau_1(47)$, $\tau_4(17)$
		206	209	201	$\tau_4(57)$, $\tau_1(25)$
		292		274	CCC(44), $\tau_4(15)$
				331	$W_2(36)$, $X_\pi(35)$
400		398 s		408	CCC(37), $W_1(14)$, $X_\pi(16)$
533 m		533 ms		541	$X(26)$, CCC(23)
		(d) $_cS_{H'}$			
				55	$\tau_2(59)$, $\tau_3(40)$
				91	$\tau_3(51)$, $\tau_2(34)$
				185	$\tau_4(38)$, $\tau_1(20)$, $W_2(20)$
		194		193	$\tau_1(43)$, $W_1(15)$, CCC(15)
				236	CCC(22), $W_1(20)$, $\tau_1(20)$
		238	241	241	$\tau_4(28)$, $W_2(20)$, $X_\pi(20)$
				320	$X_\pi(55)$
400		398 s		381	CCC(29), $X(25)$, $W_2(23)$
533 m		533 ms		530	CCC(31), $W_1(26)$, $X(12)$

* Ref. [20].
† τ_2 = CH_2—CHCl torsion, X_π = C—C—Cl bending, W = combined bending of C—C—Cl, C—C—C, C—C—H and H—C—Cl. (See Ref. [2] for details.)

Far infrared data are also available on 3-chloropentane. Normal coordinate calculations were done for the four rotational isomers of this molecule, using the refined force field. The results are given in Table 5. Observed bands at 72 cm^{-1} and 80 cm^{-1} in the Raman spectrum of 3-chloropentane are assigned to CH_2—CHCl torsions and correlate well with the same torsions in 2-chlorobutane calculated at 77, 83 and 72 cm^{-1}. The methyl torsions in $_HS_H$ 3-chloropentane were calculated at 197 and 202 cm^{-1}. These values lend additional support to our prediction that the CH_3—CH_2 torsional mode in 2-chlorobutane will remain in the vicinity of 200 cm^{-1}. The C—C—Cl bending mode in 3-chlorpentane is predicted at 258 cm^{-1} and assigned

to an observed absorption at 241 cm^{-1}. This discrepancy could reflect the fact that the CH_2—CHCl—CH_2 environment was not included in the refinement procedure, or that the actual geometry deviates from the tetrahedral geometry and standard conformational angles used.

Conclusions

We have assigned the far infrared spectra of a group of representative secondary chlorides. To do this it was necessary to include torsional modes in the existing force field for secondary chlorides and to subject this complete force field to a refinement procedure. The good agreement between observed and calculated far infrared frequencies of 2-chloropropane, 2-chlorobutane, *dl*- and meso-2,4-dichloropentanes supports our assignments and force field. Our study indicates that with respect to torsional force constants, transferring these from hydrocarbons to secondary chlorides is not justified. The complete general valence force field for secondary chlorides [25], and the results of extending this force field to other chlorides [26] and to poly(vinyl chloride) [27], will be reported later.

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