Vibrational analysis of 2,3,4-trichloropentanes

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Abstract—One *meso* form and the *racemic* isomer of 2,3,4-trichloropentane have been synthesized, and their infrared and Raman spectra analysed on the basis of a general force field refined for multiply-chlorinated hydrocarbons. Previous results on 2,3-dichlorobutane have been incorporated in this study, thus providing a force field for detailed analyses of vicinally-chlorinated hydrocarbons.

INTRODUCTION

VIBRATIONAL spectra of chlorinated normal hydrocarbons have been studied extensively in order to elucidate their conformational structures and to interpret the spectra of polymers that contain chlorine [1–6]. The bands arising from the stretching of the carbon–chlorine bond are relatively intense and have been shown experimentally to be sensitive to the geometry of the carbon chain around the chlorine atom [7, 8]. Normal mode analysis has convincingly established that the conformational structures of simple chlorinated hydrocarbons containing isolated secondary chlorines, such as 2-chlorobutane or 2,4-dichloropentanes, can be correlated with the observed frequencies of the carbon–chlorine stretch modes in the region of 500–700 cm^{-1} [3, 4]. However, carbon–chlorine stretch is highly delocalized in the range of 300–800 cm^{-1} as chlorine atoms appear vicinally along the chain, as in 2,3-dichlorobutanes [6].

In highly chlorinated hydrocarbons, structure determination, either configurational or conformational, becomes more complicated because of the overlap of many bands. For such molecules, normal mode analysis is indispensable in helping to analyse the spectral complexity. Since the calculated frequencies depend on the force constants used, the refinement procedure is very important. For the general application of normal mode analysis to highly chlorinated hydrocarbons, such as chlorinated poly(vinyl chloride) (CPVC), force constants have to be refined for the particular types of structures present, such as: 1) the isolated Cl, as in 2-chlorobutane, 2,4-dicholoropentanes, and 2,4,6-trichloroheptanes, which could be models for poly(vinyl chloride) (PVC); 2) the geminal Cl, as in 2,2-dichloropropane and 2,2-dichlorobutane, which could be models for poly(vinylidene chloride); 3) the vicinal Cl, as in 2,3-dichlorobutanes and 2,3,4-trichloropentanes, which could be models for chlorinated polyethylenes and CPVC; and 4) mixtures of geminal and vicinal Cl, as in 2,2,3-trichlorobutane, which could also be a model for structures in CPVC.

Force constants for the isolated type of secondary chlorine have been developed by OPASKAR and KRIMM [2] and MOORE and KRIMM [3]. Their force constants could successfully explain conformational structures of the monochlorohydrocarbons [3], 2,4-dichloropentanes [3,4], 2,4,6,-trichloroheptanes [4], and crystalline syndiotactic PVC [5]. Force constants applicable to the geminal Cl structure have been refined by WU et al. [9]. Recently, JING and KRIMM [6] have refined force constants for the vicinal type of secondary chlorine, using 2,3-dichlorobutanes. However, for secondary chlorines appearing in triplets along the chain, as in CPVC, specific force constants should be refined for general applications involving these structures. In addition to these, the mixed types of geminal and vicinal Cl structures should be considered together in the refinement procedures.

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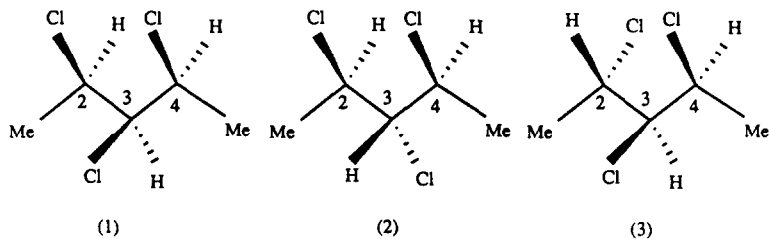
Fig. 1. Configurations of 2,3,4-trichloropentanes: (1) and (2) *meso*, (3) *racemic*.

We have synthesized one *meso* form and *racemic*-2,3,4-trichloropentane, as well as 2,2,3-trichlorobutane, in order to refine detailed force fields for such structures. We present here the analysis of the vibrational spectra of the former. The following papers give the analysis of 2,2,3-trichlorobutane [10] and the comprehensive force field refined for the various multiply-chlorinated hydrocarbons [11].

EXPERIMENTAL

2,3,4-Trichloropentane (2,3,4-TCP) has two *meso* forms (1, 2) and one *racemic* form (3), the chemical structures being shown in Fig. 1. CLIFFORD and EWING [12] synthesized a mixture of *meso* (2) and *racemic* (3) forms of TCP. However, they failed to separate the isomers. We have used a new method to prepare each isomer exlcusively.

3-Penten-2-ol, purchased from Aldrich, which was mainly the *trans* isomer, was dissolved in methylene chloride and chlorinated by bubbling chlorine gas through the solution, which was cooling in an ice bath. The reaction vessel was wrapped with aluminium foil to protect it from light. After 3 h, the chlorine gas was replaced by nitrogen gas. The cut distilled between 45 and 60°C at *ca* 20 mmHg contained two isomers of 3,4-dichloropentan-2-ol. These were tosylated at room temperature and the tosylates were then separated by crystallization in hexane–acetone (2:1) solution. The isomer that crystallized first showed chemical shifts of 5.1, 4.06, and 3.98 and 3.71 ppm for the secondary protons. Each tosylate was treated with the tetra-*n*-butylammonium chloride in N,N-dimethylformamide solution at 80°C. One *meso* isomer (2) and the *racemic* isomer (3) were obtained. The ^{1}H NMR spectra of these isomers are given in Fig. 2. Their identification followed that in [12]. However, since the above identifications by ^{1}H NMR spectra might be accidentally interchanged, the structure of one tosylate, that which gives the *meso* isomer, was determined by X-ray crystallography. Since the tosyl group is replaced by the S_{N2} mechanism
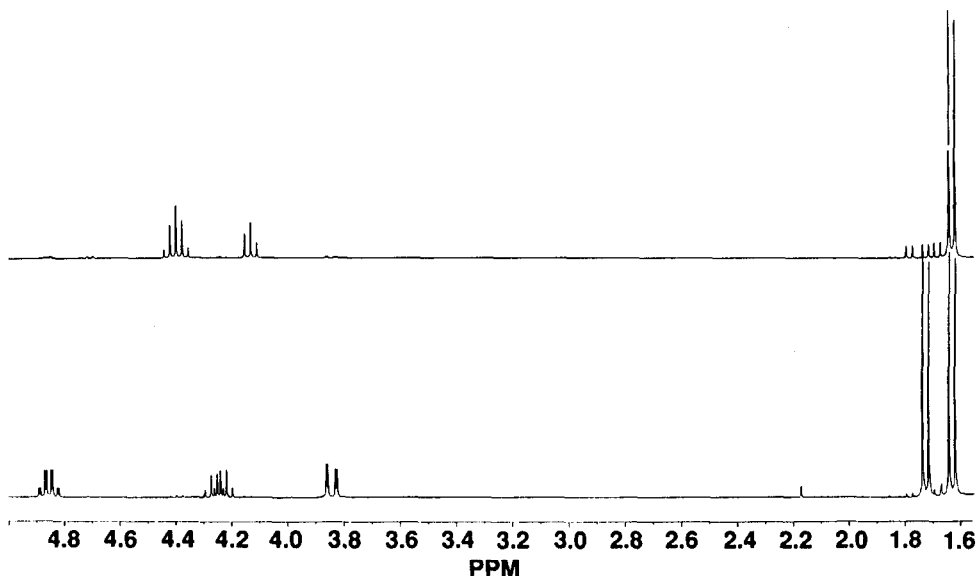

Fig. 2. ^{1}H NMR spectra of 2,3,4-trichloropentanes: upper *meso*; lower *racemic*.

[13, 14], the structure of the daughter molecule can be determined from the structure of the mother compound. The X-ray crystallography result [15] shows that the previous identification of each isomer by ^{1}H NMR is correct.

Infrared spectra were obtained on a Bomem DA-3 FTIR spectrometer, at 2 cm^{-1} resolution, and Raman spectra were obtained on a Spex 1403 spectrometer with Ar${}^+$ laser 514.5 nm excitation, also at 2 cm^{-1} resolution.

NORMAL MODE ANALYSIS

As will be seen in the Raman spectra, there are no bands that disappear upon solidifying the samples. This implies that only one conformation is present in both the liquid and solid states for each isomer. The stable conformations are the *trans–gauche* (TG), $S_{HCl} S_{ClH'} S_{CH}$, form of the *meso* isomer and the TT, $S_{HCl} S_{ClH} S_{HH}$, form of the *racemic* isomer. (The S notation for the secondary chlorides follows that used in [8].)

Normal mode analyses were performed for the above two stable conformations, using the force constants refined by JING and KRIMM (J-K hereafter) for 2,3-dichlorobutane (2,3-DCB) [6], which should be a good starting force field for TCP. However, the preliminary calculations gave relatively large discrepancies from the observed frequencies. Since the secondary chlorine atoms in TCP occur in a triplet, some new force constants are obviously required. These were estimated for the initial calculations by transferring from the J-K force field. In the refinement procedure, some force constants were adjusted to provide a better match to observed frequencies of 2,3,4-TCP and 2,3-DCB while not damaging the assignments for the *trans* form of the MRSM configuration of 2,3-DCB [6]. Since the *trans* form of MRSM has C_i symmetry, to which the mutual exclusion rule applies, the assignments of bands in its spectra can be made with greater confidence.

We used the same definitions of the local symmetry coordinates as in J-K (see also [11]), and constructed a set of molecular symmetry coordinates to take advantage of the C_i symmetry. The structural parameters were: $r(C–H)=1.09$ Å$/r(C–C) = 1.54$ Å and $r(C–Cl) = 1.79$ Å; all bond angles were assumed to be tetrahedral, and dihedral angles were taken to be 180° and ±60° for *trans* and *gauche* conformations, respectively.

RESULTS AND DISCUSSIONS

Meso-2,3,4-*trichloropentane*

As mentioned earlier, since all bands observed in the liquid persist in the solid, the same conformations must be present in both states. The stable conformation of *meso*-2,3,4,-TCP is the TG, $S_{HCl} S_{ClH'} S_{CH}$, form, in which the chlorine atoms on the 2- and 4-carbons are on the same side of an extended carbon backbone. The backbone is rotated to the TG conformation to minimize repulsive interactions between these two chlorines. This is consistent with the results of energy calculations for *meso*-2,4-dichloropentane, 2,4-DCP [16, 17]. The observed i.r. and Raman spectra are shown in Figs 3 and 4, respectively. (The i.r. spectrum below 500 cm^{-1} is from a 1:1 mixture of the *meso* and *racemic* isomers, since we did not have enough of the pure isomer.) The calculated frequencies and proposed assignments are given in Table 1, with their potential energy distributions (PED). (Some very weak bands are not assigned to fundamentals; they are probably combinations or overtones.)

In the CH stretch (s) region, we expect three types of modes: the antisymmetric (as) and symmetric (ss) stretch modes of the methyl (M) groups, and the CH s of the CHCl group. These modes are evident in the i.r. spectra of both isomers, with the force field easily reproducing their frequencies near 2990, 2875 and 2940 cm^{-1}, respectively. This region is quite complex, however, with overtones and combinations of CH bend interacting with CH s fundamentals through Fermi resonances [18]. The effects are particularly dominant in the Raman spectrum [18], and this may account for some of the structure seen (cf. Fig. 4). Because of this, our assignments of fundamental frequencies

must be considered tentative. It should also be noted that the M groups in the *meso* isomer are not in equivalent environments with respect to intramolecular non-bonded interactions, and some differences in their observed frequencies might be expected because these interactions are not incorporated in the normal mode calculations. Of course, additional shifts and splittings could occur in the solid state as a result of intermolecular interactions, which may account for the rich Raman spectrum of the crystalline *meso* isomer. The band near 2956 cm^{-1} (at 2961 cm^{-1} and intense in the crystal) is not readily accounted for; it may be due to the interactions referred to above [18].

The antisymmetric (ab) and symmetric (sb) methyl bend modes, near 1450 and 1380 cm^{-1}, respectively, are well accounted for. In the CH bend region, a medium strong band at 1328 cm^{-1} in the i.r. appears as a weak band in the Raman at room temperature. In 2,3-DCB(MRSM), an observed band at 1329 cm^{-1}, of medium intensity in i.r. and weak in the Raman, could be uniquely assigned to CH out-of-plane bend (ob), with a PED of 60%, of the *gauche* isomer. The modes in both molecules are contributed to mainly by the CH ob of the S_{CH} chlorine, which in both molecules is in a similar chemical and geometrical environment. Since the initial calculation for 2,3,4-TCP gave a frequency for this mode close to 1328 cm^{-1}, which did not change much during the refinement, we accepted this assignment even though the i.r. band becomes very weak on solidification. The final calculated frequency was 1329 cm^{-1}, with 67% of the PED in CH ob. The other CH ob and CH in-plane bend (ib) modes were relatively easily
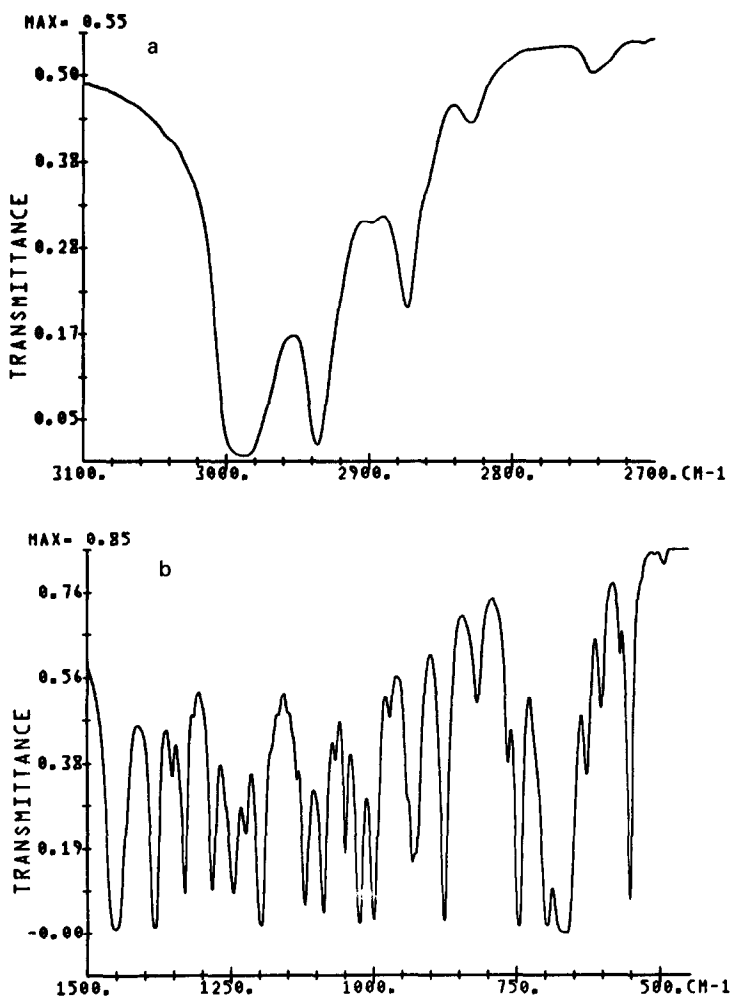

Fig. 3. Infrared spectrum of *meso*-2,3,4-trichloropentane in liquid (room temperature) state. (Region below 500 cm^{-1} from a 1:1 mixture of *meso* and *racemic* isomers.)
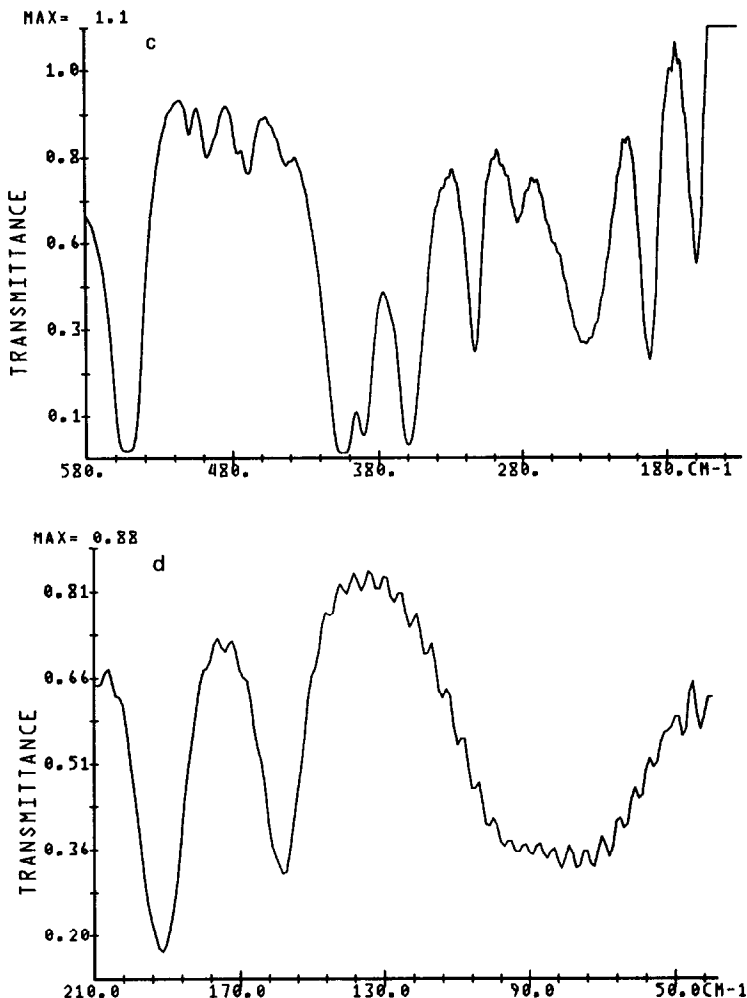
Fig. 3 (*continued*)

assigned, although there may be questions about the 1228 cm^{-1} band since it appears in the spectrum of the *racemic* isomer and the *meso* sample contains a small amount of this isomer. In the solid sample, three bands are observed in the Raman: 1257 ms, 1241 m, and 1227 mw cm^{-1}. The new band at 1257 cm^{-1} is probably a result of Fermi resonance in the crystal between the fundamental, near 1249 cm^{-1}, and the combination of two strong fundamentals, $552 + 697 = 1249$ cm^{-1}, giving rise to the split pair at 1241 and 1257 cm^{-1}. We therefore assign the observed 1228 cm^{-1} band as a fundamental, which is in agreement with the prediction of two bands in this region, their calculated values being 1247 and 1227 cm^{-1}.

In the region of 1150 to 850 cm^{-1}, CC s and M rock (r) are highly mixed, and eight bands are expected. All the bands are observed in the liquid and solid samples, making the assignments straightforward.

In the CCl s region, four strong i.r. and Raman bands are observed, near 745, 697, 668, and 552 cm^{-1}. Although CCl s contributes down to 300 cm^{-1}, being mixed with other coordinates, the first three bands are the main CCl s modes, with the 552 cm^{-1} band having a relatively large stretch component. The two bands at 697 and 668 cm^{-1} are assignable to C_4Cl s, S_{CH}, and C_2Cl s, S_{HCl}, respectively. The 3-chlorine atom, $S_{CIH'}$, contributes mainly to 745 and 552 cm^{-1}, which are mixed CCl s modes.

In the case of CC torsion (tor), the bands are highly separable. The MC tor modes are assigned to 284 cm^{-1} as a fundamental. Jing and Krimm [6] assigned the torsion bands to 280 and 264 cm^{-1} for 2,3-DCB. For this torsion, 2,3,4-TCP should have values close to 2,3-DCB due to the similar chemical environments. For the CC tor modes, we observe a
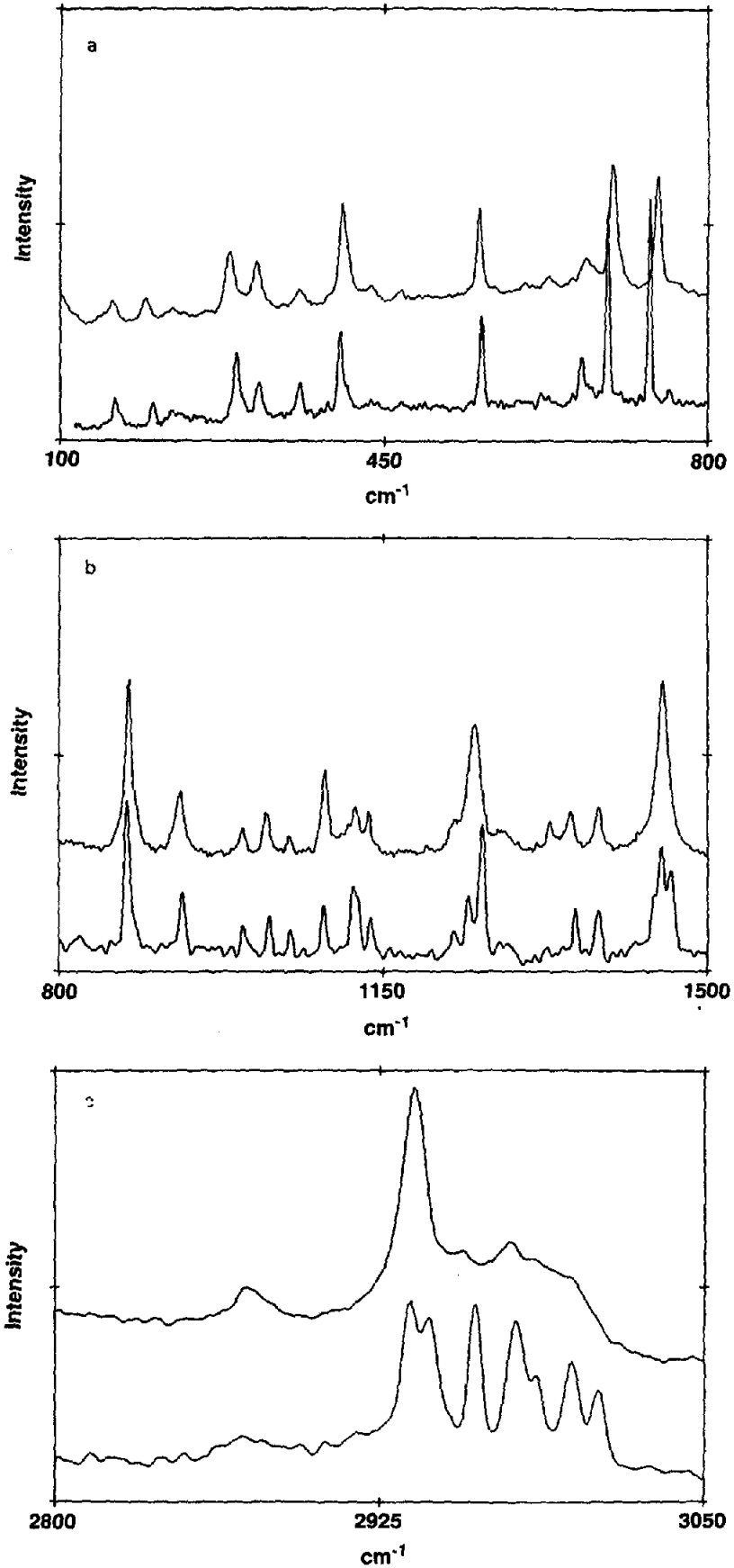
Fig. 4. Raman spectra of *meso*-2,3,4-trichloropentane, in liquid (upper) and solid (lower) states.

Table 1. Observed and calculated frequencies of *meso*-2,3,4-trichloropentane

Observed			
Infrared	Raman	Calc.	Potential energy distribution*
	2999 w	2991	M as1(98)
2989 vs	2992 vw	2991	M as1(98)
	2983 w	2990	M as2(96)
	2975 w	2990	M as2(96)
	2956 w		
		2941	CH s(98)
2935 s	2938 s	2936	CH s(98)
		2932	CH s(99)
2897 vw			
2873 m	2874 mw	2874	M ss(98)
		2874	M ss(98)
2828 w			
		1451	M ab1(52) M ab2(35)
1451 s	1452 ms	1450	M ab1(50) M ab2(43)
		1449	M ab2(54) M ab1(39)
		1449	M ab2(49) M ab1(44)
1381 s	1383 mw	1383	M sb(89)
		1380	M sb(98)
1350 w	1353 mw	1354	CH ob(44) CH ib(21) CC s(11)
1328 ms	1330 w	1329	CH ob(67) MC s(12)
1281 ms	1281 w	1286	CH ib(37) CH ob(32) MC s(10)
1244 m	1249 ms	1247	CH ib(87)
1223 w	1228 w	1227	CH ib(49) CC s(32)
1196 s	1196 vw	1191	CH ob(53) CH ib(23) CC s(12)
1133 w	1134 w	1137	CC s(24) MC s(24) M rl(11) CHX def(10)
1119 ms	1119 w	1126	CC s(37) MC s(16) CH ob(20) CH ib(10)
1086 ms	1087 m	1080	MC s(31) M r2(21)
1048 m	1049 w	1057	M rl(31) M r2(11) CH ob(10)
1023 s	1025 mw	1017	M r2(54) M rl(16)
998 s	999 w	1010	M r2(40) M rl(19) MC s(12)
930 ms	931 m	943	M rl(27) CC s(20) MC s(22) M r2(11)
874 s	876 ms	880	CC s(35) M rl(25) MC s(15) CHX def(10)
745 s	745 vs	742	C3X s(24) C3HX def(20) C3X ib(14) C4X s(13) C2X ib(10)
696 s	697 vs	701	C4X s(42) C4HX def(20) C3X ib(14) C2X s(12)
667 vs	668 mw	672	C2X s(57) C3X s(17) C2HX def(13)
551 s	552 s	553	C4X ib(33) C3X s(26) C3X ob(10)
442 vw	436 w	425	C2X ib(38) C4HX def(16) C4X s(16)
405 s	405 s	408	C2X ib(25) C4X s(18) C2X ob(13)
359† ms	358 mw	354	C2HX def(20) C2X s(18) C4X ob(13) C3X s(12)
313† m	312 m	313	C4X ob(32) C2X ob(17) C4X ib(14) C4HX def(13)C3X s(12)
283† w	284 m	275	MC tor(90)
		273	MC tor(94)
235† m	242 vw	241	C2HX def(30) C2X ib(28) C4X ib(19)
191† m	193 mw	201	C3X ib(47) C2X ib(16) C4HX def(15) C2X ob(13)
158† m	157 mw	168	C3X ob(68) C3HX def(14) C3H ob(13) C2HX def(11) C4X ob(11) C4HX def(11)
	149 w	143	C3HX def(29) C3X ob(23) C2X ob(19) C4X ib(15)C3H ob(10)
~80		80	CC tor(90)
		73	CC tor(87)

* s, stretch; as, antisymmetric stretch; ss, symmetric stretch; ab, antisymmetric bend; sb, symmetric bend; ib, in-plane bend; ob, out-of-plane bend; def, deformation; r, rock; tor, torsion (see [6] or [11] for definitions of these local symmetry coordinates). M = methyl, X = Cl. Contributions to the PED of 10 or larger.

† Peaks obtained from a 1:1 mixture of *meso* and *racemic* isomers.

very broad peak covering ~100–70 cm^{-1} in the i.r. JING and KRIMM also observed bands at 88 (MRSM) and 102 cm^{-1} (MRRM) for the torsions in 2,3-DCB [6]. These values are within the range found in this work. Our calculated frequencies are 80 and 73 cm^{-1}.

Racemic-2,3,4-*trichloropentane*

The plausible conformations of *racemic*-2,3,4-TCP are the TT, S_{HCl} S_{ClH} S_{HH}, and GG, S_{HC} S_{CH} S_{HC}, forms. They are analogous to *racemic*-2,4-DCP, except for the 3-chlorine atom. Thus, the analysis of *racemic*-2,4-DCP can give us insights into the spectra and conformations of *racemic*-2,3,4-TCP.

In *racemic*-2,4-DCP, the lowest energy conformation is the TT form and the second lowest one is the GG form [16, 17]. Experimentally, there are two strong bands at 606 and 627 cm^{-1} in the region of CCl s, which are contributed to by the S_{HH} type of secondary chlorine, i.e. the *trans* conformation. Two weak bands at 682 and 718 cm^{-1} are attributable to the GG and TG forms, respectively. However, the weakness of the 682 cm^{-1} band means that the population of the GG compared to the TT form is very low.

In the case of *racemic*-2,3,4-TCP, the GG conformation is likely to be less stable energetically than the corresponding GG form of 2,4-DCP, since the 3-chlorine atom in TCP will make the molecule more polar, thus increasing the repulsive interactions between the three Cl atoms. Accordingly, the energy difference between TT and GG conformations should be much larger compared with that of 2,4-DCP. Thus, the TT conformation should be present predominantly or solely. All bands observed in the liquid sample persist in the solid. This implies that only the TT conformation is present in the liquid and solid states. The observed i.r. and Raman spectra are shown in Figs 5 and 6, respectively. The observed bands are given in Table 2, with the calculated frequencies and proposed assignments and PEDs. (The i.r. bands below 100 cm^{-1} are taken from the spectra of the mixture of *racemic* and *meso* isomers.)

In the CH s region, there are three strong bands at 2989, 2982, and 2933 cm^{-1}, and a medium weak band at 2874 cm^{-1} in the i.r. The strong bands at 2989 and 2982 cm^{-1} appear as weak bands in the Raman at 2990 and 2984 cm^{-1}, respectively. The Raman spectrum of the solid sample shows these bands more clearly, some of which, as in the case of the *meso* isomer, may be due to Fermi resonance. Assignments of M as, M ss, and CH s similar to those for the *meso* isomer can readily be made for the *racemic* molecule.

The M ab and M sb modes are observed and calculated at about the same frequencies as in the *meso* isomer. The CH ob and CH ib modes are also well accounted for, particularly the ~15 cm^{-1} decrease in the 1329 cm^{-1} mode of the *meso* isomer to 1314 cm^{-1} in the *racemic* structure. The eight CC s and M r modes in the 1150 to 850 cm^{-1} region are similarly well predicted. We assign the 1112 ms i.r. and 1105 m cm^{-1} Raman bands as fundamentals since both are present in the Raman spectrum, with intensities obviously inverted as compared to the i.r.

The CCl s modes are clearly very different from those of the *meso* isomer. The highest frequency band, at 765 cm^{-1}, is mostly C_3Cl ib whereas in the *meso* isomer the 745 cm^{-1} band was mostly C_3Cl s. The next two strong bands, at 673 and 626 cm^{-1}, are C_2Cl s and C_4Cl s, respectively, reversed from the main contributions to the 697 and 668 cm^{-1} bands of the *meso* isomer. And while the 552 cm^{-1} band of the *meso* isomer is mainly C_4Cl ib, the 553 cm^{-1} band of the *racemic* isomer is mainly C_3Cl s. The excellent reproduction of these very different frequencies indicates that the CCl s part of the force field is quite good. Since the force constants are the same and only the conformations are different, this indicates that there is no significant dependence of these force constants on conformation.

In the region below 300 cm^{-1}, the discrepancies between observed and calculated frequencies are relatively larger. The MC tor modes are assigned to bands near 286 cm^{-1}, whose intensity is very weak in the i.r. but medium strong in the Raman. This value is close to that of the *meso* isomer and to the assigned value for 2,3-DCB [6]. The main difficulty is with the 239 cm^{-1} band, for which the calculated frequency is 257 cm^{-1}. When the calculated value is brought closer to 239 cm^{-1}, using the Jacobian matrix in the refinement procedure, a calculated band at 1092 cm^{-1} shifts downward, so that its discrepancy with the observed 1105 cm^{-1} band becomes larger. Since two medium bands are observed near 1100 cm^{-1}, we gave a greater weight to the 1092 cm^{-1} mode than to the

257 cm^{-1} mode. In the solid sample, a new band appears at 109 cm^{-1} with medium intensity in the Raman. We do not find a band near 109 cm^{-1} in the liquid state, either in the Raman or the i.r.. Thus, this band is considered to be a lattice vibration of the crystalline sample, particularly since no band is calculated near this value. The calculated bands for CC tor are placed within the observed broad peak at 100–70 cm^{-1}, as in the case of the *meso* isomer.
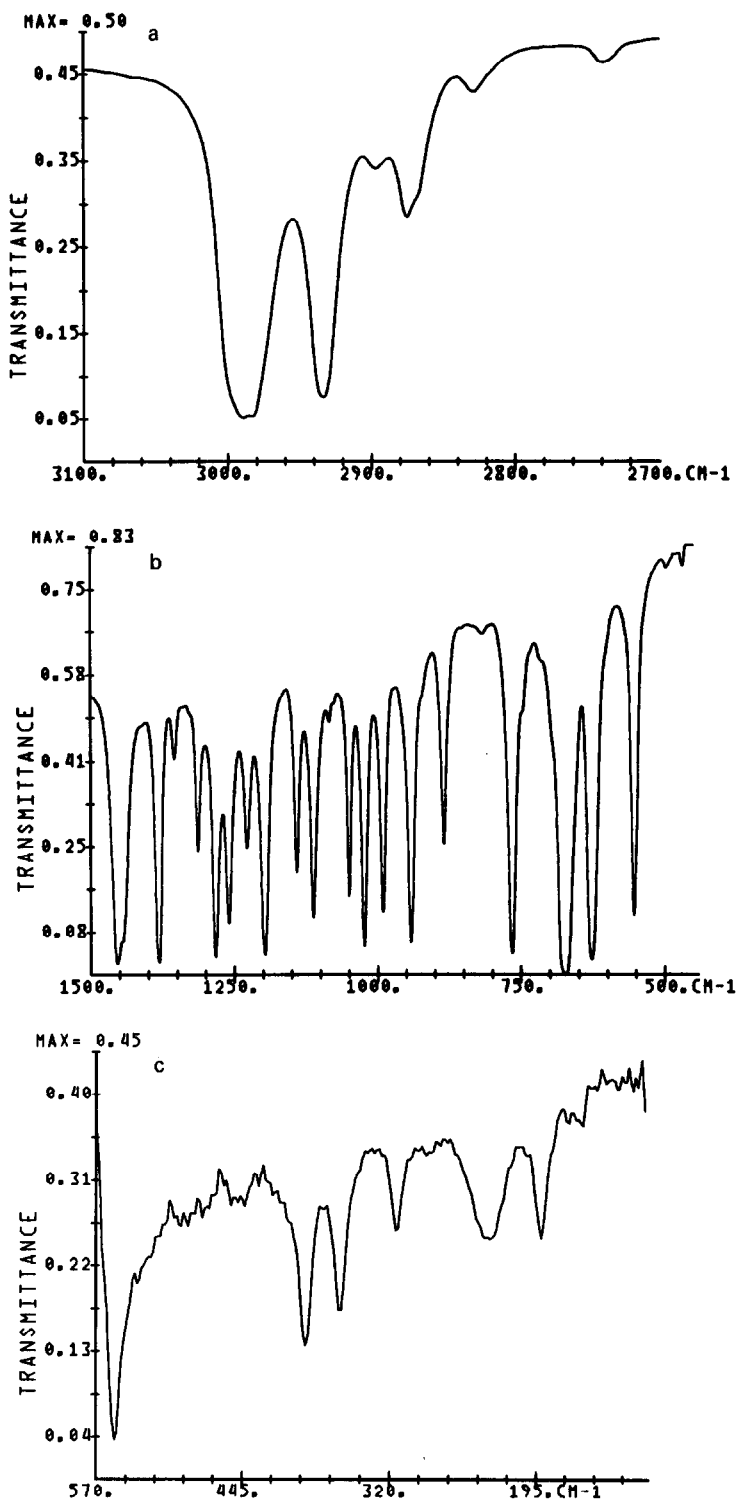
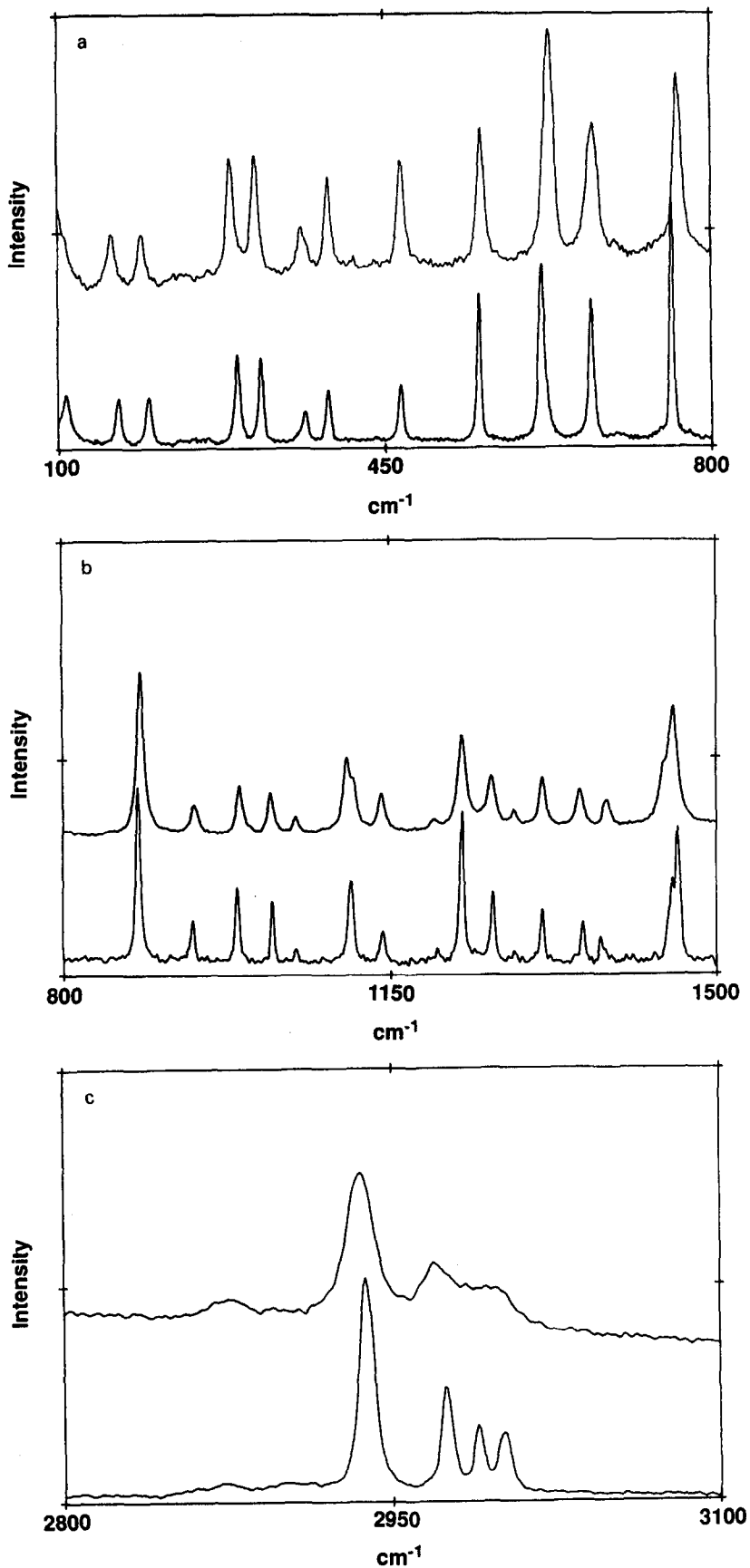Fig. 5. Infrared spectrum of *racemic*-2,3,4-trichloropentane in liquid (room temperature) state.

Fig. 6. Raman spectra of *racemic*-2,3,4-trichloropentane, in liquid (upper) and solid (lower) states.

Table 2. Observed and calculated frequencies of *racemic*-2,3,4-trichloropentane

Observed		Calc.	Potential energy distribution*
Infrared	Raman		
	2998 w	2991	M as1(97)
2989 vs	2990 w	2991	Mas1(97)
2982 vs	2984 w	2990	M as2(96)
	2970 mw	2990	M as2(96)
		2941	CH s(99)
2933 s	2936 s	2936	CH s(98)
		2932	CH s(98)
2896 w	2896 vw		
2874 mw	2878 w	2874	M ss(98)
		2874	M ss(98)
2828 w			
1453 s	1455 ms	1451	M ab1(49) M ab2(38)
		1450	M ab1(51) M ab2(37)
1444 sh	1445 sh	1449	M ab2(63) M ab1(26)
		1449	M ab1(49) M ab2(44)
1380 s	1383 w	1384	M sb(88)
		1381	M sb(97)
1353 w	1353 mw	1356	CH ob(42) CH ib(20)
1312 mw	1313 mw	1314	CH ob(63) MC s(19)
1282 s	1282 w	1283	CH ob(62) CH ib(15)
1259 ms	1259 mw	1252	CH ib(80)
1227 mw	1228 m	1235	CH ib(47) CC s(34)
1196 s	1197 w	1195	CH ob(35) CH ib(35) CC s(19)
1141 m	1142 mw	1139	CC s(40) MC s(12)
1112 ms	1111 sh	1115	MC s(44)
	1105 m	1092	CH ob(20) CC s(12) CH ib(11) M rl(17)
1049 ms	1050 w	1052	MC s(22) M rl(23) M r2(18)
1022 s	1023 mw	1021	M r2(38) M rl(31)
990 ms	990 mw	997	M r2(62)
941 s	944 w	948	MC s(35) CC s(21) M rl(16) M r2(10)
884 ms	884 s	887	M rl(46) CC s(41)
764 s	765 s	765	C₃X ib(28) C₃X s(21) C₂H ob(10) C₄X s(10)
672 vs	673 ms	672	C₂X s(69) C₂HX def(15) C₃X s(10) C₃X ob(10)
626 s	626 vs	616	C₄X s(68) C₃X s(13) C₄HX def(11) C₄X ib(10)
553 s	553 s	549	C₃X s(17) C₄X s(16) C₄X ib(13)
468 w	468 ms	471	C₃HX def(14) C₄X ib(13) C₄X ob(10)
390 m	390 m	400	C₂X ib(54) C₄HX def(17)
361 m	362 mw	357	C₂X s(21) C₂HX def(21) C₄X ob(12) C₂X ob(10) C₃X s(10)
313 mw	312 ms	314	C₄X ob(31) C₄HX def(15) C₂X ob(14) C₄X ib(13)C₃X s(11)
288 vw	286 ms	273	MC tor(92)
		273	MC tor(95)
239 mw	239 vw	257	C₂X ob(37) C₄HX def(21) C₂HX def(19)
190 mw	190 m	200	C₃X ob(39) C₃X ib(24) C₂HX def(21)
158 w	158 m	164	C₃X ob(46) C₂X ob(26) C₄X ib(24) C₃HX def(15) C₃H ob(15)
		147	C₃X ib(27) C₄X ob(26) C₃HX def(19)
~80		85	CC tor(92)
		65	CC tor(88)

* See footnote* of Table 1.

2,3-*Dichlorobutanes*

2,3-DCBs have two configurations, MRSM and MRRM. The *trans* conformations of these two isomers were used in the refinement of the comprehensive force field, MRSM being given greater weight throughout the refinement procedure because the band assignments are more certain due to its C_i symmetry. The final band assignments are the same as in JING and KRIMM [6]. The average difference between observed and calculated frequencies is 4.4 cm⁻¹ for both isomers [15], which is a slight improvement over the results of the earlier calculation [6].

Table 3. Observed and calculated frequencies of 2,3-dichlorobutane
(MRSM-G)

Observed*	Calc.	Potential energy distribution†
2995	2991	M as 1(96)
2991	2991	M as1(93)
2991	2990	M as2(92)
2986	2990	M as2(97)
2938	2936	CH s(98)
2935	2935	CH s(99)
2874	2874	M ss(99)
2874	2874	M ss(99)
1457	1452	M ab1(79) M ab2(12)
1454	1450	M ab2(70) M ab1(19)
1447	1449	M ab2(84)
1443	1448	M ab1(74) M ab2(18)
1385	1381	M sb(95)
1379	1380	M sb(97)
1329‡	1336	CH ob(68) MC s(16)
1311‡	1301	CH ob(49) CC s(33) CH ib(11)
1235‡	1235	CH ib(70) CH ob(25)
	1230	CH ib(70) CC s(25)
1150‡	1143	MC s(23) CH ib(18) M rl(13) CH ob(12) CC s(11)
1090‡	1096	MC s(32) M r2(20) CH ob(19)
1057‡	1071	M r2(30) M rl(24) CX ib(12) MC s(10)
	1027	M rl(48) M r2(20)
980‡	985	M r2(55) M rl(17)
967	971	MC s(33) M r2(29) CH ob(17) M rl(16)
847	845	CC s(45) M rl(29) MC s(20)
697	708	CX s(59) CHX def(34) CX ib(13) M r2(11)
650‡	649	CX s(57) CX ib(38) CHX def(17)
532‡	529	CX s(42) CX ib(36)
420‡	427	CX s(33) CX ob(17) CX ib(15)
344	343	CX ob(64) CHX def(28)
302‡	296	CX ob(35) CHX def(29) CX ib(17) MC tor(15)
280	275	MC tor(92)
262	267	MC tor(78) CX ob(11)
231	237	CHX def(68) CX ib(39)
187‡	178	CX ob(65) CX ib(39)
98	90	CC tor(92)

* From [6].
† See footnote* of Table 1.
‡ Observed bands uniquely assignable to MRSM-G as a result of disappearance on solidification.

Using the refined force constants, normal mode frequencies were calculated for the G conformations of MRSM and MRRM. The band assignments for these two *gauche* conformations are essentially the same as those in [6]. The results of these calculations are given in Tables 3 and 4, the PEDs being slightly different (as might be expected) from the previous ones [6].

For the G conformer of MRSM, the observed band at 1235 cm^{-1}, uniquely associated with this conformation, is assigned to two CH ib modes, with calculated values at 1235 and 1230 cm^{-1}. In the previous study [6], these bands were calculated at 1250 and 1234 cm^{-1}, with the former being assigned to an observed liquid and solid band at 1252 cm^{-1}; it seems possible that the latter is associated only with the *trans* conformer. The average difference between observed and calculated frequencies is ~6 cm^{-1}.

For the G conformer of MRRM, our present force field results in several changes in assignments. Instead of 1295 we calculate a mode at 1277 cm^{-1}, and therefore the previously assigned 1303 cm^{-1} band (present in solid as well as liquid) is assigned only to the *trans* conformer. The highest CCl s frequency is now calculated at 723 rather than 703 cm^{-1}; we therefore tentatively assign the 729 cm^{-1} i.r. band to it, which previously

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Table 4. Observed and calculated frequencies of 2,3-dichlorobutane
(MRRM-G)

Observed*	Calc.	Potential energy distribution†
3000	2991	M as1(94)
2994	2991	M as1(99)
2987	2990	M as2(99)
2980	2990	M as2(94)
2943	2936	CH s(99)
2937	2936	CH s(99)
2877	2874	M ss(100)
2873	2874	M ss(99)
1455	1452	M ab1(70) M ab2(20)
1450	1450	M ab2(66) M ab1(27)
	1449	M ab2(71) M ab1(20)
1447	1448	M ab1(66) M ab2(28)
1383	1382	M sb(96) MC s(12)
1379	1381	M sb(97) MC s(12)
1347	1338	CH ob(78) MC s(16)
	1277	CH ib(82)
1255	1246	CC s(39) CH ob(50) MC s(12)
1227	1225	CH ib(86)
1167	1175	CC s(19) CH ob(30) MC s(26)
1113	1116	MC s(34) M r1(18) M r2(18) CX ib(16)
1052	1044	M r2(68)
1021	1018	M r1(46) M r2(32)
995	1003	M r1(50) MC s(28) CH ob(14)
956	954	MC s(36) M r2(34) CH ob(14)
831‡	838	CC s(46) M r1(22) MC s(26)
729	723	CX s(46) CHX def(38) CH ob(18) M r2(18) CX ib(18)
650	653	CX s(98)
560	568	CX ib(66) CHX def(22) M r1(12)
370‡	375	CX s(42) CHX def(16) CX ib(16)
342‡	339	CX ob(72) CHX def(20)
280	283	MC tor(51) CX ob(22) CX ib(16)
	277	MC tor(90)
264	261	MC tor(46) CX ib(22) CX ob(22)
	216	CX ob(62) CHX def(44) CX ib(26) CH ob(14)
208‡		
	213	Ch def(40) CX ib(30) CX ob(18)
102	93	CC tor(94)

* From [6].
† See footnote* of Table 1.
‡ Observed bands uniquely assignable to MRRM-G as a result of disappearance on solidification.

had to be assigned to a combination band. This implies that the former assignment of the very strong 694 cm^{-1} liquid and solid Raman band to this mode cannot be supported, and the explanation of the strong 706 (i.r.), 694 (Raman) pair in the liquid and comparable 698, 701 pair in the solid may have to be sought in Fermi resonance interactions in the *trans* conformer (note, for example, that 2×354 (obs)[6] = 708). A similar situation exists for a strong liquid and solid band near 597 cm^{-1}, previously assigned both to the *trans* conformer as well as to a calculated band at 593 cm^{-1} for the *gauche* conformer. We now calculate this mode at 568 cm^{-1} and tentatively assign a weak band near 560 cm^{-1} to it. Such assignments will obviously need further verification, but they result from our present more globally refined force field.

CONCLUSIONS

A vibrational analysis of the i.r. and Raman spectra of known *meso* and *racemic* isomers of 2,3,4-trichloropentane that we have synthesized has permitted us to assign the

spectra of these molecules in detail. The calculated normal mode frequencies, based on a force field co-refined to the spectra of *trans* isomers of 2,3-dichlorobutane, agree with the observed bands with an average error of $5.2\,cm^{-1}$. If the 2,3-dichlorbutane frequencies are included, the overall average error is $5.1\,cm^{-1}$.

Since the force field was refined so as to be consistent with those of related chlorinated hydrocarbons [2, 6], assignments in some previously studied molecules have had to be modified very slightly. This is particularly true of the *gauche* conformers of 2,3-dichlorobutanes, and details have been given.

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