Comprehensive force field for multiply-chlorinated hydrocarbons

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Abstract—A force field is presented that has been optimized for chlorinated hyrocarbons containing isolated, vicinal, and geminal secondary chlorines. For carbon–chlorine stretch modes, 74 frequencies in 10 molecules are reproduced with an average error of $4.5 \, \mathrm{cm^{-1}}$. This force field can therefore serve to study these conformation-dependent modes in multiply-chlorinated hydrocarbons.

INTRODUCTION

IN the previous two papers [1, 2] we presented the results of force field refinements for vicinal and geminal secondary chlorides, as derived from vibrational analyses of *racemic* and *meso* 2,3,4-trichloropentanes and *trans*, *gauche* and *gauche'* 2,2,3-trichlorobutanes, respectively. In the former case [1], the refinement was optimized to include data on 2-chlorobutane, 3-chloropentane, and *racemic* and *meso* 2,4-dichloropentanes [3–5], as well as the vicinal chlorines of *racemic* and *meso* 2,3-dichlorobutane [6]. In the latter case [2], data on 2,2-dichloropropane [7] and *trans* and *gauche* 2,2-dichlorobutane [8] were included in the refinement.

In this paper we present the comprehensive force field encompassed by the above kinds of secondary chloride structures. The general approach to refining this force field was as follows. We developed a program to list all possible environments of each force constant in a chlorinated hydrocarbon chain, focussing on the segments that are likely to occur in chlorinated poly(vinyl chloride). The model compounds listed above were used to refine force constants for many of these different environments, with all molecules containing a given environment being refined together. Since some possible environments were not available in our model compounds, we have (for completeness) tentatively suggested values for these equal to the most closely similar environments for which we have refined constants.

This force field should serve not only to interpret the spectra of multiply-chlorinated hydrocarbonss, but should also be suitable for the analysis of the spectra of chlorinated polymers, such as chlorinated polyethylene, poly(vinyl chloride) [9], and chlorinated poly(vinyl chloride). Since the CCl stretch frequencies are very sensitive to the local backbone conformation [10, 11], they can be an important method of studying chain conformation in such polymers. We also present the observed and calculated frequencies for these modes in the molecules studied. The results for other modes are given in [12].

FORCE FIELD

The local symmetry coordinates used in the normal mode calculations are defined in Table 1, based on the atom designations of Fig. 1. The structural parameters were: $r(\mathrm{C–H}) = 1.09 \, \text{Å}$, $r(\mathrm{C–C}) = 1.54 \, \text{Å}$ and $r(\mathrm{C–Cl}) = 1.79 \, \text{Å}$; all angles were assumed to be tetrahedral, and dihedral angles were taken to be 180° and ±60° for *trans* and *gauche* conformations, respectively. The force field is presented in Table 2.

At first we tried a minimally differentiated force field, i.e. using one force constant, independent of the environment, where possible. For example, a single value was first

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Table 1. Local symmetry coordinates of CH_3-, $-CHX-$ and $-CX_2-$ in chlorinated hydrocarbons

Group	Coordinate	Symbol*	Definition†
CH_3	Symmetric stretch	M ss	$CH^1 + CH^2 + CH^3$
	Antisymmetric stretch 1	M as1	$2CH^1 - CH^2 - CH^3$
	Antisymmetric stretch 2	M as2	$CH^2 - CH^3$
	Symmetric bend	M sb	$H^2CH^3 + H^1CH^3 + H^1CH^2 - CCH^1$ $- CCH^2 - CCH^3$
	Antisymmetric bend 1	M ab1	$2H^2CH^3 - H^1CH^3 - H^1CH^2$
	Antisymmetric bend 2	M ab2	$H^1CH^3 - H^1CH^2$
	Rock 1	M r1	$2CCH^1 - CCH^2 - CCH^3$
	Rock 2	M r2	$CCH^2 - CCH^3$
CHX	CH stretch	CH s	CH
	CX stretch	CX s	CX
	CH out-of-plane bend	CH ob	$C'CH - HCC''$
	CH in-plane bend	CH ib	$2HCX - C'CH - HCC''$
	CX out-of-plane bend	CX ob	$C'CX - XCC''$
	CX in-plane bend	CX ib	$C'CX + XCC'' + C'CC'' - C'CH$ $- HCC - HCX$
	Deformation	CHX def	$C'CC'' - C'CX - XCC''$
CX_2	Symmetric stretch	CX_2 ss	$CX + CX'$
	Antisymmetric stretch	CX_2 as	$CX - CX'$
	Deformation	CX_2 def	$5C'CC'' - C'CX - C'CX' - XCC''$ $- X'CC'' - XCX'$
	Bend	CX_2 b	$4XCX' - C'CX - C'CX' - XCC''$ $- X'CC''$
	Wag	CX_2 w	$C'CX + C'CX' - XCC'' - X'CC''$
	Rock	CX_2 r	$C'CX - C'CX' + XCC'' - X'CC''$
	Twist	CX_2 tw	$C'CX - C'CX' - XCC'' + X'CC''$

* M = methyl, X = chlorine.
† CH^1 is the bond *trans* to the non-methyl C–C bond. CH_2 has the same definition as CX_2.

assigned to the four CC stretch constants (see Table 2). In such a case, however, the frequency agreement was poor and we had to allow for different values depending on the environment. Our force field includes all interaction constants between two bonds that have an atom in common and between two angles that have a bond in common, but does not include most interactions between two angles that have only an apex atom in common or that have neither a bond nor an apex atom in common. However, interactions such as those between CCl stretch and $C'CC''$ bend, between $C'C$ stretch and HCC'' bend, and between $C'CCl$ bend and $C''CCl'$ bend are included. In cases where three successive C atoms along the chain have attached Cl atoms (one or two), some force constants related to the center C atom were allowed to refine independently; these are specifically indicated in Table 2. Similar force constants in different environments, such as $CH_3(=M)$, $CH_2(=HH)$, $CHCl(=HX)$ and $CCl_2(=XX)$, were also allowed to refine independently. When specific environments were not available from our model compounds, force constants were assigned from a similar environment so that more complex structures could still be computed. Thus, HXHXXX is among the 11 possible environments for the CCC bend constant, but it is not represented in our model compounds. We are suggesting in this case that the value for the HXHXHX environment be used.
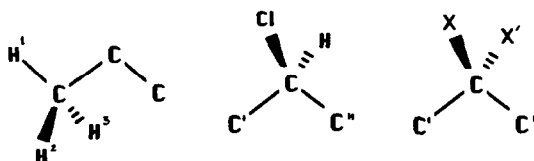

Fig. 1. Designation of atoms in local symmetry coordinates for $-CH_3$, $-CHCl-$ and $-CCl_2-$ units.

Table 2. Force constants for chlorinated hydrocarbons

Constant*	Environ.†	Value	Constant*	Environ.†	Value
MH	ME	4.7522		MEHXHH	0.2738
CH	HX	4.6932		MEXXHX	0.5867
	HH	4.4870		MEXXHH	0.5867
MC	MEHH	4.4858		MEHHHX	0.2691
	MEHX	4.7047		MEHHXX	0.2691
	MEXX	4.2576	CC,CC	HXHXHX	0.2248
CC	HXHX	4.7264		HXHXXX	0.2248
	XXHX	4.4845		XXHXHH	0.2691
	XXHH	4.3768		HXHXHH	0.2691
	HXHH	4.7778		HHHXHH	0.1738
CX	HX	2.7476		HXHHHX	0.1319
	XX	2.7433		HXHHXX	0.1319
HCH	HH	0.5084		XXHHXX	0.1319
HMH	ME	0.5397		HHXXHH	0.5867
CMH	HXME	0.6105		HHXXHX	0.5867
	HHME	0.6172		HXXXHX	0.5867
	XXME	0.6433	MC,CX	MEHX	0.6401
MCH	MEHX	0.6719		MEXX	0.4524
	MEHH	0.7041	CC,CX	HXHX	0.3959
CCH	HXHX	0.6243		HHHX	0.6401
	XXHX	0.6063		XXHX	0.3907
	XXHH	0.6382		HXXX	0.5832
	HXHH	0.6467		HHXX	0.6629
	HHHX	0.6301	CX,CX	XX	0.3644
MCX	MEHX	1.1584	CM,CMH	MEHX	0.1845
	MEXX	1.2696		MEHH	0.1845
CCX	HXHX	1.2246		MEXX	0.1510
	XXHX	1.5814	MC,MCH	MEHX	0.2067
	HHHX	0.8863		MEHH	0.3065
	HXXX	1.4457	MC,MCX	MEHX	0.1003
	HHXX	1.2605		MEXX	0.0998
HCX	HX	0.8751	MC,MCC	MEHXHX	0.3584
XCX	XX	1.0200		MEHXXX	0.3584
MCC	MEHXHX	1.0835		MEHXHH	0.3334
	MEHXXX	1.0047		MEXXHX	0.3706
	MEHXHH	1.0641		MEXXHH	0.1293
	MEXXHX	0.8865		MEHHHX	0.3165
	MEXXHH	0.8965		MEHHXX	0.3165
	MEHHXX	0.9987	CC,CCC	HXHXHX	0.4994
	MEHHHX	0.9987		HXHXXX	0.4994
CCC	HXHXHX	1.1746		XXHXHX	0.4994
	HXHXXX	1.1746		HXHXHH	0.3744
	HXHXHH	1.0918		HHHXXX	0.3584
	XXHXHH	1.0047		HHHXHX	0.3584
	HHHXHH	0.9218		XXHXHH	0.1226
	HXHHHX	1.2269		HXHHHX	0.1700
	HXHHXX	1.2269		HXHHXX	0.1700
	XXHHXX	1.2269		XXHHHX	0.1700
	HHXXHH	0.8965		XXHHXX	0.1700
	HHXXHX	0.8865		HHXXHH	0.2064
	HXXXHX	0.8865		HHXXHX	0.3706
M.C	MEHX	0.1410		HXXXHH	0.2912
	MEXX	0.1410		HXXXHX	0.2912
	MEHH	0.0784		HHHXHH	0.1200
C.C	HXHX	0.2733	CC,CCH	HXHX	0.0395
	HXXX	0.2733		XXHX	0.1000
	HXHH	0.1432		HHHX	0.1000
	XXHH	0.2733		HXHH	0.1200
MH,MH	ME	0.0010		XXHH	0.0483
CH,CH	HH	0.0167	(CC,CCH)‡	-HX-	0.1603
MC,CC	MEHXHX	0.2691	CC,CCX	HXHX	0.2614
	MEHXXX	0.2691		XXHX	0.2022

Table 2 (*continued*)

Constant*	Environ.†	Value	Constant*	Environ.†	Value
	HXXX	0.1533		XXHXHX	−0.0160
	HHXX	0.2061		HHHXHX	−0.0160
	HHHX	0.2061		HHHXHH	−0.0160
(CC,CCX)‡	–HX–	0.4070		HXXXHX	−0.0503
	–XX–	0.4070		HXXXHH	−0.0503
CC,CCM	HXHXME	0.3744		HHXXHX	−0.0456
	HHHXME	0.3754		HHXXHH	−0.0503
	XXHXME	0.1226	CX,CCX′	HXXX	−0.0645
	HXXXME	0.2912		HHXX	−0.0664
	HHXXME	0.2064	CX,MCX′	MEXX	−0.0893
	HXHHME	0.2064	CX,CCC	HXHXHX	−0.0549
	XXHHME	0.2064		HXHXXX	−0.0549
CX,HCX	HX	0.0996		HXHXHH	−0.0878
CX,XCX	XX	0.2099		HHHXHH	−0.1500
CX,MCX	MEHX	0.3922		HHXXHH	−0.0480
	MEXX	0.4052		HHXXHX	−0.1793
CX,CCX	HXHX	0.5727		HXXXHX	−0.1793
	XXHX	0.6100	HMH,HMH	ME	0.0091
	HXXX	0.6635	HMH,CMH	MEHX	0.0039
	HHHX	0.4095		MEXX	0.0182
	HHXX	0.5611		MEHH	0.0039
CX,MCC	MEHXHX	−0.0693	CMH,CMH	MEHX	−0.0237
	MEHXXX	−0.1602		MEHH	−0.0237
	MEHXHH	−0.0300		MEXX	−0.0212
	MEXXHX	−0.1793	CCH,CCH′	HXHH	−0.0300
	MEXXHH	−0.0840		XXHH	−0.0423
MC,HCC	MEHXHX	−0.0256		HHHH	−0.0400
	MEHHHX	−0.0218	MCH,MCH′	MEHH	−0.0032
	MEHHXX	−0.0256	MCH,HCX	MEHX	0.1483
	MEHXXX	−0.0218	CCH,HCX	HXHX	0.1583
	MEHXHH	−0.0730		XXHX	0.1022
CC,HCM	HXHXME	−0.0803		HHHX	0.1528
	XXHXME	−0.0865	(CCH,HCX)‡	–HX–	0.1507
	HHHXME	−0.1443	MCH,HCC	MEHXHX	0.0293
	HXHHME	−0.0543		MEHXXX	0.0240
	XXHHME	−0.0400		MEHXHH	0.0338
	HHHHME	−0.0543		MEHHHX	0.0240
CC,HCC′	HXHXHX	−0.0142		MEHHXX	0.0440
	HXHXXX	−0.0142	CCH,HCC′	HXHXHX	0.0135
	XXHXHX	−0.0142		HXHXHH	0.0293
	HXHXHH	−0.0803		HXHXXX	0.0135
	HHHXXX	−0.0218		HHHXHH	0.0000
	HHHXHX	−0.0256		HHHXXX	0.0240
	HXHHHX	−0.0862		HXHHHX	0.0036
	HXHHXX	−0.0862		HXHHXX	0.0036
	XXHHHX	−0.0862		XXHHXX	0.0036
	XXHHXX	−0.0862	MCH,MCX	MEHX	0.0999
	HHHXHH	−0.0698	CCH,CCX	HXHX	−0.2683
	XXHXHH	−0.0865		HHHX	−0.1945
MC,XCC	MEHXHX	−0.0130		XXHX	−0.1000
	MEHXHH	−0.0130	MCX,HCX	MEHX	−0.0551
	MEHXXX	0.0000	CCX,HCX	HXHX	−0.1603
	MEXXHX	−0.0456		HHHX	−0.0111
	MEXXHH	−0.0651		XXHX	−0.3567
CC,XCM	HXHXME	−0.0240	(CCX,HCX)‡	–HX–	−0.0115
	XXHXME	0.0000	MCX,XCC	MEHXHX	0.0100
	HHHXME	−0.0300		MEHXXX	0.0100
	HXXXME	−0.0503		MEHXHH	0.0100
	HHXXME	−0.0503		MEXXHX	0.0948
CC,XCC′	HXHXHX	−0.0160		MEXXHH	0.1233
	HXHXXX	−0.0160	MCC,MCH	MEHXHX	−0.0470
	HXHXHH	−0.0240		MEHXHH	−0.2188

Table 2 (*continued*)

Constant*	Environ.†	Value	Constant*	Environ.†	Value
	MEHXXX	−0.0783		MEHXHX	0.0080
	MEHHHX	−0.1301		MEHXXX	0.0080
	MEHHXX	−0.1301		MEHXHH	0.0080
MCC,CCH	MEHXHX	−0.1364		MEHHXX	0.0080
	MEHXHH	−0.0540		MEHHHX	0.0080
	MEHXXX	−0.0599		MEHHHH	0.0080
	MEHHHX	−0.0898	C.C,C.C	HXHXHX	0.0080
	MEHHXX	−0.0898		HXHXHH	0.0080
CCC,CCH	HXHXHX	−0.1500		HXHXXX	0.0080
	HXHXXX	−0.1500		HHHXHH	0.0080
	HXHXHH	−0.1364		HHHXXX	0.0080
	XXHXHX	−0.1500		HHXXHH	0.0080
	XXHXHH	−0.0783		HHXXHX	0.0080
	HHHXXX	−0.0599		HXXXHX	0.0080
	HHHXHX	−0.0470		HXHHHX	0.0080
	HHHXHH	−0.1100		HXHHXX	0.0080
	HXHHHX	−0.0688		XXHHXX	0.0080
	HXHHXX	−0.0688	$(HMC,MCH)_T$	MEHX	0.0706
	XXHHHX	−0.0688		MEHH	0.1037
	XXHHXX	−0.0688	$(HMC,MCH)_G$	MEHX	−0.0194
MCC,MCX	MEHXHX	−0.0133		MEHH	−0.0460
	MEHXXX	−0.0236	$(HMC,MCXS)_T$	MEHX	−0.1542
	MEHXHH	−0.0107		MEXX	−0.2234
	MEXXHX	−0.0533	$(HMC,MCX)_G$	MEHX	−0.1222
	MEXXHH	−0.1442		MEXX	−0.0617
CCC,CCX	HXHXHX	−0.4488	$(CCM,CMH)_T$	HXHXME	0.0456
	HXHXXX	−0.4488		HHHXME	0.1316
	HXHXHH	−0.3724		XXHXME	0.0050
	HHHXXX	−0.1985		HXXXME	0.0745
	HHHXHH	−0.1473		HHXXME	0.0580
	XXHXHX	−0.4488		HXHHME	0.0545
	HHHXHX	−0.3724		XXHHME	0.0545
	XXHXHH	−0.3649	$(CCM,CMH)_G$	HXHXME	−0.0517
	HXXXHH	−0.1985		HHHXME	−0.0570
	HHXXHX	−0.0236		XXHXME	−0.0473
	HXXXHX	−0.4488		HXXXME	−0.0864
	HHXXHH	−0.0179		HHXXME	−0.0864
MCC,CCX	MEHXHX	−0.3724		HXHHME	−0.0864
	MEHXHH	−0.3582		XXHHME	−0.0864
	MEHXXX	−0.2174	$(MCC,CCX)_T$	MEHXHX	−0.1218
	MEXXHX	−0.1985		MEHXXX	−0.1218
	MEXXHH	−0.0179		MEHHHX	−0.1218
MCX,XCX	MEXX	−0.1824		MEHHXX	−0.1826
CCX,XCX	HXXX	−0.2858		MEXXHX	−0.0070
	HHXX	−0.1000		MEXXXX	−0.0070
CCX,CCX'	HXXX	0.0492	$(MCC,CCX)_G$	MEHXHX	−0.0044
	HHXX	0.2500		MEHXXX	−0.1435
(MCX,XCC)§	MEXXHX	0.0533		MEHHHX	−0.0299
	MEXXHH	0.0040		MEHHXX	−0.0841
MCX,MCX'	MEXX	0.1646		MEXXHX	−0.2498
CCX,XCC	HXHXHX	0.0100		MEXXXX	−0.2498
	HXHXHH	0.0100	$(MCC,CCH)_T$	MEHXHX	−0.1504
	HXHXXX	0.0100		MEHXHH	−0.1300
	HHHXHH	0.0100		MEXXHX	−0.2564
	HHXXHH	0.0948		MEXXHH	−0.4449
	HHXXHX	0.0948		MEHHHX	−0.1300
	HXXXHX	0.0948	$(MCC,CCH)_G$	MEHXHX	−0.1168
(CCX,XCC)§	HXXXHX	0.0533		MEHXHH	−0.0695
	HXXXHH	0.0533		MEXXHX	−0.1815
	HHXXHH	0.0040		MEXXHH	−0.1515
M.C,C.C	MEXXHX	0.0080		MEHHHX	−0.1168
	MEXXHH	0.0080	$(HCC,CCX)_T$	HXHX	−0.1261

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Table 2 (continued)

Constant*	Environ.†	Value	Constant*	Environ.†	Value
	HXXX	−0.1509		HHHXHX	−0.0903
	HHHX	−0.1029		XXHXHX	−0.0903
	HHXX	−0.2993		HXHXHH	−0.0903
(HCC,CCX)$_G$	HXHX	−0.2988		HHHXHH	−0.1300
	HXXX	−0.1723		XXHXHH	−0.0903
	HHHX	−0.1620		HXXXHX	−0.0903
	HHXX	−0.0208		HXXXHH	−0.0903
(XCC,CCX)$_T$	HXHX	−0.1579		HHXXHX	−0.0903
	HXXX	−0.2647		HHXXHH	−0.0903
(XCC,CCX)$_G$	HXHX	0.0121		XXHHHX	−0.0930
	HXXX	0.1028		HXHHHX	−0.0930
(HCC,CCH)$_T$	HXHX	0.0636	(CCC,CCH)$_G$	HXHXHX	−0.0966
	HXHH	0.0852		HHHXHX	−0.0966
(HCC,CCH)$_G$	HXHX	−0.0403		XXHXHX	−0.0966
	HXHH	−0.0403		HXHXHH	−0.0966
(CCC,CCX)$_T$	HXHXHX	−0.1218		HHHXHH	−0.0481
	HHHXHX	−0.1218		XXHXHH	−0.1815
	XXHXHX	−0.1218		HXXXHX	−0.0966
	HXHXXX	−0.1218		HXXXHH	−0.1815
	HHHXXX	−0.1218		HHXXHX	−0.1815
	XXHHXX	−0.1668		HHXXHH	−0.1515
	HXHHXX	−0.1668		XXHHHX	−0.1246
	HXHHHX	−0.1668		HXHHHX	−0.1246
	XXHHHX	−0.1668	(MCC,CCC)$_T$	M–C–C–C–	−0.0889
	HXXXHX	−0.1218	(MCC,CCC)$_G$	M–C–C–C–	−0.1302
	HHXXHX	−0.1218	(MCC,CCM)$_T$	MEHHHHME	−0.0889
(CCC,CCX)$_G$	HXHXHX	0.0754		MEHXHHME	−0.0889
	HHHXHX	0.0754		MEHXHXME	−0.0889
	XXHXHX	0.0754		MEXXHHME	−0.0719
	HXHXXX	0.0754		MEXXHXME	−0.0719
	HHHXXX	0.0754	(MCC,CCM)$_G$	MEHHHHME	−0.1302
	XXHHXX	0.0100		MEHXHHME	−0.1302
	HXHHXX	0.0100		MEHXHXME	−0.1302
	HXHHHX	0.0100		MEXXHHME	−0.3143
	XXHHHX	0.0100		MEXXHXME	−0.0932
	HXXXHX	0.0754	(CCC,CCC)$_T$	–C–C–C–C–	−0.0889
	HHXXHX	0.0754	(CCC,CCC)$_G$	–C–C–C–C	−0.1302
(CCC,CCH)$_T$	HXHXHX	−0.0903			

* M = Methyl carbon; X = chlorine; T = *trans*; G = *gauche*; AB = AB stretch; ABC = ABC bend; Y,Z = YZ interaction; A.B = AB torsion. See Fig. 1 for designation of atoms in groups.

† ME = methyl group; HH = CH$_2$; HX = CHCl; XX = CCl$_2$.

‡ (Y,Z)‡ = interaction for center C in a triplet containing Cl atoms (neighboring C atoms may have one or two Cl atoms).

§ (Y,Z)§ = cross interaction; i.e. (CCX,XCC)§ = (CCX,X'CC') in C–XCX'–C'–.

Such an empirical refined force field is, of course, not unique. However, since the number of frequencies used in the refinement was about twice the number of independent force constants (which was about 260), we feel that the force field will give a good representation of the normal modes and their frequencies for a wide range of multiply-chlorinated hydrocarbons.

CARBON–CHLORINE STRETCH FREQUENCIES

Since normal mode calculations can be particularly useful in studying the conformation-sensitive carbon–chlorine stretch frequencies [3–5, 9–11], we have given particular attention to the refinement of this part of the force field. In Table 3 we bring together the results for this part of the spectrum for all of the molecules used in our

refinement (details for other parts of the spectrum can be found in the references cited or in [12]).

It can be seen from Table 3 that the agreement between observed and calculated frequencies is very good. For the 74 observed bands, the average error is 4.5 cm^{-1}, with

Table 3. Observed and calculated CCl stretch frequencies of chlorinated hydrocarbons

Mol.*	Obs.*	Calc.	Conformer†	Potential energy distribution‡
2-CB	670	678	G′	CX s(71) CHX def(19) CH$_2$ def(13)
	627	630	G	CX s(81) CX ib(19) CHX def(10)
	607	614	T	CX s(92) CHX def(16)
3-CP	668	684	GG	CX s(62) CH$_2$ def(11) CX ib(11) CHX def(11)
	657	664	TG′	CX s(63) CH$_2$ r(15) CH$_2$ def(14) CHX def(13)
	633	626	TG	CX s(72) CX ib(19) CH$_2$ r(11) CH$_2$ def(10)
	606	603	TT	CX s(93) CHX def(11) CH$_2$ r(10)
2,4-DCP	718	718	GG(r)	C$_2$X s(30) C$_4$X s(30) CH$_2$ def(17)
	682	678	TG(r)	C$_4$X s(73) C$_4$HX def(18) CH$_2$ def(10)
	631	624	TT(r)	C$_2$X s(47) C$_4$X s(47)
	611	615	TT(r)	C$_2$X s(47) C$_4$X s(47) C$_2$HX def(11) C$_4$HX def(11)
	685	679	TG(m)	C$_4$X s(72) C$_4$HX def(19) CH$_2$ def(11)
	645	635	TG′(m)	C$_4$X s(67) C$_4$X ib(17) C$_2$X s(11) C$_4$HX def(10)
	618	619	TG(m)	C$_2$X s(94) C$_2$HX def(17)
2,4,6-TCH	725	724	TTGG(s)	C$_6$X s(28) C$_4$X s(26) C$_5$H$_2$ def(20) C$_6$HX def(10)
	632	631	TTGG(s)	C$_6$X s(44) C$_4$X s(40) C$_2$X s(14)
	632	628	TTTT(s)	C$_2$X s(35) C$_6$X s(35) C$_4$X s(26)
	632	625	TTTT(s)	C$_2$X s(39) C$_6$X s(39) C$_2$HX def(11) C$_6$HX def(11)
	608	618	TTGG(s)	C$_2$X s(79) C$_2$HX def(16) C$_4$X s(10)
	608	610	TTTT(s)	C$_4$X s(69) C$_2$X s(13) C$_6$X s(13) C$_4$HX def(12)
	688	702	G′TTG(i)	C$_2$X s(28) C$_6$X s(28) C$_3$H$_2$ def(12) C$_5$H$_2$ def(12) C$_2$HX def(11) C$_6$HX def(11)
	688	694	TGTG(i)	C$_4$X s(30) C$_6$X s(28)
		670	TGTG(i)	C$_6$X s(43) C$_4$X s(35) C$_6$HX def(10)
		668	G′TTG(i)	C$_2$X s(41) C$_6$X s(41)
	635	637	TTTT(i)	C$_4$X s(40) C$_2$X s(28) C$_6$X s(28)
	619	619	TGTG(i)	C$_2$X s(92) C$_2$HX def(17)
	614	614	G′TTG(i)	C$_4$X s(94) C$_4$HX def(13)
	688	689	TTTG(h)	C$_6$X s(62) C$_6$HX def(19) C$_5$H$_2$ def(16)
	688	685	TTG′T(h)	C$_4$X s(63) C$_4$HX def(14) C$_5$H$_2$ def(13)
	628	624	TTTG(h)	C$_2$X s(68) C$_4$X s(24) C$_2$HX def(12)
	620	623	TTG′T(h)	C$_6$X s(48) C$_2$X s(46)
	620	616	TTG′T(h)	C$_2$X s(46) C$_6$X s(44)
	610	611	TTTG(h)	C$_4$X s(71) C$_2$X s(22) C$_4$HX def(11)
PVC	640	636	(s)	CX s(96) CX ib(20) CHX def(12)
	604	609	(s)	CX s(96) CHX def(26)
2,3-DCB	703	706	MRSM(T)	CX s(45) CX ib(20) CHX def(24) CH ob(21) M r2(21)
	652	655	MRSM(T)	CX s(97)
	344	352	MRSM(T)	CX s(48) CHX def(27)
	706	700	MRRM(T)	CX s(50) CX ib(46) M r2(18) CHX def(14)
	597	602	MRRM(T)	CX s(94) CHX def(18)
	519	511	MRRM(T)	CX s(50) CX ib(26) CX ob(12)
	697	708	MRSM(G)	CX s(59) CHX def(34) CX ib(13) M r2(11)
	650	649	MRSM(G)	CX s(57) CX ib(38) CHX def(17)
	532	529	MRSM(G)	CX s(42) CX ib(36)
	420	427	MRSM(G)	CX s(33) CX ob(17) CX ib(15)
	729	723	MRRM(G)	CX s(46) CHX def(38) CH ob(18) M r2(18) CX ib(18)
	650	653	MRRM(G)	CX s(98)
	370	375	MRRM(G)	CX s(42) CHX def(16) CX ib(16)
2,3,4-TCP	765	765	TT(r)	C$_3$X ib(28) C$_3$X s(21) C$_2$H ob(10) C$_4$X s(10)
	673	672	TT(r)	C$_2$X s(69) C$_2$HX def(15) C$_3$X s(10)
	626	616	TT(r)	C$_4$X s(68) C$_3$X s(13) C$_4$HX def(11) C$_4$X ib(10)
	553	549	TT(r)	C$_3$X s(17) C$_4$X s(16) C$_4$X ib(13)
	745	742	TG(m)	C$_3$X s(24) C$_3$HX def(20) C$_3$X ib(14) C$_4$X s(13) C$_2$X ib(10)
	697	701	TG(m)	C$_4$X s(42) C$_4$HX def(20) C$_3$X ib(14) C$_2$X s(12)
	668	672	TG(m)	C$_2$X s(57) C$_3$X s(17) C$_2$HX def(13)

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Table 3 (*continued*)

Mol.*	Obs.*	Calc.	Confermer†	Potential energy distribution‡
	552	553	TG(m)	C_4X ib(33) C_3X s(26) C_3X ob(10)
2,2-DCPr	656	653		CX_2 as(97) CX_2 r(44) M r2(13)
	559	561		CX_2 ss(66) CX_2 def(11)
2,2-DCB	645	646	T	CX_2 as(114) CX_2 r(56)
	544	547	T	CX_2 ss(81)CX_2 b(13)
	276	269	T	CX_2 b(80) CX_2 ss(16) CX_2 def(10)
	692	691	G	CX_2 as(85) CX_2 r(50) CH_2 def(16)
	567	569	G	CX_2 ss(59) CX_2 as(17) CX_2 def(14) CX_2 b(10)
	413	417	G	CX_2 w(26) CX_2 ss(18) CH_2 def(16) CX_2 as(10)
2,2,3-TCB	733	727	T	CX_2 r(52) CX_2 as(49) CX ib(20) CX s(13)
	668	668	T	CX s(60) CX_2 as(20) CX_2 ss(10)
	570	565	T	CX_2 ss(52) CX_2 as(32) CX_2 b(11)
	361	362	T	CX s(21) CX_2 as(17) CX_2 ss(11)
	733	737	G	CX_2 as(53) CX_2 r(48) CHX def(26) CX s(16)
	681	672	G	CX s(58) CX_2 as(32)
	625	624	G	CX_2 ss(44) CX_2 def(26) CX ib(26)
	439	437	G	CX ib(23) CX_2 ss(21) CX_2 def(10)
	721	723	G′	CX_2 as(64) CX_2 r(48) CX ib(17)
	699	687	G′	CX s(61) CHX def(23) CX_2 def(18)
	562	558	G′	CX_2 ss(60) CX_2 as(23) CX_2 b(14)
	483	471	G′	CX_2 w(22) CX s(19) CX ib(16) CX_2 as(11)

* 2-CB: 2-chlorobutane [4]; 3-CP: 3-chloropentane [4]; 2,4-DCP: 2,4-dichloropentane [5]; 2,4,6-TCH: 2,4,6-trichloroheptane [5]; PVC: poly(vinyl chloride) [9]; 2,3-DCB: 2,3-dichlorobutane [6]; 2,3,4-TCP: 2,3,4-trichloropentane [1]; 2,2-DCPr: 2,2,-dichloropropane [7]; 2,2-DCB: 2,2-dichlorobutane [8]; 2,2,3-TCB: 2,2,3-trichlorobutane [2].

† T = *trans*; G = *gauche*; s = syndiotactic; i = isotactic; h = heterotactic; M = methyl; for R and S see [6]; r = *racemic*; m = *meso*.

‡ See Table 1 for definitions of local symmetry coordinates. *n* in C_nX refers to carbon atom number in molecular backbone. Contributions to PED of 10 or larger.

only 8 bands having errors of $10\,\mathrm{cm}^{-1}$ or more. (The error could probably be reduced if non-standard torsion angles were used for some of the conformers [4].) This force field should therefore be suitable for predicting the normal mode frequencies of different conformations of multiply-chlorinated hydrocarbons, including polymers.

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