Vibrational analysis of 2,2,3-trichlorobutane and a force field for 2,2-dichloropropane

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Abstract—The infrared and Raman spectra of 2,2,3-dichlorobutane have been analysed in terms of normal modes calculated from a force field for secondary dichlorides refined using this molecule as well as 2,2-dichlorobutane and 2,2-dichloropropane. A force field specific to the latter molecule is presented.

INTRODUCTION

IN the previous paper [1], we presented the results of a refinement of a force field for vicinal secondary chlorides, based on vibrational analyses of 2,3,4-trichloropentanes and 2,3-dichlorobutanes. Normal mode analyses showed that the calculated frequencies agreed very well with the observed bands. Such a force field should, therefore, be applicable to structures found in complex chlorinated polymers, such as chlorinated poly(vinyl chloride). However, such systems may also have geminal secondary dichlorides as well as mixtures of these two types. Since it is not simple to analyse for such structures, vibrational spectroscopy can be a very important tool in defining structure in these complex chlorinated hydrocarbons. In order to do this, we need a good force field for the geminal and mixed types of secondary chlorides.

WU *et al.* [2] refined force constants related to geminal secondary dichlorides, i.e. –C–C(Cl$_2$)–C–, in order to interpret the spectra of poly(vinylidene chloride). The model compounds they used were 2,2-dichloropropane and 2,2-dichlorobutane. Their results showed relatively large differences between observed and calculated frequencies for two C–C–C backbone angles that they used, viz. 120° and tetrahedral.

In order to obtain force constants generally applicable to various secondary chlorides, we synthesized 2,2,3-trichlorobutane and used its spectra in a force field refinement together with 2,2-dichloropropane and 2,2-dichlorobutane. In this refinement we assumed tetrahedral bond angles for all the molecules. The refined force constant set for multiply-chlorinated hydrocarbons is presented in the subsequent paper [3], in the form of a comprehensive force field for various types of secondary chlorides. In this paper we present the force field specific to 2,2-dichloropropane.

EXPERIMENTAL

2,2,3-Trichlorobutane (2,2,3-TCB) was prepared by the reaction of 2-chloro-3-butanone and PCl$_5$[4]. Phosphorus pentachloride (0.1 mole) was charged into a three-necked round-bottom flask with a paddle stirrer and reflux condenser, then 2-chloro-3-butanone (0.1 mole) was added drop by drop for 2 h at 60 °C. The reaction was maintained at 60 °C for 10 h. 2,2,3-TCB was then obtained by distillation with flowing N$_2$ gas.

Infrared spectra were obtained on a Bomem DA-3 FTIR spectrometer at 2 cm^{-1} resolution (except for the 500–150 cm^{-1} region, which was obtained on a Nicolet 60SX FTIR spectrometer). Raman spectra were obtained on a Spex 1403 spectrometer with Ar$^+$ laser 514.5 nm excitation, also at 2 cm^{-1} resolution.

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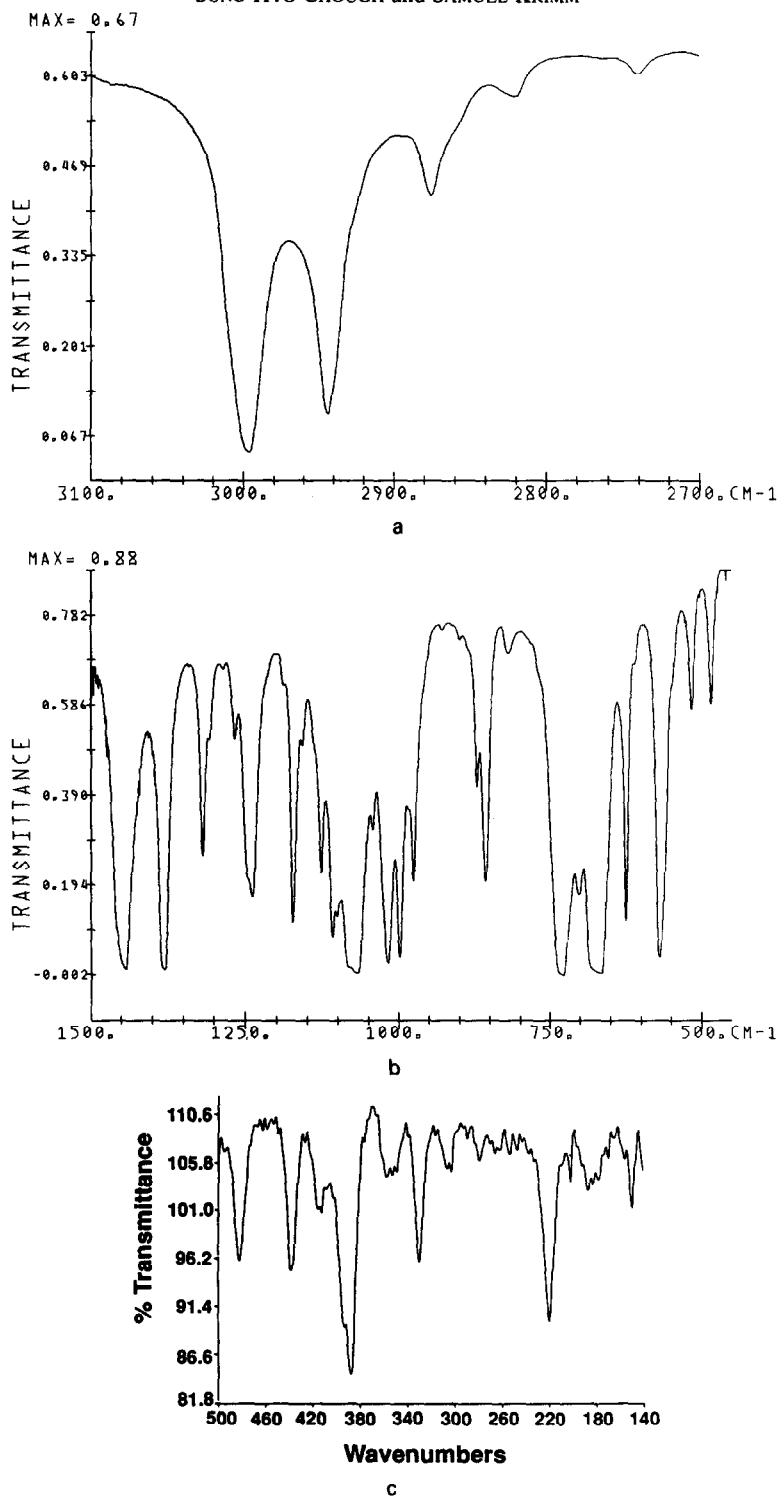
Fig. 1. Infrared spectrum of 2,2,3-trichlorobutane in liquid (room temperature) state.

RESULTS AND DISCUSSION

2,2,3-Trichlorobutane

Infrared spectra of 2,2,3-TCB are given in Fig. 1 and Raman spectra are given in Fig. 2. The observed and calculated frequencies are listed in Tables 1–3. 2,2,3-TCB can have three conformations, *trans*(T), *gauche* (G) and *gauche'* (G'), as shown in Fig. 3.
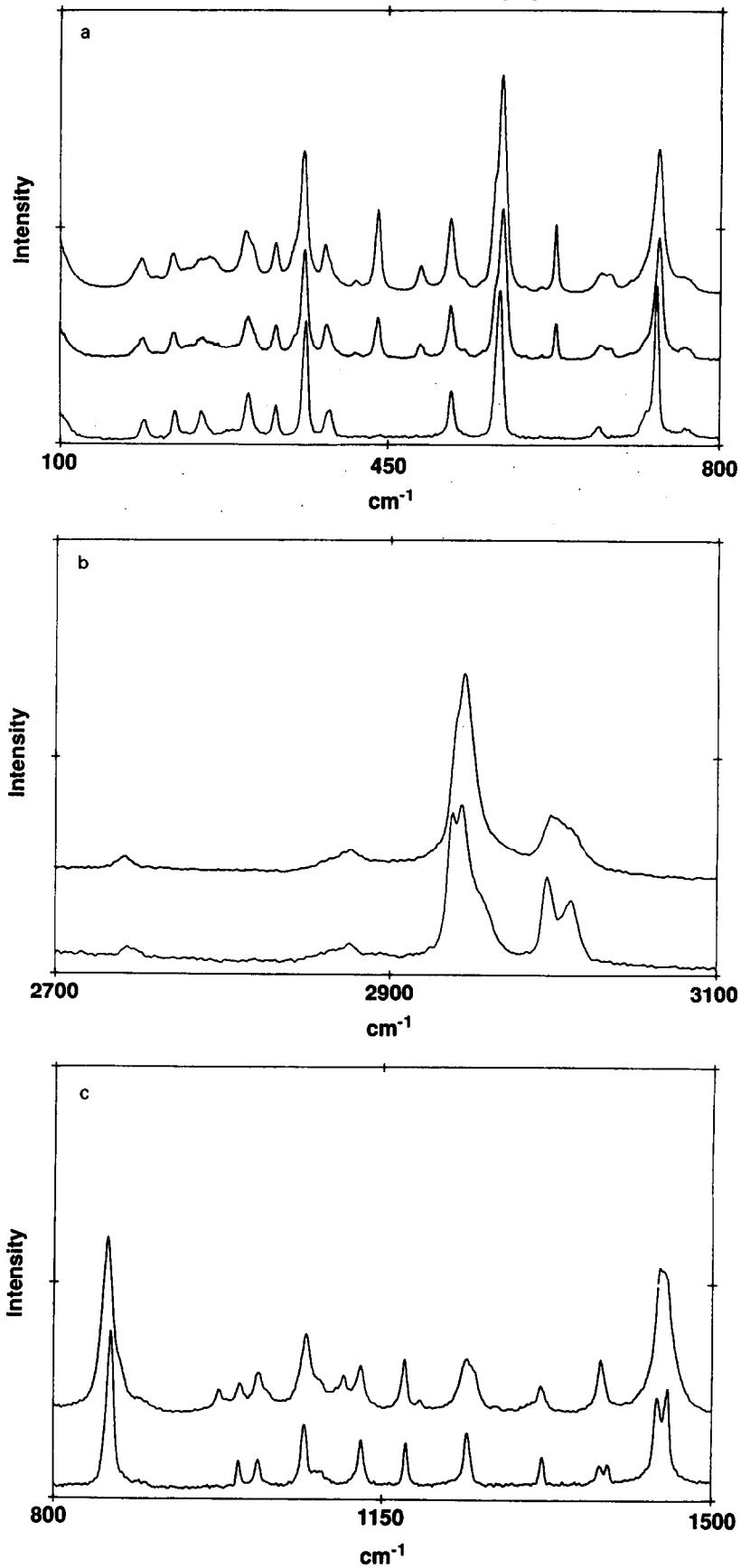
Fig. 2. Raman spectra of 2,2,3-trichlorobutane, in liquid (upper) and solid (lower) states. Middle spectrum in 100–800 cm^{-1} region is from pre-frozen state.

Table 1. Observed and calculated frequencies of *trans*-2,2,3-trichlorobutane

Observed			
Infrared	Raman	Calc.	Potential energy distribution*
	3009 sh	2991	M as1(100)
		2991	M as1(90)
2997 vs	2998 mw	2990	M as2(90)
		2990	M as2(99)
2944 s	2944 vs	2936	CH s(99)
	2940 sh		
2875 mw	2877 w	2874	M ss(98)
		2874	M ss(98)
	1450 sh	1451	M ab1(65) M ab2(26)
		1449	M ab2(67) M ab1(25)
1446 s	1444 s	1445	M ab2(94)
		1443	M ab1(93)
	1389 sh	1380	M sb(98) CC s(10)
1381 s	1382 mw	1376	M sb(92)
1318 m	1319 w	1320	CH ob(51) CC s(21) CH ib(14)
1238 ms	1239 mw	1249	CH ib(72) CH ob(17)
1173 ms	1174 mw	1173	CC s(67) M r1(16) CX_2 w(13)
1126 m	1126 mw	1130	CC s(34) M r1(33) CX_2 def(12)
1068 s	1067 m	1069	CC s(54) M r2(24)
1025 sh	1028 vw	1030	M r2(53) M r1(24) CX_2 r(10)
1017 s	1019 m	1011	M r1(45) CC s(23) M r2(20)
997 ms	998 w	994	M r2(71)
856 ms	857 s	855	CC s(58) M r1(41)
732 vs	733 s	727	CX_2 r(52) CX_2 as(49) CX ib(20) CX s(13)
668 vs	672 w	668	CX s(60) CX_2 as(20) CX_2 ss(10)
569 s	570 vs	565	CX_2 ss(52) CX_2 as(32) CX_2 b(11)
516 mw	515 m	516	CX ib(27) CX_2 w(18) CC s(16) CHX def(11)
390 m	388 w	387	CX ob(29) CX_2 w(22) CX_2 def(22)
358 w	361 s	362	CX s(21) CX_2 as(17) CX_2 ss(11)
330 mw	331 w	325	CX_2 tw(39) CC r(34)
305 w	300 mw	287	CX_2 b(64) CX_2 ss(16)
	255[†] sh	275	MC tor(99)
	252 w	272	MC tor(91)
220 mw	223 w	226	CX ob(35) CX_2 tw(26) CX_2 w(14) CX_2 def(14) CX_2 b(13) CHX def(11)
187 w	188 w	192	CHX def(28) CX ib(26) CX_2 w(24) CX_2 def(18)
		173	CX_2 def(34) CX ob(16) CHX def(15) CX_2 r(14) CX_2 tw(13)
		79	CC tor(96)

* s, stretch; as, antisymmetric stretch; ss, symmetric stretch; b, bend; ab, antisymmetric bend; sb, symmetric bend; ib, in-plane bend; ob, out-of-plane bend; def, deformation; w, wag; r, rock; tw, twist; tor, torsion (see [3] for definition of these local symmetry coordinates). M = methyl, X = Cl. Contribution to the PED of 10 or larger.

[†] Visible in the solid state.

Our MM2 calculated energies of the three conformers were 10.73 kcal mol^{-1} for T, 11.78 kcal mol^{-1} for G, and 13.23 kcal mol^{-1} for G'. On solidifying the sample, some bands disappear and others become sharper, the frequency shifts being small. The frequencies for the T isomer are taken as the liquid state frequencies that remain in the solid state Raman spectrum. In order to assign the bands for G and G' conformations, intensity changes in the spectra were observed at various temperatures down to freezing. We expected that the intensities of some bands that are uniquely assignable to G or G' might change at low temperatures due to the energy difference between these con-formers. However, there were no significant changes to distinguish the G and G' conformations, even though very different frequencies are associated with them. These

Table 2. Observed and calculated frequencies of *gauche*-2,2,3-trichlorobutane

Observed			
Infrared	Raman	Calc.	Potential energy distribution*
	3009 sh	2991	M as1(96)
		2991	M as1(97)
2997 vs	2998 m	2990	M as2(92)
		2990	M as2(98)
2944 s	2944 vs	2937	CH s(99)
	2940 sh		
2875 mw	2877 mw	2874	M ss(99)
		2874	M ss(99)
	1450 sh	1451	M ab1(67) M ab2(24)
		1449	M ab2(68) M ab1(23)
1446 s	1444 s	1445	M ab2(94)
		1443	M ab1(92)
1381 s	1382 mw	1380	M sb(98) CC s(10)
		1375	M sb(95)
1310 sh	1307† vw	1309	CH ob(53) CH ib(20) CC s(15)
1246 sh	1246† sh	1251	CH ib(61) CH ob(24)
1190 vw	1191† w	1189	CC s(40) M r1(16) M r2(15) CX ib(12)
1108 m	1109† w	1106	CC s(40) M rl(16) M r2(15) CX ib(12)
1080 sh	1083 sh	1071	CC s(42) M r1(20)
1045 w		1035	M r2(54) M r1(20)
997 ms	998 w	1005	M r2(75) M r1(14)
975 m	977† w	964	CC s(36) M r2(23) CH ob(19) M r1(18)
871 w	871† sh	866	CC s(59) M r1(32) CX₂ ss(10)
732 vs	733 s	737	CX₂ as(53) CX₂ r(48) CHX def(26) CX s(16)
681 sh	681† w	672	CX s(58) CX₂ as(32)
624 s	625† m	624	CX₂ ss(44) CX₂ def(26) CX ib(26)
439 mw	439† m	437	CX ib(23) CX₂ ss(21) CX₂ def(10)
390 m	388 w	389	CX₂ w(52) CX ob(22) CX₂ ss(11)
349 w	348† sh	358	CX₂ as(27) CX₂ r(17) CX s(15) CHX def(10)
305	307† sh	303	CX₂ tw(36) CHX def(24) CX₂ r(15) CX₂ b(12)
	300 mw	297	CX₂ b(34) CX₂ tw(24) CX₂ ss(15) CX ob(11)
	267† w	275	MC tor(97)
266 vw	261† w	274	MC tor(81)
247 vw	247† w	245	CX ib(26) CX₂ def(20) CX₂ w(14) CX ob(13)
			CX₂ b(11) MC tor(10)
203 w	204† vw	203	CX₂ def(47) CX₂ b(21) CHX def(19) CX ob(16)
			CX ib(13) CX₂ tw(10)
179 w	181† sh	170	CX₂ r(23) CX₂ tw(21) CHX def(19) CX ob(18)
			CX₂ def(12)
		79	CC tor(96)

* See footnote* of Table 1.
† Disappears in the solid state.

spectral results may indicate that the energy difference between the G and G′ conformers is small, despite the results of the MM2 calculations.

To assign the bands of G and G′, we first refined the force field using the *trans* form of 2,2,3-TCB, 2,2-dichloropropane (2,2-DCPr), and the *trans* and *gauche* forms of 2,2-dichlorobutane (2,2-DCB). The starting force constants were transferred from our previously refined force field as well as those of Wu et al. [2]. From the normal mode calculations based on these refined force constants, the bands in the 400–700 cm⁻¹ region that disappear on solidification could be uniquely assigned to the G and G′ conformations. Finally, with all bands assigned to T, G and G′ conformations of 2,2,3-TCB, to 2,2-DCPr, and to T and G conformations of 2,2-DCB, we refined the combined force constant set again.

Trans-2,2,3-*trichlorobutane*. Observed and calculated frequencies of *trans*-2,2,3-TCB are listed in Table 1 together with their potential energy distributions (PED).

Table 3. Observed and calculated frequencies of *gauche'*-2,2,3-trichlorobutane

Observed			
Infrared	Raman	Calc.	Potential energy distribution*
	3009 sh	2991	M as1(99)
		2991	M as1(90)
2997 vs	2998 m	2990	M as2(87) M as1(10)
		2990	M as2(99)
2944 s	2944 vs	2937	CH s(99)
	2940 sh		
2875 mw	2877 mw	2874	M ss(99)
		2874	M ss(100)
	1450 sh	1451	M ab1(66) M ab2(25)
		1449	M ab2(68) M ab1(24)
1446 s	1444 s	1445	M ab2(94)
		1443	M ab1(91)
1381 s	1382 mw	1380	M sb(93)
		1375	M sb(90)
1310 sh	1307† vw	1314	CH ob(52) CH ib(17) CC s(22)
1246 sh	1244† sh	1249	CH ib(69) CH ob(20)
1173 ms	1174 mw	1179	CC s(57) M r1(24)
1108 m	1109† w	1105	CC s(69)
1100 vw	1101† vw	1090	CC s(35) M r2(26) CX ob(11) M r1(11)
1045 w		1036	M r1(39) M r2(22) CC s(15)
997 ms	998 w	1006	M r2(66) M r1(15) CC s(11)
975 m	977† w	988	M r2(51) M r1(37)
871 w	871† sh	877	CC s(51) M r1(20)
	721 w	723	CX_2 as(64) CX_2 r(48) CX ib(17)
699 w		687	CX s(61) CHX def(23) CX_2 def(18)
	562† sh	558	CX_2 ss(60) CX_2 as(23) CX_2 b(14)
482 mw	484† w	471	CX_2 w(22) CX s(19) CX ib(16) CX_2 as(11)
413 w	415† vw	411	CX ob(31) CX_2 w(16) CX_2 as(13)
353 w		351	CHX def(20) CX s(16) CX_2 def(15) CX ob(12)
330 mw	331 w	326	CX_2 tw(46) CX_2 r(40)
279 vw		285	CX_2 b(63) CX_2 ss(16)
	267† w	275	MC tor(93)
266 vw	261† w	274	MC tor(82)
247 vw	247† w	242	CX_2 def(32) CHX def(25) CX ob(18) CX_2 b(18) CX_2 w(12)
187 w	188 w	187	CX_2 tw(31) CX ib(31) CX_2 r(21) CHX def(16)
179 w	181† sh	173	CX_2 def(32) CX ob(23) CX_2 w(19) CHX def(11)
		77	CC tor(95)

* See footnote* of Table 1.
† Disappears in the solid state.

In the CH stretch (s) region, the antisymmetric (as) and symmetric (ss) stretch modes of the methyl (M) groups are readily assigned in general, as is (Cl)CH s, on the basis of force constants that we refined for other chlorinated hydrocarbons [1]. Of course, small differences may be expected because of the locally different chemical environments. Fermi resonances with overtones and combinations of bending modes are also known to affect this region [5]. In the absence of such a detailed analysis, we have not modified this part of the force field.

The antisymmetric (ab) and symmetric (sb) M bend modes are well accounted for, as are the CH in-plane (ib) and out-of-plane (ob) bend and CC s modes. It should be noted that the modes calculated at 1320 and 1130 cm^{-1} are unique to the T conformer. We considered the possibility that the weak ~1080 cm^{-1} band, present in both liquid and solid, might be a fundamental, but this hypothesis is not supported in the refinement. It seems possible that this band is a combination: 733 + 361 = 1094. Although the 1028 cm^{-1} band in the Raman weakens on solidification, it still seems to be present in the solid and

thus may justify our assignment of the 1030 cm^{-1} mode. The other M rock (r) and CC s modes are well predicted.

In the CCl s region, the symmetric and antisymmetric stretches of CCl$_2$ are coupled with CCl s and distributed from 733 to 300 cm^{-1}. A weak band at 721 cm^{-1}, also present in the solid, may be an overtone of a strong band at 361 cm^{-1}: $2 \times 363 = 722$ cm^{-1}. In this region, the calculated frequencies are very close to the observed bands, except for that at ~303 cm^{-1}, which is calculated as a mixed bend and symmetric stretch of CCl$_2$ at 287 cm^{-1}. When the latter is brought closer to 303 cm^{-1}, the other CCl s bands deviate more. A similar mode in trans-2,2-DCB is observed at 276 cm^{-1} and calculated at 269 cm^{-1} (see below). With allowance for the effect of the third Cl atom adjacent to CCl$_2$, we believe that the band at 303 cm^{-1} is probably correctly assigned to this mixed mode. It should be noted that the 516 and 565 cm^{-1} modes are also unique to the T conformer.

The methyl–carbon torsion (tor) frequencies are difficult to assign: the calculated values are at 275 and 272 cm^{-1}, but the only observed bands in this region are at 279 and 266 cm^{-1} in the i.r. and a broad band from ~270 to 250 cm^{-1} in the Raman. The 279 cm^{-1} band is most reasonably assigned to the G′ isomer, while a Raman peak at ~247 cm^{-1} can be associated with modes of the G and G′ isomers. Since the broad 270–250 cm^{-1} Raman band collapses to a sharp band at 252 cm^{-1} in the solid, we have assigned this band to MC tor in the T isomer, reserving the disappearing bands at 267 and 261 cm^{-1} for the G and G′ structures. If we try to decrease the discrepancy for the 252 cm^{-1} band in the refinement, torsion frequencies in other molecules become worse. We have therefore left the torsion force constants unchanged, pending further investigations of this region. It should be noted that the 226 cm^{-1} mode is another one unique to the T conformer.

Gauche- and gauche′-2,2,3-trichlorobutane. The proposed band assignments and calculated frequencies for G- and G′-2,2,3-TCB are listed in Tables 2 and 3, respectively, with their PEDs. Many bands overlap those of the T conformation, but some are unique to each structure.

For the G conformation, unique frequencies are found for modes calculated at 1189, 624, 437 and 203 cm^{-1}. These as well as other bands involve specifically predicted large shifts from the frequencies of the T conformer, e.g. 1320–1309, 1173–1189, 1130–1106, 994–964, 565–624, 516–437 and 325–303 cm^{-1}, and these shifts are indeed observed. A similar situation exists for the G′ conformation, with unique modes calculated at 471 and 411 cm^{-1} and shifts that are comparable to those of the G conformer.

In the case of 2,3-dichlorobutane, JING and KRIMM [6] identified the S$_{HCl}$ CCl s frequency as occuring near 650 cm^{-1}, between S$_{HH}$ at ~600 and S$_{HC}$ at ~690 cm^{-1}. It is interesting to note that in 2,2,3-TCB, while CCl s (S$_{HC}$) for the G′ conformer is observed near its expected value, viz. at 699 cm^{-1}, the S$_{HCl}$ CCl s frequencies of the T and G conformers are found at higher-than-expected frequencies, 668 cm^{-1} for T and 681 cm^{-1} for G. This is probably due to the presence of the neighboring CCl$_2$ group in 2,2,3-TCB.

2,2-Dichlorobutane

2,2-Dichlorobutane has two conformations, T and G. Spectra have been obtained by OHNO et al. [7] and by CROWDER and LIN [8]. The spectra of the T conformer can be
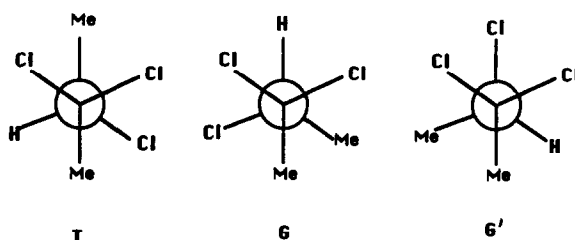

Fig. 3. Conformers of 2,2,3-trichlorobutane.

Table 4. Observed and calculated frequencies of *trans*-2,2-dichlorobutane

Sym.	Observed*	Calc.	Potential energy distribution[†]
A'	2980	2991	M as1(99)
		2991	M as1(99)
	2866	2874	M ss(99)
		2874	M ss(99)
	2848	2839	CH_2 ss(99)
	1463	1453	M ab1(80)
	1454	1443	M ab1(92)
	1427	1433	CH_2 b(88)
	1382	1382	M sb(93)
		1376	M sb(91)
	1342	1330	CH_2 w(69) CC s(16)
	1170	1163	M r1(43) CC s(28) CX_2 def(12)
	1120	1124	MC·s(71) CX_2 w(19) CC s(18)
	1037	1028	MC s(85)
	999	989	M r1(66)
	859	861	M r1(45) CC s(42)
	544	547	CX_2 ss(81) CX_2 b(13)
	490	481	CH_2 def(39) CX_2 w(36) MC s(12)
	358	348	CX_2 def(50) CX_2 w(19)
	276	269	CX_2 b(80) CX_2 ss(16) CX_2 def(10)
	202	192	CH_2 def(46) CX_2 w(34) CX_2 def(23)
A"	2980	2991	M as2(99)
		2990	M as2(99)
	2930	2901	CH_2 as(99)
	1454	1449	M ab2(91)
		1445	M ab2(94)
	1279	1288	CH_2 tw(58) M r2(14)
	1037	1040	M r2(44) CH_2 tw(34) CH_2 r(27)
	999	1002	M r2(85)
	808	799	CH_2 r(61) M r2(47)
	645	646	CX_2 as(114) CX_2 r(56)
	358	364	CX_2 r(66)
	276	290	CX_2 tw(67) M_1C_2 tor(24)
	252	271	M_1C_2 tor(75) CX_2 tw(24)
	202	198	M_4C_3 tor(88)
		120	CC tor(77) CX_2 tw(13)

* From [7].
[†] See footnote* of Table 1.

obtained from the solid sample, while the bands that disappear on solidification are attributable to the G conformer. The T conformation has C_s symmetry, and the normal modes are divided into 21 modes of *A'* and 15 of *A"* symmetry. The results of our normal mode calculations for the T and G conformations are given in Tables 4 and 5, respectively.

Wu et al. [2] used normal mode analysis to refine the force constants for both tetrahedral and 120° C–C–C bond angles, but their results showed large discrepancies with observation. They initially used the spectra assigned by OHNO et al. [7]. However, in the *A"* block for the T conformation, they assigned the methyl rock mode to a band at 1088 cm⁻¹, which is very weak in the solid sample. OHNO et al. [7] did not assign this band to the T conformer. Recently, CROWDER and LIN [8] also measured the spectra of this molecule, but they did not observe the band at 1088 cm⁻¹ in the solid sample. We assigned the band at 1037 cm⁻¹ to a methyl rock, following OHNO et al. [7], because our preliminary calculations gave 1044 cm⁻¹ for this mode. This is in agreement with the assignment of CROWDER and LIN [8].

In the CH s region, there is a large discrepancy for the CH_2 as mode of the T conformer. However, when the calculated frequency of 2901 cm⁻¹ was adjusted to come

Table 5. Observed and calculated frequencies of *gauche*-2,2-dichlorobutane

Observed*	Calc.	Potential energy distribution†
2980	2991	M as1(98)
	2991	M as2(93)
2944	2991	M as1(94)
	2990	M as2(99)
2892	2901	CH₂ as(99)
2866	2874	M ss(98)
	2874	M ss(99)
2848	2839	CH₂ ss(99)
1463	1455	M ab1(71) CH₂ b(19)
	1449	M ab2(89)
1454	1445	M ab2(94)
1443	1444	M ab1(88)
1427	1436	CH₂ b(73) M ab1(21)
1382	1382	M sb(92)
	1375	M sb(93)
1443	1444	M ab1(88)
1427	1436	CH₂ b(73) M ab1(21)
	1382	M sb(92)
1382		
	1375	M sb(93)
1333	1331	CH₂ w(63)
1283	1289	CH₂ tw(58) M r2(13)
1146	1152	CC s(45) M r1(31) CX₂ w(13) MC s(12)
1091	1092	MC s(48) M r1(13)
1042	1048	CC s(45) M r2(18) M r1(14)
1020	1019	CC s(26) M r2(32) CH₂ tw(12)
1008	1005	M r2(73) CH₂ tw(11)
982	974	M r1(51) CH₂ w(19) CC s(12)
859	866	CC s(48) M r1(34)
796	794	CH₂ r(61) M r2(45)
692	691	CX₂ as(85) CX₂ r(50) CH₂ def(16)
567	569	CX₂ ss(59) CX₂ as(17) CX₂ def(14) CX₂ b(10)
413	417	CX₂ w(26) CX₂ ss(18) CH₂ def(16) CX₂ as(10)
367	362	CX₂ w(42) CX₂ def(38)
358	358	CX₂ r(38) CX₂ w(13) CX₂ as(11)
276	297	CX₂ tw(39) CX₂ b(20) CX₂ def(16) CH₂ def(16) CX₂ ss(10)
276	275	MC tor(96)
252	259	CX₂ b(55) CX₂ tw(30)
202	201	MC tor(88)
	180	CH₂ def(34) CX₂ def(33) CX₂ tw(30) CX₂ r(19)
	129	CC tor(82)

* From [7].
† See footnote* of Table 1.

closer to the observed band at 2930 cm⁻¹, the same mode in the G conformer showed a larger deviation. We therefore did not modify the CH₂ force constants, particularly since Fermi resonances influence this region [5].

The assignments of the other bands follow quite reasonably from the frequencies calculated from our force field for dichlorides. The major problem is in the region below 280 cm⁻¹, and in particular with the CCl₂ twist mode, calculated at 290 and observed at 276 cm⁻¹ for the T conformer and calculated at 297 and observed at 276 cm⁻¹ for the G conformer. These as well as the torsion assignments will need further study.

2,2-Dichloropropane

Many authors [9–12] have studied the vibrational spectrum of 2,2-dichloropropane. This molecule has high symmetry, C_{2v}, and the modes divide into four symmetry species,

A_1, A_2, B_1 and B_2. Each shows characteristic features in the vibrational spectrum, such as specific gas-phase band contours. These properties, and the group symmetry in the normal mode analysis, are useful in helping to assign the bands. However, there have still been some disagreements in the band assignments, primarily in the A_2, B_1 and B_2 species.

Klaboe [10] assigned the 1192 cm^{-1} band to the A_2 block because he observed it only in the Raman spectrum. However, Green and Harrison [11] and Berlandier et al. [12] observed peaks at this position also in the i.r.. Green and Harrison [11] pointed out that the absorption at 1192 cm^{-1} persists weakly in the gas spectrum, with a shape that seems like a C-type contour. Berlandier et al. [12] observed that the 1192 cm^{-1} band was sharp in the liquid and broader in the gas. The above two studies suggest that the contour is of the C-type, which indicates that the band at 1192 cm^{-1} should be assigned to the B_1 species.

The band at 1121 cm^{-1} has an A-type contour according to Berlandier et al. and others [10, 11], implying that it should be assigned to the B_2 species. However, Berlandier et al. [12] also assigned this band to the A_2 species, although they noted that this may not be reliable. Green and Harrison [11] assigned a 1018 cm^{-1} band, which may correspond to a 1012 cm^{-1} Raman band of Berlandier et al. [12], to the A_2 species. In view of these studies, we have assigned the band at 1012 cm^{-1} to the A_2 species, retaining the assignment of 1121 cm^{-1} to the B_2 species.

In the B_2 species, Klaboe [10] assigned the 1034 cm^{-1} band to the methyl rock mode. However, Berlandier et al. [12] could not observe a band at 1034 cm^{-1} and assigned this mode to a band at 1121 cm^{-1}, which shifted to 1110 cm^{-1} in the liquid. Green and Harrison [11] obtained a similar result.

Our work follows the assignments of Berlandier et al. [12], except for the 1012 cm^{-1} band in the A_2 block, and uses the liquid phase frequencies. The observed and calculated

Table 6. Observed and calculated frequencies of 2,2-dichloropropane

Sym.	Observed	Calc.	Potential energy distribution*
A_1	3000	2992	M as(99)
	2937	2874	M ss(100)
	1434	1446	M ab1(93)
	1386	1386	M sb(90)
	1156	1156	M r1(47) MC s(39) CX$_2$ def(13) CX$_2$ ss(11)
	910	903	MC s(54) M r1(40)
	559	561	CX$_2$ ss(66) CX$_2$ def(11)
	362	362	CX$_2$ def(61) CX$_2$ b(19)
	259	259	CX$_2$ b(75) CX$_2$ def(33) CX$_2$ ss(19)
A_2	3003	2991	M as2(99)
	1444	1442	M ab2(95)
	1012	1004	M r2(93)
	287	293	MC tor(64) CX$_2$ tw(35)
		278	CX$_2$ tw(63) MC tor(36)
B_1	2988	2990	M as1(99)
	2935	2874	M ss(100)
	1454	1442	M ab1(94)
	1372	1367	M sb(99)
	1188	1186	MC s(63) M r1(23) CX$_2$ w(18)
	950	958	M r1(69) MC s(25)
	389	388	CX$_2$ w(84)
B_2	3000	2991	M as2(99)
	1444	1444	M ab2(94)
	1110	1115	M r2(77) CX$_2$ r(16) CX$_2$ as(11)
	656	653	CX$_2$ as(97) CX$_2$ r(44) M r2(13)
	357	360	CX$_2$ r(60) CX$_2$ as(13)
		268	MC tor(99)

* See footnote* of Table 1.

Table 7. Force constants for
2,2-dichloropropane

Force constant*	Value
MH	4.7522
MC	4.2576
CX	2.7433
HMH	0.5397
CMH	0.6433
XCX	1.0200
MCX	1.2696
MCM†	0.7714
M.C	0.1410
MH,MH	0.0010
MC,M'C†	0.3919
MC,CX	0.4524
CX,CX	0.3644
CM,CMH	0.1510
MC,MCX	0.0998
MC,XCM'	−0.0985
MC,MCM†	0.0104
CX,MCX	0.4052
CX,X'CM	−0.0893
CX,MCM†	0.1403
CX,XCX	0.2099
HMH,HMH	0.0091
HMH,CMH	0.0182
CMH,CMH	−0.2120
MCX,XCX	−0.1824
MCX,XCM'†	0.1203
MCX,MCX'†	−0.1826
MCX,X'CM'†	0.0129
(HMC,MCX)$_T$	−0.0568
(HMC,MCX)$_G$	−0.0617
(MCM,CMH)$_T$†	−0.1642
(MCM,CMH)$_G$†	−0.1684
(M.C)(C.M)†	0.0080

* M = methyl carbon, X = chlorine, AB = AB bond stretch, ABC = ABC angle bend, A.B = AB torsion. Units: mydn/Å for stretch and stretch–stretch; mdyn for stretch–bend; mdyn Å for all other force costants.
† Unique force constants defined for 2,2-dichloropropane.

frequencies are listed in Table 6, with the PEDs. The force constants for 2,2-dichloropropane are given in Table 7, and are the result of a least squares refinement that includes 2,2,3-TCB, 2,2-DCB and 2,2-DCPr. Thus, the 23 observed frequencies of 2,2-DCPr are used to fit 11 unique force constants in this molecule (see Table 7), the other 22 force constants (not unique to 2,2-DCPr) being part of the overall refinement involving 2,2-DCB and 2,2,3-TCB as well as 2,2-DCPr. The calculated frequencies agree well with the observed bands, except for the M ss modes in the A_1 and B_1 blocks. Throughout the refinement these modes were given zero weight.

CONCLUSIONS

We have synthesized 2,2,3-trichlorobutane and analysed its i.r. and Raman spectra in terms of normal mode calculations. These were based on a force field for secondary

dichlorides co-refined together with 2,2-dichlorobutane and 2,2-dichloropropane. In the latter case, we have re-examined the band assignments and we present a force field specific to this molecule.

The agreement between observed and calculated frequencies is quite good: the average error for three conformers of 2,2,3-trichlorobutane is $5.2 \, \text{cm}^{-1}$, for two conformers of 2,2-dichlorobutane it is $6.2 \, \text{cm}^{-1}$, and for 2,2-dichloropropane it is $4.3 \, \text{cm}^{-1}$. The overall average error for these three molecules is $5.4 \, \text{cm}^{-1}$. This force constant set is therefore a good component of a comprehensive force field for multiply-chlorinated hydrocarbons [3].

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