# Equilibrium Geometry and Vibrational Frequencies of the 1 : 2 van der Waals Complexes between Methyl Chloride and Hydrogen Chloride

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The equilibrium geometry, relative stability and vibrational frequencies for the 1:2 van der Waals complexes between  $CH_3CI$  and HCI have been investigated using MP2/6-31 + G\*\* *ab initio* calculations. The results are used to interpret the IR spectrum of the 1:2 complex observed in solutions of  $CD_3CI$ -HCI mixtures dissolved in liquefied argon, and show that in these solutions the chain complex  $CD_3CI$  · HCI · HCI is formed.

The mid- and far-IR spectra of several solutions in liquefied noble gases containing both an alkyl chloride [CD<sub>3</sub>Cl, C<sub>2</sub>D<sub>5</sub>Cl, (CD<sub>3</sub>)<sub>2</sub>CDCl, etc.] and hydrogen chloride have been described.<sup>1,2</sup> In all spectra, evidence was found for the occurrence of a 1:1 species RCl · HCl in which the HCl molecule is hydrogen bonded to the chlorine atom of the RCl molecule. In several spectra, evidence was also found for the existence of another species, the stoichiometry of which was determined to be  $(RCl) \cdot (HCl)_2$  and which was expected to have a chain structure. As can be seen in Fig. 1(a) in such a complex, further described as RCl·HCl·HCl, the second HCl molecule is hydrogen bonded to the chlorine atom of the first HCl molecule. However, by analogy with the results obtained for  $H_2O \cdot (HCl)_2$ ,<sup>3</sup> dimethylether  $\cdot (HCl)_2$ <sup>4</sup> and dimethyl sulfide  $(HCl)_2$ ,<sup>5</sup> a bifurcated structure can also be proposed, in which both HCl molecules are hydrogen bonded to the chlorine atom of the RCl molecule. Such a structure is shown in Fig. 1(b).

Note that for all the solutions described before,<sup>1,2</sup> only one band of the 1:2 species was observed in the  $v_{HC1}$  region, while both geometries are expected to give rise to two bands. Furthermore, no absorption bands of the 1:2 species were observed in the  $v_{CC1}$  region. Thus, it is clear that in the previous studies<sup>1,2</sup> a rather incomplete description of the spectra of the 1:2 complex has been given.

As little is known about the 1 : 2 complex between methyl chloride and hydrogen chloride, in this study it was decided to carry out *ab initio* calculations of the equilibrium geometry, the relative stability and the vibrational frequencies for both the bifurcated and the chain structure. As reliable information on weakly bound complexes can only be obtained at the post-Hartree–Fock level,<sup>6,7</sup> the present calculations were performed at the MP2/6-31 + G\*\* level.

Also, to complete the body of experimental data, in this study new IR experiments were carried out, studying solutions in liquefied argon of  $CD_3Cl-HCl$  and  $C_2D_5Cl-HCl$  mixtures at higher concentrations than those used before.<sup>1,2</sup> These experiments were interpreted using the results from the *ab initio* calculations.

#### (a) (b) H-CI R-CI R-CI (b) H-CI H-CI

**Fig. 1** Possible equilibrium geometries for the  $(CH_3Cl) \cdot (HCl)_2$  van der Waals complex: (a) chain structure, (b) bifurcated structure

#### Experimental

## **Computational Details**

For both the chain structure and the bifurcated structure the MP2/6-31 +  $G^{**}$  equilibrium geometry was calculated using the GAUSSIAN 92 program,<sup>8</sup> as implemented on an IBM RS/6000 workstation. For all calculations, the correlation energy was calculated using all molecular orbitals, while the Berny geometry optimization was used with the tight convergence criteria. Furthermore, no restrictions due to a possible symmetry of the species were imposed.

For both structures, the vibrational frequencies and the corresponding IR intensities were calculated using standard harmonic force fields. The latter were obtained by calculating the numeric second derivatives of the energy with respect to the Cartesian coordinates using the analytically determined first derivatives.

#### Synthesis and Spectroscopy

The sample of CD<sub>3</sub>Cl was synthesized by mixing CD<sub>3</sub>OD (Janssen Chimica 16.635.48) and a small amount of PCl<sub>3</sub> at room temperature.  $C_2D_5Cl$  was synthesized by adding an amount of  $C_2D_5I$  (MSD Isotopes, MD-211) to an excess of dry, fresh AgCl. After 48 h, the reaction mixture containing both  $C_2D_5Cl$  and  $C_2D_5I$  was collected by bulb-to-bulb distillation. The hydrogen chloride was made in small amounts by hydrolysing PCl<sub>3</sub> with water, and was purified afterwards by pumping the reaction mixture through a propan-2-ol slush. All compounds were purified on a low-pressure, low-temperature fractionation column. The argon used in this study has a stated purity of 99.9999%, and was used without further purification.

All spectra were recorded using a Bruker 113v Fouriertransform spectrometer, equipped with a Globar source, Ge/KBr beamsplitter and an  $LN_2$  cooled broadband MCT detector. The interferograms of the mid-IR spectra, recorded at a resolution of 0.5 cm<sup>-1</sup>, were averaged over 200 scans, Happ Genzel-apodized and Fourier-transformed using a zero-filling factor of 4. A detailed description of the liquid noble-gas setup was given in a previous study<sup>1</sup> and will not be repeated here.

#### **Results and Discussion**

## Equilibrium Geometry

#### CH<sub>3</sub>Cl · HCl · HCl

A starting geometry for  $CH_3Cl \cdot HCl \cdot HCl$  was obtained by combining the structural parameters of  $CH_3Cl \cdot HCl$ <sup>9</sup> and





Fig. 2 MP2/6-31 + G\*\* equilibrium geometry of  $CH_3Cl \cdot HCl \cdot HCl$ 

HCl·HCl.<sup>10</sup> At the MP2/6-31 + G\*\* level, these complexes are planar, *i.e.* the dihedral angle  $\tau_{X-Cl\cdots H-Cl}$  is equal to 0°. Therefore, for all calculations on CH<sub>3</sub>Cl·HCl·HCl, the initial value for the dihedral angles  $\tau_{R-Cl\cdots H-Cl}$  and  $\tau_{H-Cl\cdots H-Cl}$  was set at 0°. For a complete description of the relative orientation of the three molecules, the value of the dihedral angle  $\tau_{Cl\cdots H-Cl\cdots H}$  must also be given. Because at the outset no information was available on this angle, several initial geometries with a different value for  $\tau_{Cl\cdots H-Cl\cdots H}$  were refined using standard convergence criteria. All optimizations resulted in the same equilibrium geometry, which was subsequently refined using the tight convergence criteria. The equilibrium geometry obtained is shown in Fig. 2, and its structural parameters are given in Table 1.

As can be seen in Fig. 2, the equilibrium geometry of  $CH_3CI \cdot HCI \cdot HCI$  is cyclic. This structure suggests an inter-

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action between H(4) and Cl(9). Such an interaction was observed in  $(CH_3)_2CO \cdot HCl^{11}$  and in  $CH_3Cl \cdot HCl^1$  and its occurrence in  $CH_3Cl \cdot HCl \cdot HCl$  is therefore not surprising. As described before,<sup>8</sup> during the formation of  $RCl \cdot HCl$ , the structural parameters of the methyl group in  $CH_3Cl$  are hardly affected. In contrast, Table 1 shows that when a second HCl molecule is added, the distortion of the methyl group strongly increases. This proves the existence of a weak interaction  $C-H \cdots Cl-H$ .

In Table 1, the structural parameters of  $CH_3Cl \cdot HCl$  and  $HCl \cdot HCl$  and of the monomers are also given. The data show that the hydrogen-bond lengths  $Cl(2) \cdots H(6)$  and  $Cl(7) \cdots H(8)$  in  $CH_3Cl \cdot HCl \cdot HCl$  are both shorter than the corresponding bond in  $CH_3Cl \cdot HCl$ . As a decrease in bond length reflects an increase in bond strength, these differences neatly demonstrate the cooperative effect<sup>12</sup> in the 1:2 species. This effect also explains the increased H-Cl bond lengths in the 1:2 complex compared with the corresponding bonds in  $CH_3Cl \cdot HCl$ .

During the formation of CH<sub>3</sub>Cl·HCl, the C–Cl bond lengthens by 0.0036 Å, indicating a weakening of the bond. In agreement with this, the C–Cl stretch of the complex is observed at a lower frequency than that of the monomer.<sup>1,2</sup> Adding a second HCl to form the chain complex, the C–Cl bond length increases by another 0.0027 Å. Thus, the C–Cl stretch of the 1 : 2 complex must again be shifted to lower frequencies, by an amount of the same magnitude as that of the first shift. Hence, this stretching mode is expected to be observed separately in the vibrational spectra.

It is clear from Table 1 that the dihedral angles  $\tau_{R-Cl\cdots H-Cl}$ and  $\tau_{H-Cl\cdots H-Cl}$  have values significantly different from 0. Consequently, the chain complex is not planar. In this respect, the 1 : 2 complex obviously differs from CH<sub>3</sub>Cl·HCl.

Table 1 MP2/6-31 + G\*\* structural parameters of CH<sub>3</sub>Cl·HCl, HCl, HCl, CH<sub>3</sub>Cl·HCl · HCl and CH<sub>3</sub>Cl(·HCl)<sub>2</sub>

	monome	r species	1:1 s	pecies	1 : 2 spo	ecies
internal coordinate <sup>a</sup>	CH <sub>3</sub> Cl <sup>b</sup>	HCl <sup>b</sup>	HCl · HCl <sup>c</sup>	CH <sub>3</sub> Cl · HCl <sup>b</sup>	CH <sub>3</sub> Cl · HCl · HCl <sup>d</sup>	$CH_3Cl(\cdot HCl)_2^d$
bond length/Å						
r[C(1)-Cl(2)]	1.7761			1.7807	1.7834	1.7853
r[C(1)-H(3)]	1.0836			1.0832	1.0830	1.0833
r[C(1)-H(4)]	1.0836			1.0835	1.0827	1.0831
r[C(1)-H(5)]	1.0836			1.0835	1.0834	1.0831
$r[Cl(2)\cdots H(6)]$				2.4634	2.4102	2.4957
r[H(6)-Cl(7)]		1.2689	1.2700	1.2746	1.2778	1.2733
$r[Cl(7)\cdots H(8)]$			2.5926		2.5348	
r[H(8)—Cl(9)]		1.2689	1.2714		1.2739	
bond angle/degrees						
$\angle [H(3) - C(1) - Cl(2)]$	108.9			108.5	108.14	108.71
$\angle [H(4) - C(1) - Cl(2)]$	108.9			108.8	108.83	108.40
$\angle [H(5)-C(1)-Cl(2)]$	108.9			108.8	108.69	108.40
$\angle [C(1)-Cl(2)\cdots H(6)]$				93.4	100.77	92.68
$\angle [Cl(2) \cdots H(6) - Cl(7)]$				166.0	167.92	167.27
$\angle [H(6) - Cl(7) \cdots H(8)]$			105.0		90.29	
$\angle [Cl(7) \cdots H(8) - Cl(9)]$			174.6		162.93	
$\tau [H(4) - C(1) - C[(2) - H(3)]$	120.0			119.9	120.06	120.08
$\tau$ [H(5)-C(1)-Cl(2)-H(3)]	-120.0			-119.9	-119.64	-120.08
$\tau [H(3) - C(1) - C(2) \cdots H(6)]$				180.0	186.20	64.36
$\tau [C(1) - C(2) \cdots H(6) - C(7)]$				0.0	22.93	-1.60
$\tau$ (C)(2)···H(6)-C)(7)···H(8)]					15.89	
$\tau [H(6) - Cl(7) \cdots H(8) - Cl(9)]$			0.0		-12.00	
dipole moment/D <sup>e</sup>	2.04	1.46	2.57	2.78	1.98	2.37
$E/E_{\rm h}$		-460.218345	-920.440113	-959.620436	- 1419.844747	
$E_{\rm BSSE}/E_{\rm h}$			-0.001704	-0.002477	-0.005320	-0.005013
$\Delta E/E_{\rm h}$			-0.001719	-0.002921	-0.006071	-0.005080
$\Delta E/kJ mol^{-1}$			-4.51	-7.65	-15.94	-13.36

<sup>a</sup> Atom numbering as defined in Fig. 4. <sup>b</sup> Taken from ref. 8. <sup>c</sup> Taken from ref. 10. <sup>d</sup> This study. <sup>e</sup> 1 D (Debye)  $\approx$  3.33564  $\times$  10<sup>-30</sup> C m.

## CH<sub>3</sub>Cl(·HCl)<sub>2</sub>

In order to find theoretical support for the possible occurrence of a bifurcated 1:2 complex MP2/6-31 + G\*\* calculations were also carried out. The resulting equilibrium geometry is shown in Fig. 3 and the structural parameters are given in Table 1.

From Table 1 it can be seen that on going from  $CH_3Cl \cdot HCl$  to  $CH_3Cl(\cdot HCl)_2$ , the H-Cl bond length decreases from 1.2746 to 1.2733 Å. At the same time, the  $Cl \cdots H$  hydrogen-bond length increases from 2.4634 to 2.4957 Å. This shows that when a second HCl molecule is attached to the chlorine atom of  $CH_3Cl$ , the hydrogen bond loses some of its strength. Also, the addition of a second HCl causes the C-Cl bond length to increase further from 1.7807 to 1.7853 Å. The resultant C-Cl distance in  $CH_3Cl(\cdot HCl)_2$  is somewhat larger than that in the linear complex. Finally, when forming the bifurcated complex from monomers, the structural parameters of the methyl group are hardly affected, showing that in this complex, in contrast to the linear one, there is no direct interaction between the methyl grouping and the HCl molecules.

### **Relative Stability**

It has been demonstrated before<sup>8</sup> that the contribution to the energy of a van der Waals complex due to the basis set superposition error,  $\Delta E_{\text{BSSE}}$ , is of the same order of magnitude as the difference between the energy of the complex and the energies of the monomers. In order to take this into account, the energy of complexation,  $\Delta E$ , is defined as:

$$\Delta E_{\rm CH_3Cl \cdot HCl \cdot HCl} = E_{\rm CH_3Cl \cdot HCl \cdot HCl} - E_{\rm CH_3Cl} - 2E_{\rm HCl} - \Delta E_{\rm BSSE}$$
(1)

Using the full counterpoise correction method,<sup>13</sup> the value for  $\Delta E_{\text{BSSE}}$ , was estimated to be  $-0.005320 E_{\text{h}}$  (Hartree). Using this value, and the energies of the species involved, from the above equation the complexation energy  $\Delta E$  for the chain complex is found to be  $-0.006071 E_{\text{h}}$  (-15.94 kJ mol<sup>-1</sup>).

The influence of the cooperative effect on the structural parameters has been noted above, and it is of interest to see what the impact of this effect is on the energy of the complex. The stabilisation due to the cooperative effect,  $\Delta E_{coop}$ , can be estimated from the expression:

$$\Delta E_{\rm coop} = \Delta E_{\rm CH_3Cl \cdot HCl \cdot HCl} - \Delta E_{\rm CH_3Cl \cdot HCl} - \Delta E_{\rm HCl \cdot HCl}$$
(2)

Using this equation, the cooperative effect,  $\Delta E_{coop}$ , was calculated to be  $-0.001413 E_h (-3.71 \text{ kJ mol}^{-1})$ .

The complexation energy of the bifurcated complex is derived from an expression similar to the one for the chain



Fig. 3 MP2/6-31 + G\*\* equilibrium geometry of  $CH_3Cl(\cdot HCl)_2$ 

structure:

$$\Delta E_{\text{CH}_3\text{Cl}(\cdot\text{HCl})_2} = E_{\text{CH}_3\text{Cl}(\cdot\text{HCl})_2} - E_{\text{CH}_3\text{Cl}} - 2E_{\text{HCl}} - \Delta E_{\text{BSSE}}$$
(3)

In an analogous way  $\Delta E_{\rm BSSE}$  for the complex was estimated to be  $-0.005013 E_{\rm h}$ . With the above expression, the complexation energy of CH<sub>3</sub>Cl(·HCl)<sub>2</sub> is then found to be equal to  $-0.005080 E_{\rm h}$  ( $-13.36 \text{ kJ mol}^{-1}$ ). Comparison with the result for the chain structure shows that the latter is the more stable of the two. The energy difference between them is 2.58 kJ mol<sup>-1</sup>. If this calculated energy difference is believed to be an acceptable measure of the free enthalpy difference between the two types of complexes, in an environment in which the chain structure is present in a reasonable concentration, the bifurcated complex will be present in a much lower, but in principle measurable, concentration.

By considering that both hydrogen bonds in  $CH_3Cl(\cdot HCl)_2$  are weaker than that in  $CH_3Cl\cdot HCl$ , the complexation energy of the former species is expected to be smaller than twice the value of the complexation energy of  $CH_3Cl$ , thus showing an anti-cooperative effect. Using the complexation energy of  $CH_3Cl\cdot HCl$  obtained before,<sup>9</sup> the energy of  $CH_3Cl(\cdot HCl)_2$  calculated in this study confirms this anti-cooperative effect.

#### Vibrational Spectra

For both types of complexes a vibrational analysis was made in terms of a symmetry force field. The chain complex has no elements of symmetry, and no subdivision of its normal coordinates based on symmetry can be made. The point-group symmetry of  $CH_3Cl(\cdot HCl)_2$  is  $C_s$ , and the normal coordinates divide into 12 having A' and 9 having A'' symmetry. Symmetry coordinates were constructed from the internal coordinates defined in Fig. 4 for the chain complex, and in Fig. 5 for the bifurcated complex. The symmetry coordinates are given in Tables 2 and 3, respectively. These coordinates



Fig. 4 Internal coordinates for  $CH_3Cl \cdot HCl \cdot HCl$ 



Fig. 5 Internal coordinates for  $CH_3Cl(\cdot HCl)_2$ 

**Table 2** Symmetry coordinates for the  $CH_3CI \cdot HCI \cdot HCI$  van der Waals complex

approximate description	symmetry coordinate <sup>a</sup>
CH <sub>3</sub> symmetric stretch	$S_1 = r_{13} + r_{14} + r_{15}$
CH <sub>3</sub> asymmetric stretch	$S_2 = 2r_{15} - r_{13} - r_{14}$
CH <sub>2</sub> asymmetric stretch	$S_3 = r_{13} - r_{14}$
C-Cl stretch	$S_{4} = r_{12}$
CH <sub>3</sub> asymmetric deformation	$S_{5} = 2\beta_{34} - \beta_{35} - \beta_{45}$
CH <sub>3</sub> asymmetric deformation	$S_6 = \beta_{35} - \beta_{45}$
CH <sub>3</sub> symmetric deformation	$S_7 = \beta_{34} + \beta_{35} + \beta_{45}$
5.	$-\alpha_{32}-\alpha_{42}-\alpha_{52}$
CH <sub>3</sub> rocking	$S_8 = 2\alpha_{52} - \alpha_{32} - \alpha_{42}$
CH <sub>3</sub> rocking	$S_9 = \alpha_{32} - \alpha_{42}$
ClH stretch	$S_{10} = r_{26}$
H-Cl stretch	$S_{11} = r_{67}$
C-ClH in-plane deformation	$S_{12} = \theta_{16}$
Cl···H-Cl in-plane deformation	$S_{13} = \theta_{27}$
CH <sub>3</sub> torsion	$S_{14} = \tau_{12}$
C - Cl - H - Cl torsion	$S_{15} = \tau_{26}$
Cl···H stretch	$S_{16} = r_{78}$
H-Cl stretch	$S_{17} = r_{89}$
C-Cl····H in-plane deformation	$S_{18} = \theta_{68}$
ClH-Cl in-plane deformation	$S_{19} = \theta_{79}$
Cl. H-Cl. H torsion	$S_{20} = \tau_{67}$
H-Cl···H-Cl	$S_{21} = \tau_{78}$
<u> </u>	

" Not normalised.

were used to transform the Cartesian force field by GAUSS-IAN 92 into a symmetry force field. Applying Wilson's FG matrix method<sup>14</sup> then led to the vibrational frequencies and potential-energy distributions. These are collected in Tables 4 and 5.

From the vibrational eigenvectors, and using the Cartesian dipole derivatives produced by GAUSSIAN 92, the IR intensities of the fundamental transitions were calculated. The intensities have been included in Tables 4 and 5.

Table 3 Symmetry coordinates for the  $CH_3Cl(\cdot\,HCl)_2$  van der Waals complex

approximate description	symmetry coordinate <sup>a</sup>
CH <sub>3</sub> asymmetric stretch	$S_1 = 2r_{13} - r_{14} - r_{15}$
CH <sub>3</sub> symmetric stretch	$S_2 = r_{13} + r_{14} + r_{15}$
CH <sub>3</sub> asymmetric deformation	$S_{3} = 2\beta_{A5} - \beta_{34} - \beta_{35}$
CH <sub>3</sub> symmetric deformation	$S_4 = \beta_{34} + \beta_{35} + \beta_{45}$
	$-\alpha_{32} - \alpha_{42} - \alpha_{52}$
CH <sub>3</sub> rocking	$S_5 = 2\alpha_{32} - \alpha_{42} - \alpha_{52}$
C—Cl stretch	$S_6 = r_{12}$
H-Cl stretch, in-phase	$S_7 = r_{67} + r_{89}$
Cl···H-Cl in-plane deformation,	$S_8 = \theta_{27} + \theta_{29}$
in-phase	
C - C - C - C + C + C + C + C + C + C +	$S_9 = \tau_{26} + \tau_{28}$
Cl···H stretch, in-phase	$S_{10} = r_{26} + r_{28}$
C-Cl···H in-plane deformation,	$S_{11} = \theta_{16} + \theta_{18}$
in-phase	
$H \cdots Cl \cdots H$ bending	$S_{12} = \chi$
A''	
A CH asymmetric stratch	S _ n
$CH_{3}$ asymmetric deformation	$S_{13} = r_{15} - r_{14}$
$CH_{3}$ asymmetric deformation	$S_{14} = p_{34} - p_{35}$
U = Cl stretch out of phase	$S_{15} = a_{32} - a_{42}$
Clush-Clip plane deformation	$S_{16} = r_{67} - r_{89}$
out of phase	$S_{17} = \theta_{27} - \theta_{29}$
C = C + H = C + c + c	S _ z _ z
Clust H stretch out of phase	$S_{18} = t_{26} - t_{28}$
$C = C   \dots H$ in plane deformation	$S_{19} = r_{26} - r_{28}$ $S_{19} = \theta_{10} - \theta_{10}$
out-of-phase	$b_{20} = b_{16} - b_{18}$
CH. torsion	$S = \tau$
0113 10101011	$c_{21} - c_{12}$

<sup>a</sup> Not normalised.

Table 4MP2/6-31 + G\*\*vibrational frequencies, IR intensitiesand potential energy distributions for the  $CH_3Cl \cdot HCl \cdot HCl$  van derWaals complex

$\tilde{v}/cm^{-1}$	IR intensity /km mol <sup>-1</sup>	P.E.D. <sup><i>a</i></sup>
3299.5	0.5	$S_3(86) + S_2(13)$
3289.7	3.0	$S_{2}(86) + S_{3}(13)$
3170.6	15.9	$S_1(100)$
3056.6	195.4	$S_{17}$ (96)
2998.7	309.7	$S_{11}$ (96)
1531.7	6.7	$S_5(74) + S_6(20)$
1527.1	7.0	$S_{6}(74) + S_{5}(20)$
1464.2	17.6	S <sub>7</sub> (97)
1084.7	3.3	S <sub>9</sub> (95)
1079.5	2.2	S <sub>8</sub> (96)
766.5	27.2	S <sub>4</sub> (96)
434.5	38.1	$S_{13}(50) + S_{18}(42)$
357.0	50.6	$S_{20}(53) + S_{15}(45)$
275.7	62.0	$S_{19}(49) + S_{13}(29)$
263.6	31.3	$S_{15}(46) + S_{20}(35) + S_{21}(10)$
107.6	9.7	$S_{10}(38) + S_{13}(12)$
90.8	1.4	$S_{16}(77)$
80.8	3.9	$S_{14}(35) + S_{12}(18) + S_{13}(12) + S_{16}(12)$
61.3	1.0	$S_{14}(47) + S_{15}(28)$
29.3	1.1	$S_{20}(38) + S_{15}(24) + S_{12}(18) + S_{18}(13)$
17.1	2.1	$S_{18}^{20}(32) + S_{20}^{20}(31) + S_{15}^{12}(20)$

<sup>a</sup> Symmetry coordinates defined in Table 2.

Table 4 shows that  $CH_3Cl \cdot HCl \cdot HCl$  is characterized by two well separated fundamentals in the  $v_{HCl}$  region, at 2998.7 and 3056.2 cm<sup>-1</sup>, respectively. The C—Cl stretching fundamental of the complex is predicted to appear at 766.5 cm<sup>-1</sup>, which is lower than the frequencies of 772.0 and 781.9 cm<sup>-1</sup> calculated for  $CH_3Cl \cdot HCl$  and  $CH_3Cl$ , respectively.<sup>9</sup> For the methyl vibrations small frequency shifts have been calculated on going from  $CH_3Cl$  to  $CH_3Cl \cdot HCl$ .<sup>1</sup> It can be seen in Table 4 that a similar effect is predicted for  $CH_3Cl \cdot HCl \cdot HCl$ . For example, the antisymmetric  $CH_3$ stretches of the latter are calculated at 3299.5 and 3289.7

Table 5MP2/6-31 + G\*\*vibrational frequencies, IR intensitiesand potential-energy distributions for the  $CH_3Cl(\cdot HCl)_2$  van derWaals complex

$\bar{\nu}/cm^{-1}$	IR intensity /km mol <sup>-1</sup>	P.E.D. <sup>a</sup>
A'		
3298.8	1.02	$S_{1}(100)$
3170.1	13.71	$S_{2}(100)$
3062.1	63.5	$S_{7}^{2}(99)^{\prime}$
1524.0	8.4	$S_{3}(94)$
1462.7	12.6	$S_{4}^{(98)}$
1079.3	2.3	S <sub>5</sub> (95)
762.9	27.1	$S_{6}^{2}(96)$
321.7	79.5	$S_8(69) + S_{11}(17) + S_{10}(13)$
269.6	20.3	S <sub>9</sub> (97)
78.6	0.6	$S_{10}$ (96)
28.2	4.4	$S_{11}(61) + S_8(36)$
11.1	0.7	$S_{12}^{(70)}$
A″		
3295.1	1.5	$S_{13}$ (100)
3056.1	324.8	$S_{16}^{15}$ (99)
1522.0	2.4	$S_{14}^{(94)}$
1081.5	2.7	$S_{15}^{+}(96)$
303.9	22.9	$S_{17}(68) + S_{20}(19) + S_{18}(12)$
299.3	62.4	$S_{18}(90)$
110.0	8.1	$S_{19}(91)$
63.2	45.4	$S_{21}(87)$
45.4	5.9	$S_{20}^{-1}(54) + S_{17}(39)$

<sup>a</sup> Symmetry coordinates defined in Table 3.

cm<sup>-1</sup>, while at the same level they are calculated at 3281.9 cm<sup>-1</sup> for CH<sub>3</sub>Cl.<sup>1</sup> The corresponding fundamentals for CH<sub>3</sub>Cl·HCl were calculated at 3290.7 and at 3287.2 cm<sup>-1</sup>.<sup>9</sup> Thus, the frequency splitting of these modes in the chain complex, 9.8 cm<sup>-1</sup>, is much larger than that in the 1:1 complex. This again illustrates the increased perturbation of the methyl group in CH<sub>3</sub>Cl·HCl HCl as a consequence of the cyclic nature of the structure.

The H–Cl stretches of CH<sub>3</sub>Cl(·HCl)<sub>2</sub> appear as a symmetric and an antisymmetric combination. The asymmetric stretch is calculated to be at 3056.1 cm<sup>-1</sup>, while the symmetric combination is calculated to be at a slightly higher frequency, at 3062.1 cm<sup>-1</sup>, with an intensity which is less than 20% that of the antisymmetric stretch. The  $v_{CCl}$  fundamental of CH<sub>3</sub>Cl(·HCl)<sub>2</sub> is calculated to be at 762.9 cm<sup>-1</sup>, *i.e.* at a frequency somewhat lower than the 766.5 cm<sup>-1</sup> obtained for CH<sub>3</sub>Cl·HCl·HCl. This is in agreement with the longer C–Cl bond length in the bifurcated complex. Small frequency shifts were also calculated for the vibrational modes localized in the methyl group. The shifts for the bifurcated structure vary between 1.3 and 2.2 cm<sup>-1</sup>, which is substantially less than some of the shifts calculated for the chain structure.

#### **Comparison with Experimental Results**

No direct structural study of the 1:2 complex between methyl chloride and hydrogen chloride has been published. Therefore, the identification of the 1:2 complex observed in liquefied argon at the present stage has to rely on a comparison with *ab initio* data.

The experimental values for the enthalpies of complexation of the 1:1 and 1:2 complexes have been published.<sup>1</sup> These data show a cooperative, and not an anti-cooperative effect. As it is unlikely that the thermal and solvent influences that are included in the enthalpy differences differ strongly between the 1:1 and the 1:2 complex, the observed cooperative effect strongly suggests that in liquefied argon the chain complex is formed.

Supplementary evidence for the chain structure of the observed 1 : 2 complex can be obtained from a detailed comparison of the calculated and the experimental IR spectra. Even when the absolute values of the calculated vibrational frequencies are not as accurate as desired, experience suggests for instance, from conformational analysis, that the relative positions of the calculated frequencies in general are reliable. The situation with calculated IR intensities is somewhat less favourable, as even relative intensities sometimes differ from the experimental values by an order of magnitude, for reasons not always understood. Consequently, in the analysis below emphasis will be placed on the comparison of frequencies.

From the discussion above it is clear that the *ab initio* calculations predict a doublet in the H-Cl stretching region for each of the complexes, with substantial differences in frequency splitting and relative intensity of the components. In Fig. 6, the H-Cl stretching region of the experimental IR spectra of two different CD<sub>3</sub>Cl-HCl mixtures in liquefied argon are compared with the spectrum of a solution containing only HCl. A previous analysis of the spectra showed that only one band in the H-Cl stretching region could be attributed to a 1 : 2 complex.<sup>1,2</sup> Therefore, considerations based on the above differences cannot be exploited to identify the nature of the experimentally observed complex. Comparison of the vibrational frequencies obtained here with those calculated for the 1:1 complex,<sup>9</sup> shows that both components of the  $v_{HCI}$  doublet of the bifurcated complex are calculated at a higher frequency than the  $v_{HCl}$  of the 1 : 1 complex, while for



**Fig. 6** H—Cl stretching region of the IR spectra of CD<sub>3</sub>Cl–HCl mixtures dissolved in liquefied argon. (a)  $1.5 \times 10^{-3}$  mol dm<sup>-3</sup> CD<sub>3</sub>Cl and  $50.0 \times 10^{-3}$  mol dm<sup>-3</sup> HCl, 95 K; (b)  $1.5 \times 10^{-3}$  mol dm<sup>-3</sup> CD<sub>3</sub>Cl and  $2 \times 10^{-3}$  mol dm<sup>-3</sup> HCl, 95 K; (c)  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup> HCl, 95 K; (c)  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup> HCl, 96 K. The bands marked D and T are due to the HCl dimer and trimer, respectively. The bands marked with 1 : 1 and 1 : 2 are assigned to the CD<sub>3</sub>Cl·HCl and CD<sub>3</sub>Cl·(HCl)<sub>2</sub> complexes, respectively.

the chain complex one component is predicted on the high-frequency side, and the other on the low-frequency side of the CH<sub>3</sub>Cl·HCl frequency. In the experimental spectra, the H—Cl stretch due to a 1:2 complex in all cases was observed at a frequency lower than the HCl stretch of the 1:1 complex.<sup>1,2</sup> This suggests that the observed band is due to the complex having the chain structure. This, of course, is in agreement with the conclusion drawn from the cooperative effect.

The ab initio calculations predict that the chain structure must have a second absorption band, with a slightly weaker intensity, in the HCl stretching region. In the search for an experimental band due to the second HCl stretching, the frequency predicted for this vibration cannot be used without rescaling, as becomes clear from a comparison of the predicted and observed frequencies of the H-Cl stretches. The H-Cl stretches predicted at the same level for  $CH_3Cl \cdot HCl$ and for HCl are 3040 and 3120 cm<sup>-1</sup>, respectively, and the experimental values are 2765 and 2869 cm<sup>-1</sup>. The ratio of experimental to calculated frequency for both molecules produces a frequency scaling factor of ca. 0.91. This factor leads to a frequency of 2681 cm<sup>-1</sup> for the low-frequency H-Cl stretch of the 1:2 complex, which is experimentally observed at 2713 cm<sup>-1</sup>. This discrepancy suggests that the frequency of the other H-Cl stretch calculated with this scaling factor, 2788 cm<sup>-1</sup>, presumably is also not very accurate. Therefore, another estimate of the frequency of this mode was made in the following way. Recently, the HCl stretching frequencies of several  $B \cdot HCl$  and  $B \cdot H_aCl \cdot H_bCl$  complexes observed in solid matrices have been analysed.<sup>15</sup> In that study, the observed frequencies were expressed through their difference,  $\Delta \bar{v}$ , from the frequency of monomer HCl in the same environment. It was found that  $\Delta \bar{v}_a$  and  $\Delta \bar{v}_b$ , the shifts of  $v_{H_aCl}$  and  $v_{H_{b}Cl}$ , respectively, can be expressed as a second-degree polynomial in  $\Delta \bar{v}_s$ , the frequency shift observed for the 1:1 complex  $B \cdot HCl$ . As the environmental influence of a solid argon matrix will not be too different from that of an argon solution, it may be hoped that the results of the matrices will



Fig. 7 Mid-IR spectra of CD<sub>3</sub>Cl-HCl mixtures dissolved in lique-fied argon. (a)  $1.5 \times 10^{-3}$  mol dm<sup>-3</sup> CD<sub>3</sub>Cl and  $50.0 \times 10^{-3}$  mol dm<sup>-3</sup> HCl, 108 K; (b)  $1.5 \times 10^{-3}$  mol dm<sup>-3</sup> CD<sub>3</sub>Cl and  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup> HCl, 90 K; (c)  $1.5 \times 10^{-3}$  mol dm<sup>-3</sup> CD<sub>3</sub>Cl and  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup> HCl, 105 K.

be applicable to the solutions studied here. With the polynomials obtained in ref. 15, and using the value of 104 cm<sup>-1</sup> for  $\Delta \bar{\nu}_s$  observed for CH<sub>3</sub>Cl·HCl,<sup>1</sup>  $\Delta \bar{\nu}_a$  and  $\Delta \bar{\nu}_b$  for CH<sub>3</sub>Cl·HCl·HCl are calculated to be 152.5 and 55.0 cm<sup>-1</sup>. This brings the predicted frequencies at 2716.5 and 2814 cm<sup>-1</sup>. The former agrees quite well with the experimentally observed value of 2713 cm<sup>-1</sup>, and it is assumed that the value of the other frequency has a similar accuracy. Note that the frequency predicted by this method is substantially higher than the rescaled *ab initio* value.

In an attempt to detect experimentally the high-frequency H-Cl stretch of the 1:2 complex, new HCl-CD<sub>3</sub>Cl solutions in liquefied argon were investigated. The goal of these experiments was to increase the concentrations of the complexes. This can be achieved by increasing the concentrations of the monomers. Unfortunately, owing to the limited solubility of CD<sub>3</sub>Cl, the concentration of this monomer could not be increased compared with the previous study.<sup>1</sup> Hydrogen chloride, on the other hand, is quite soluble, and in this study concentrations of up to  $50.0 \times 10^{-3}$  mol dm<sup>-3</sup> have been used. The region of the spectra in the vicinity of the frequency of 2814 cm<sup>-1</sup> was carefully checked, but no bands attributable to the 1:2 complex could be identified. One reason for this is the complexity of the spectra in this region of solutions containing considerable concentrations of HCl, due to the presence of dimers, trimers and higher oligomers of HCl itself.<sup>16</sup> This complexity is obvious from Fig. 6(a). Also, it is likely that, in agreement with the ab initio predictions, Table 4, the intensity of the high-frequency  $v_{HCI}$  is somewhat lower than that of the low-frequency stretching, so that in the spectra of the solutions the band escapes detection.



Fig. 8 Mid-IR spectra of  $C_2D_5Cl$ -HCl mixtures dissolved in liquefied argon. (a)  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>  $C_2D_5Cl$  and  $45.0 \times 10^{-3}$  mol dm<sup>-3</sup> HCl, 103 K; (b)  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>  $C_2D_5Cl$  and  $3.5 \times 10^{-3}$ mol dm<sup>-3</sup> HCl, 104 K.

In addition to the band observed in the  $v_{HCl}$  region, the complex CD<sub>3</sub>Cl · HCl also gives rise to a well separated isotopic doublet in the  $v_{CC1}$  region. Although a similar doublet was calculated for the 1:2 species, in a previous study<sup>1</sup> no such doublet was observed owing to the relatively low concentration of CD<sub>3</sub>Cl · HCl · HCl and to the medium IR intensity of this fundamental. Therefore, the IR spectra recorded in this study were also carefully checked in the C-Cl stretching region. In Fig. 7, this region of a solution containing  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup> CD<sub>3</sub>Cl and  $50.0 \times 10^{-3}$  mol dm<sup>-3</sup> HCl, recorded at 108 K [Fig. 7(a)], is compared with that of a solution containing  $1.5 \times 10^{-3}$  mol dm<sup>-3</sup> CD<sub>3</sub>Cl and  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup> HCl, recorded at 90 K [Fig. 7(b)] and at 105 K [Fig. 7(c)]. On the low-frequency side of the monomer bands at 697.5 and 691 cm<sup>-1</sup>, two bands can be observed at 689 and 683 cm<sup>-1</sup> [Fig. 7(b)]. These have been assigned to the CD<sub>3</sub>Cl · HCl complex.<sup>1</sup> Next to these bands, in the region between 677 and 688  $cm^{-1}$  several bands of solid CD<sub>3</sub>Cl can be observed. In the spectrum of the more concentrated solution, Fig. 7(a), apart from the bands due to  $CD_3Cl$  and  $CD_3Cl \cdot HCl$ , two weak bands are detected at 685 and 679 cm<sup>-1</sup>, while in this spectrum no bands due to solid  $CD_3Cl$  are observed. The 685 and 679 cm<sup>-1</sup> bands therefore are assigned to the C-Cl stretching fundamentals of the 1:2 complex. The ab initio calculations above show that on going from CH<sub>3</sub>Cl to CH<sub>3</sub>Cl · HCl, the C-<sup>35</sup>Cl stretching fundamental undergoes a red shift of 9.9  $\text{cm}^{-1}$ . In contrast, the red

shift induced by the addition of a second HCl molecule is predicted to be only  $5.5 \text{ cm}^{-1}$ . Taking into account an average scaling factor for stretching frequencies, these values agree quite well with the experimental shifts of 8.5 and 4.0 cm<sup>-1</sup>, respectively, deduced from the data above.

The behaviour of  $C_2H_5Cl$  dissolved in liquefied argon with respect to the formation of 1:1 and 1:2 complexes with HCl was found to be similar to that of methyl chloride.<sup>2</sup> Therefore, it is reasonable to expect that in the IR spectra a  $v_{CCI}$ doublet due to the 1:2 complex must be present. As such a doublet was not observed in the previous study, in this study the spectra of C<sub>2</sub>D<sub>5</sub>Cl-HCl mixtures dissolved in liquefied argon were re-investigated at higher concentrations of HCl. In Fig. 8, the C-Cl stretching region of the mid-IR spectrum of a liquefied argon solution containing  $2.0 \times 10^{-3}$  mol  $dm^{-3}$  C<sub>2</sub>D<sub>5</sub>Cl and 3.5 × 10<sup>-3</sup> mol  $dm^{-3}$  HCl is compared with that of a solution containing  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup> C<sub>2</sub>D<sub>5</sub>Cl and  $45.0 \times 10^{-3}$  mol dm<sup>-3</sup> HCl, recorded at the same temperature. In the former spectrum, Fig. 8(b), four bands belonging to either  $C_2D_5Cl$  or  $C_2D_5Cl$ ·HCl are observed at 622, 617, 613, 608  $\text{cm}^{-1}$ . When a large excess of HCl is added to the solution [Fig. 8(a)], in agreement with the behaviour of the CD<sub>3</sub>Cl solutions, two new weak bands appear at 610 and 605 cm<sup>-1</sup>. By analogy with the results described above, these bands are assigned to the  $C^{-35}Cl$  and the C- $^{37}$ Cl stretching fundamental in the 1:2 species  $C_2D_5Cl \cdot HCl \cdot HCl.$ 

### Conclusions

In this study,  $MP2/6-31 + G^{**}$  calculations have been made on two different structures of the complex formed between methyl chloride and two hydrogen chloride molecules.

The chain structure  $CH_3Cl \cdot HCl \cdot HCl$  is found to be cyclic, and is more stable, by 2.58 kJ mol<sup>-1</sup>, than the bifurcated structure  $CH_3Cl(\cdot HCl)_2$ .

The experimentally observed cooperative effect in the enthalpy difference for the 1:2 complex formed in liquefied argon shows that the complex must have the chain structure.

By comparing the pattern observed in the H—Cl stretching region of the IR spectra of  $CD_3Cl$ –HCl mixtures dissolved in liquefied argon with the *ab initio* force field calculations, it is concluded that the observed band is due to the complex with the chain structure.

At higher concentrations of HCl, in the C—Cl stretching region of the IR spectra of  $CD_3Cl$ -HCl mixtures in liquefied

argon, the isotopic  $v_{CC1}$  doublet due to the 1:2 complex is detected. Its shift from the monomer frequency is in agreement with the *ab initio* calculations for the chain complex.

Finally, in the IR spectra of  $C_2D_5Cl-HCl$  mixtures dissolved in liquefied argon, the  $v_{CCl}$  isotopic doublet of the 1 : 2 complex has been observed.

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