

IR spectra, relative stability and angular geometry of vinyl chloride–HCl, vinyl bromide–HCl and allyl chloride–HCl van der Waals complexes observed in liquefied argon

W. A. Herrebout and B. J. van der Veken†

Department of Chemistry, Universitair Centrum Antwerpen, Groenenborgerlaan 171, B2020-Antwerpen, Belgium

The mid-IR spectra ($4000\text{--}400\text{ cm}^{-1}$) of vinyl chloride–HCl, vinyl bromide–HCl and allyl chloride–HCl mixtures, dissolved in liquefied argon at 105 K, have been examined. In all spectra, evidence was found for the existence of a 1 : 1 van der Waals complex. At higher concentrations of hydrogen chloride, in the spectra of the vinyl chloride–HCl mixtures, absorption bands of a 1 : 2 species were also observed. Using spectra recorded at several temperatures between 95 and 120 K, the complexation enthalpies of $\text{CH}_2=\text{CHCl}\cdot\text{HCl}$ and $\text{CH}_2=\text{CHCl}\cdot(\text{HCl})_2$ were determined to be $-6.5 \pm 0.2\text{ kJ mol}^{-1}$ and $-10.6 \pm 0.3\text{ kJ mol}^{-1}$, respectively.

A structural study, using *ab initio* calculations at the MP2/6-31 + G** level, indicates that the complexation between vinyl chloride and HCl can occur either *via* the chlorine atom or *via* the π -bond. From a comparison of the experimental with the *ab initio* vibrational frequencies it was concluded that all observed bands of the 1 : 1 complex are due to a species complexed *via* the chlorine atom. A similar conclusion applies to the vinyl bromide and allyl chloride complexes.

The formation of complexes of some vinyl and allyl halides and pseudo-halides with hydrogen chloride has been investigated using matrix isolation IR spectroscopy.^{1,2} In the spectra, weak bands were detected that were interpreted as being due to complexes in which HCl is hydrogen bonded to the halogen or the pseudo-halogen. *Ab initio* calculations on the vinyl fluoride–HCl system³ confirm that such a σ -complex can be formed. At the same time, these calculations show also that a π -complex, in which the HCl is attached to the π -bond, can form, and that the dissociation energies of the σ - and π -complexes are very similar. Thus, it must be expected that both types of complexes occur simultaneously. It cannot be excluded that the absence of the π -complexes in matrices, which are deposited under non-equilibrium conditions, is caused by kinetic effects favouring the formation of the σ -complexes. However, cryosolutions in thermodynamical equilibrium, containing mixtures of vinyl fluoride and HCl, have been investigated and only the formation of the σ -complex was observed.³ While fluorides often exhibit behaviour not completely in line with that of other halides, it would be interesting to see which complexes are formed under equilibrium conditions by other vinyl and allyl halides. Hence, we report an IR study of mixtures of vinyl chloride, vinyl bromide and allyl chloride with HCl, dissolved in liquefied argon. As will be described below, formation of complexes was observed. Where possible, stoichiometry and complexation enthalpy have been determined, and comparison with *ab initio* vibrational frequencies suggests that also for the present Lewis bases only σ -complexes have been detected.

In cryosolutions, halides have been observed to form 1 : 2 complexes with HCl.^{3–5} In the vinyl and allyl halide matrices^{1,2} such complexes were not observed. Therefore, in this study also special attention was given to the detection of these species.

Experimental

Vinyl chloride was synthesized by condensing a small amount of 1,2-dichloroethane (Janssen Chimica 16.776.92), previously

dried over 4 Å molecular sieves, onto a solution of sodium ethoxide in ethanol. After the mixture had been allowed to warm up slowly, the volatile fraction of the reaction mixture was collected by bulb-to-bulb distillation and fractionated using a low-temperature, low-pressure fractionation column. For vinyl bromide, a similar synthesis was carried out using 1,2-dibromoethane (Janssen Chimica 22.036.17). The sample of allyl chloride (Fluka Chemika 05880) was obtained commercially and was used without further purification. The HCl was synthesized in small amounts by hydrolysing PCl_3 with H_2O and was purified by pumping the reaction mixture through a propan-2-ol slush (180 K), followed by fractionation on a low-temperature, low-pressure fractionation column. The argon used has a stated purity of 99.9999% and was used without further purification.

The IR spectra were recorded on a Bruker IFS 66v or a Bruker IFS 113v Fourier transform spectrometer, using a Globar source in combination with a Ge/KBr beamsplitter and a broadband MCT detector. The interferograms were averaged over 200 scans, Happ Genzel apodized and Fourier transformed using a zero filling factor of 4, to yield spectra at a resolution of 0.5 cm^{-1} . A description of the liquefied noble gas set-up was given previously⁶ and will not be repeated here.

Spectra of crystalline vinyl chloride, vinyl bromide and allyl chloride were obtained by condensing a small amount of the compound onto a window cooled to 10 K, followed by annealing until no further changes were observed in the IR spectrum. For all solid-state experiments, a Leybold ROK 10-300 double-stage cryostat with closed-cycle helium cooling was used.

Results

Ab initio calculations

For vinyl chloride, the possibilities of complex formation were investigated using *ab initio* calculations, at the MP2/6-31 + G** level. Comparisons made for simple systems, as for instance in ref. 7, show that, with such a basis set, at the MP2 level of treating electron correlation, the van der Waals bond

† E-mail: bvdveken@ruca.ua.ac.be

length has basically converged, so that reliable structural predictions are made. All calculations described below were carried out using the GAUSSIAN 92 program.⁸ For all calculations, the correlation energy was calculated using all molecular orbitals, while the Berny optimization⁹ was used with the tight convergence criteria. The complexation energies of the complexes were calculated by subtracting the energies of the monomers from that of the complex, and these energies were corrected for basis set superposition error (BSSE), using the counterpoise correction method described by Boys *et al.*¹⁰ For all equilibrium geometries, the vibrational frequencies and the IR intensities were calculated using standard harmonic force fields.

Equilibrium geometry. The relative orientation of the molecules in the Cl \cdots H-bonded isomer σ -CH₂=CHCl \cdots HCl must be expected to be similar to that in other Cl \cdots H hydrogen-bonded species, such as HCl \cdots HCl¹¹ and CH₃Cl \cdots HCl.^{4,12} For a complete description of the present complex, however, the dihedral angle $\tau_{C=C\cdots H}$ must also be specified. Because no information was available for this angle, several different initial geometries were proposed and refined using standard convergence criteria. These optimizations resulted in two different equilibrium geometries, which were subsequently refined using the tight convergence criteria. The resulting geometries, described below as conformers a and b of isomer I, are shown in Fig. 1. Their structural parameters and those of the monomers are collected in Table 1.

From Table 1 it is clear that, when forming the complex **Ia**, the C—Cl bond length increases from 1.7281 to 1.7341 Å, while the H—Cl bond length increases from 1.2689 to 1.2730 Å. This shows that both bonds are slightly weakened by complexation. On the other hand, the structural parameters describing the geometry of the vinyl group are hardly affected by the approaching HCl molecule. Similar phenomena were observed for **Ib**. In fact, when passing from **Ia** to **Ib**, the C—Cl, H—Cl and Cl \cdots H bond lengths do not show significant changes.

In a next step, the potential curve for the internal rotation of the HCl molecule around the C—Cl bond was calculated. For several values of the dihedral angle, all other internal parameters were refined and the energy of the complex was calculated. During the internal rotation, the C(2)—Cl(1) \cdots H(7) and the Cl(1) \cdots H(7)—Cl(8) bond angles were calculated to change, from 85.8° to 102.7° and from

157.4° to 173.3°, respectively. Hence, upon changing the dihedral angle $\tau_{C=C\cdots H}$, the relative orientation of both molecules changes strongly. This, of course, will influence the BSSE. However, no attempts were made to correct the potential for BSSE.

The resulting potential is shown in Fig. 2. It can be seen that the height of the barrier separating **Ia** from **Ib** is a mere 0.5 kJ mol⁻¹; evidently, the calculated energy difference between the conformers is even lower. Even at the relatively low temperatures used in our experiments, the rotational barrier is lower than *kT*. Therefore, a substantial fraction of the complex molecules will be thermally excited to levels above the barrier. These molecules perform a large amplitude torsional motion, so that their conformational identity is lost. The *ab initio* calculations predict further (*vide infra*) that the spectroscopic differences between **Ia** and **Ib** are quite subtle. As the presence of thermally excited species will cause some broadening, the detection of conformational splittings in the IR spectra must be anticipated to be very unlikely.

The equilibrium geometry was also calculated for π -CH₂=CHCl \cdots HCl, isomer **II** in Fig. 1. The structural parameters of this complex are summarized in Table 2. Upon formation of the π -complex, the C=C distance is calculated to increase from 1.3338 to 1.3362 Å, *i.e.* the C=C bond is slightly weakened in the complex. At the same time, the H—Cl bond length increases, from 1.2689 to 1.2732 Å. This value is similar to that (1.2730 Å) obtained for the σ -complex. In contrast, Table 2 also shows that the C—Cl bond length decreases from 1.7281 to 1.7258 Å.

Relative stability. The MP2/6-31 + G** complexation energies of **Ia**, **Ib** and **II**, the corresponding values for the BSSE, ΔE_{BSSE} and the corrected complexation energies, ΔE_{corr} , are given in Table 3. The π - and σ -complexes have very similar complexation energies and hence, in an environment in which complex formation between vinyl chloride and HCl is taking place, the simultaneous occurrence of both σ - and π -complexes must be expected.

Vibrational spectra. In Table 4, the predicted vibrational frequencies and IR intensities calculated for **Ia**, **Ib**, **II** and vinyl chloride are summarized, together with the complexation shifts $\Delta\bar{\nu}$, defined as $\bar{\nu}_{complex} - \bar{\nu}_{monomer}$.

On going from vinyl chloride to a σ -complex, the ν_{C-Cl} fundamental is calculated to undergo a red shift of some 7.5

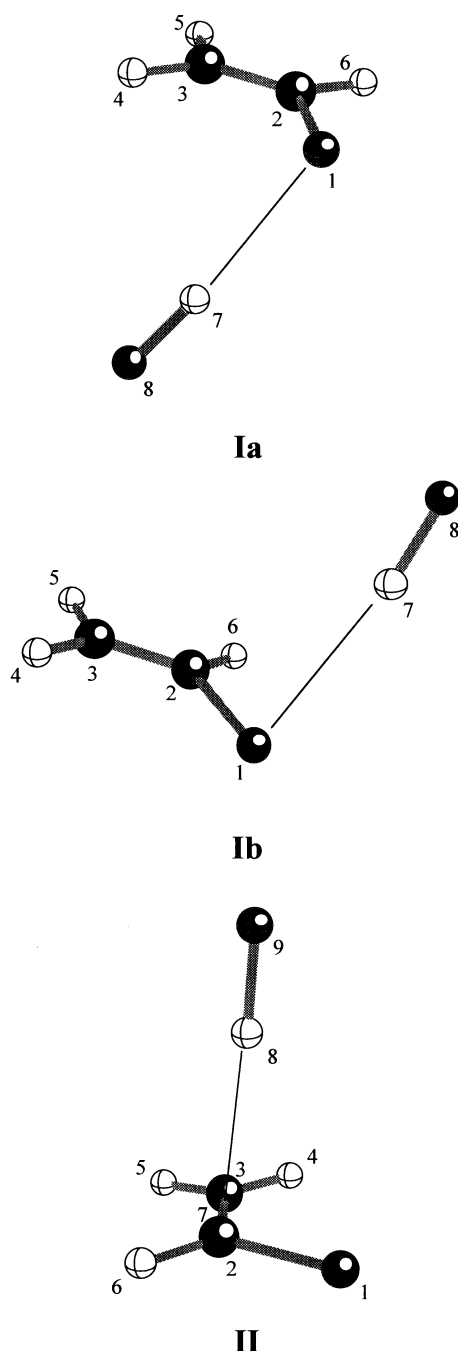
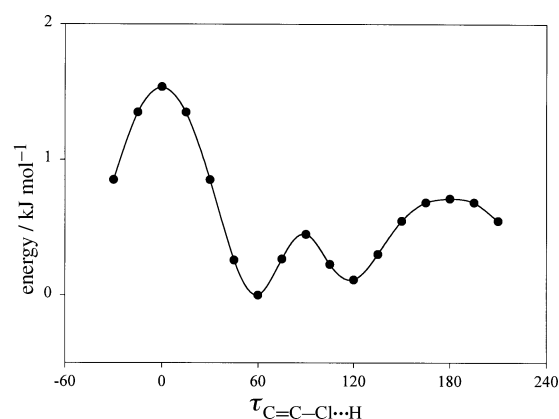
Table 1 MP2/6-31 + G** structural parameters (bond lengths in Å, bond angles in degrees) for the σ -complexes CH₂=CHCl \cdots HCl, for CH₂=CHCl and for HCl

	CH ₂ =CHCl \cdots HCl		CH ₂ =CHCl	HCl
	Ia	Ib		
<i>r</i> [Cl(1)—C(2)]	1.7341	1.7344	1.7281	
<i>r</i> [C(2)—C(3)]	1.3330	1.3327	1.3338	
<i>r</i> [H(4)—C(3)]	1.0791	1.0790	1.0790	
<i>r</i> [H(5)—C(3)]	1.0792	1.0792	1.0792	
<i>r</i> [H(6)—C(2)]	1.0788	1.0791	1.0792	
<i>r</i> [Cl(1) \cdots H(7)]	2.5158	2.5237		
<i>r</i> [H(7)—Cl(8)]	1.2730	1.2730		1.2689
\angle [C(3)—C(2)—Cl(1)]	123.00	122.94	123.30	
\angle [H(4)—C(3)—C(2)]	122.40	122.21	122.06	
\angle [H(5)—C(3)—C(2)]	118.99	119.01	119.06	
\angle [H(6)—C(3)—C(2)]	123.83	123.74	123.33	
\angle [H(7) \cdots Cl(1)—C(2)]	90.16	87.68		
\angle [Cl(8)—H(7) \cdots Cl(1)]	173.26	165.09		
τ [H(4)—C(2)—C(3)—Cl(1)]	0.39	0.15	0.00	
τ [H(5)—C(2)—C(3)—Cl(1)]	180.39	179.94	180.00	
τ [H(6)—C(2)—C(3)—Cl(1)]	179.71	179.76	180.00	
τ [H(7) \cdots Cl(1)—C(2)—C(3)]	59.00	117.32		
τ [Cl(8)—H(7) \cdots Cl(1)—C(2)]	− 24.21	10.54		
dipole moment/D	2.34	2.21	1.48	1.22
energy/ <i>E</i> _h	− 957.591 301	− 957.591 258	− 537.367 939	− 420.218 345

Table 2 MP2/6-31 + G** structural parameters (bond lengths in Å, bond angles in degrees) for π -CH₂=CHCl · HCl (**II**)

$r[\text{Cl}(1)-\text{C}(2)]$	1.7258	$\angle [\text{C}(2)-\text{X}(7)\cdots\text{H}(8)]$	90.00
$r[\text{C}(2)-\text{C}(3)]$	1.3362	$\angle [\text{X}(7)\cdots\text{H}(8)-\text{Cl}(9)]$	178.42
$r[\text{H}(4)-\text{C}(3)]$	1.0798	$\tau[\text{H}(4)-\text{C}(3)-\text{C}(2)-\text{Cl}(1)]$	0.97
$r[\text{H}(5)-\text{C}(3)]$	1.0796	$\tau[\text{H}(5)-\text{C}(3)-\text{C}(2)-\text{Cl}(1)]$	179.76
$r[\text{H}(6)-\text{C}(2)]$	1.0798	$\tau[\text{H}(6)-\text{C}(2)-\text{C}(3)-\text{Cl}(1)]$	179.90
$r[\text{C}(2)-\text{X}(7)]^a$	0.8090	$\tau[\text{H}(8)\cdots\text{X}(7)-\text{C}(2)-\text{Cl}(1)]$	-78.28
$r[\text{X}(7)\cdots\text{H}(8)]$	2.4617	$\tau[\text{H}(8)\cdots\text{X}(7)-\text{C}(2)-\text{H}(6)]$	101.61
$r[\text{H}(8)-\text{Cl}(9)]$	1.2732	$\tau[\text{H}(8)\cdots\text{X}(7)-\text{C}(3)-\text{H}(4)]$	79.25
$\angle [\text{C}(3)-\text{C}(2)-\text{Cl}(1)]$	123.33	$\tau[\text{H}(8)\cdots\text{X}(7)-\text{C}(3)-\text{H}(5)]$	-101.96
$\angle [\text{H}(4)-\text{C}(3)-\text{C}(2)]$	122.13	$\tau[\text{C}(3)\cdots\text{X}(7)-\text{H}(8)-\text{C}(2)]$	180.00
$\angle [\text{H}(5)-\text{C}(3)-\text{C}(2)]$	119.16	$\tau[\text{C}(2)\cdots\text{X}(7)-\text{H}(8)-\text{Cl}(9)]$	-139.81
$\angle [\text{H}(6)-\text{C}(3)-\text{C}(2)]$	123.10	$\tau[\text{C}(3)\cdots\text{X}(7)-\text{H}(8)-\text{Cl}(9)]$	40.19
$\angle [\text{C}(2)-\text{X}(7)-\text{C}(3)]$	180.00		
dipole moment/D	2.38		
energy/ E_h	-997.590 845		

^a X₇ is a dummy situated in the C=C bond, at the perpendicular projection of the H(Cl) atom.

**Fig. 1** MP2/6-31 + G** equilibrium geometries for the 1 : 1 complexes between vinyl chloride and HCl**Fig. 2** Potential-energy function for the internal rotation around the C—Cl bond in CH₂=CHCl · HCl. The *cis*-conformation of HCl with respect to the C=C bond was chosen as the origin of $\tau_{\text{C}=\text{Cl}\cdots\text{H}}$.

cm^{-1} . Also, for the CH₂ wagging a shift of 12 cm^{-1} and for the C(2)—H(6) stretching fundamental a shift of -7.4 cm^{-1} is calculated. Upon complexation with vinyl chloride, a red shift of 60 cm^{-1} is calculated for the H—Cl stretching fundamental of the proton donor molecule. Also, it is clear that the predicted conformational splittings are invariably very small.

Upon forming a π -complex, the C=C stretching is calculated to red shift by 10.7 cm^{-1} , while for the CH₂ twist, the CH₂ wagging and the CH₂ rocking blue shifts of 13.8, 20.5 and 10.9 cm^{-1} , respectively, are calculated. In contrast, the C—Cl stretching fundamental is much less affected, complexation resulting in a small blue shift. Small frequency shifts, varying from -3.6 to -4.6 cm^{-1} , are calculated for the C—H stretching fundamentals. For the H—Cl stretching in the proton donor molecule, a red shift of *ca.* 61 cm^{-1} is calculated. This shift is close to those predicted for the σ -complexes.

Table 3 MP2/6-31 + G** complexation energies for the σ - and π -complexes of vinyl chloride with HCl^a

	Ia	Ib	II
$\Delta E^b/E_h$	-0.005 017	-0.004 974	-0.004 561
$\Delta E_{\text{BSSE}}^c/E_h$	-0.002 820	-0.002 913	-0.002 677
$\Delta E_{\text{corr}}^d/E_h$	-0.002 197	-0.002 061	-0.001 884
$\Delta E_{\text{corr}}/\text{kJ mol}^{-1}$	-5.77	-5.41	-4.95

^a Numbering of the complexes refers to Fig. 1. ^b Calculated using the expression $\Delta E = E_{\text{CH}_2=\text{CHCl}\cdots\text{HCl}} - E_{\text{CH}_2=\text{CHCl}} - E_{\text{HCl}}$. ^c Calculated using the full counterpoise correction. ^d Calculated using the expression $\Delta E_{\text{corr}} = \Delta E - \Delta E_{\text{BSSE}}$.

Table 4 MP2/6-31 + G** vibrational frequencies (cm^{-1}) and IR intensities (km mol^{-1}) for **Ia**, **Ib**, **II** and $\text{CH}_2=\text{CHCl}^a$

approximate description	$\text{CH}_2=\text{CHCl} \cdot \text{HCl}$									$\text{CH}_2=\text{CHCl}$	
	Ia			Ib			II			$\bar{\nu}$	int.
	$\bar{\nu}$	int.	$\Delta\bar{\nu}$	$\bar{\nu}$	int.	$\Delta\bar{\nu}$	$\bar{\nu}$	int.	$\Delta\bar{\nu}$	$\bar{\nu}$	int.
CH_2 antisym. stretch	3364.2	1.0	1.0	3365.0	0.7	1.8	3359.5	0.5	−3.7	3363.2	1.9
CH stretch	3312.3	3.9	7.4	3309.0	3.4	4.1	3301.1	4.4	−3.7	3304.9	5.5
CH_2 sym. stretch	3254.4	0.3	1.1	3254.6	0.2	1.3	3248.8	0.5	−4.6	3253.3	0.1
H—Cl stretch ^b	3064.1	170.6	−60.0	3064.3	180.4	−59.8	3059.2	198.9	−61.0		
C=C stretch	1686.3	45.8	−3.0	1687.8	48.2	−1.5	1676.6	51.4	−10.7	1686.3	53.4
CH_2 deformation	1449.5	11.7	1.3	1447.9	10.2	−0.3	1448.6	11.8	0.4	1448.2	12.2
C=C—H in plane def.	1345.3	8.7	−2.3	1349.0	8.0	1.3	1348.2	6.8	0.6	1347.6	8.0
CH_2 rocking	1070.6	17.1	−2.9	1071.3	17.1	−2.2	1075.9	18.1	2.4	1073.5	18.3
C=C—H out of plane def.	990.1	49.6	−2.2	991.6	50.2	−0.7	1003.2	52.6	10.9	992.4	46.9
CH_2 wagging	906.0	32.9	12.0	904.9	33.9	10.9	914.4	48.3	20.4	893.9	38.2
C—Cl stretch	749.4	34.1	−7.5	748.5	33.5	−8.3	759.4	35.1	2.6	756.8	34.9
CH_2 twist	632.7	13.4	−1.8	635.3	12.9	0.9	648.2	13.3	13.7	634.4	13.5
C=C—Cl in plane def.	408.3	0.4	0.2	407.5	0.3	−0.6	410.0	0.2	1.9	408.1	0.2
	282.9	34.2		305.3	53.1		263.9	24.9			
	277.1	38.6		266.3	35.3		208.0	24.6			
	85.5	1.5		89.4	3.4		85.4	0.3			
	49.8	0.5		61.7	2.7		67.6	2.4			
	40.1	2.0		22.3	0.9		34.5	0.6			

^a Numbering of the complexes refers to Fig. 1. ^b HCl monomer: 3120.1 cm^{-1} ; 26.3 km mol^{-1} .

Vibrational spectra

Vinyl chloride. The vibrational bands observed for a solution of vinyl chloride in liquid argon at 108 K, and their assignments, obtained by comparing the vibrational frequencies observed in this study and those observed in other phases,¹³ are summarized in Table 5.

Owing to the occurrence of ^{35}Cl and ^{37}Cl , in all spectra of vinyl chloride in LAr, two separate bands are observed in the $\nu_{\text{C-Cl}}$ region, at 718 and 712 cm^{-1} , respectively. Moreover, near the strong band at 1609 cm^{-1} , assigned to the $\nu_{\text{C=C}}$ fundamental, in the spectra of vinyl chloride, two weak bands, assigned to the $^{13}\text{CH}_2=\text{CHCl}$ or the $\text{CH}_2=^{13}\text{CHCl}$ isotopomers, can be observed at 1586 and 1582 cm^{-1} , respectively.

When larger amounts of vinyl chloride are condensed in the cell, a weak doublet, with maxima at 699 and 695 cm^{-1} appears. In the spectra of solid, crystalline vinyl chloride, bands at the same frequencies are observed. The bands are, therefore, assigned to crystalline particles of vinyl chloride dispersed in the solutions.

Compared with the spectra of the individual components, in the HCl-stretching region of the spectrum of a vinyl chloride–HCl mixture dissolved in liquid argon (108 K), a new band occurs at 2800 cm^{-1} . This indicates that a van der Waals complex between vinyl chloride and HCl is formed. In the spectra of argon matrices containing both vinyl chloride and HCl a new band, assigned to $\text{CH}_2=\text{CHCl} \cdot \text{HCl}$, is observed at 2786 cm^{-1} .^{1,2} Taking into account that the fundamental ν_{HCl} of weakly bound complexes $\text{B} \cdots \text{HCl}$ red shifts by *ca.* 10 – 20 cm^{-1} when passing from solution to solid matrices,¹³ the matrix band at 2786 cm^{-1} must be due to the species that causes the 2800 cm^{-1} band in solution.

The ν_{HCl} region of spectra of a vinyl chloride–HCl mixture recorded at different temperatures between 101 and 116 K are compared in Fig. 3. Upon decreasing the temperature of the solution, the intensity of the band at 2800 cm^{-1} is seen to increase strongly. Near this band, two weaker bands appear, at 2830 and 2758 cm^{-1} . The former band is due to the HCl dimer.⁶ However, the 2758 cm^{-1} band has to be assigned to a complex formed between vinyl chloride and HCl. The intensity ratio of the bands at 2800 and 2758 cm^{-1} clearly changes with the temperature of the solution, thus, these bands are due to species with a different stability. Furthermore, when the

concentration of HCl is decreased, the band at 2758 cm^{-1} disappears rapidly; showing that this band belongs to a complex containing more than one HCl molecule. Evidently,

Table 5 Observed^a frequencies (cm^{-1}) and assignments for vinyl chloride

liq. argon	rel. int. ^a	gas ^b	ν_i	approximate description
3210	vw			$2\nu_4$
3118	w	3121	ν_1	CH_2 antisym. stretch
3084		3087	ν_2	CH stretch
3029		3033		$\nu_4 + \nu_7 + \nu_{12}$
3020			ν_3	CH_2 sym. stretch
2957		2961		$\nu_4 + \nu_8$
2328	w			$\nu_4 + \nu_{10}$
2322	vw,sh			$\nu_4 + \nu'_{10}$
2306				$\nu_5 + \nu_9$
1874		1877		$2\nu_8$
1833		1836		$\nu_8 + \nu_9$
1794		1798		$2\nu_9$
1744	w			$\nu_7 + \nu_{10}$
1738	vw,sh			$\nu_7 + \nu'_{10}$
1677	vw	1678		
1675	vww,sh			$\nu_6 + \nu_{12}$
1647	vww			$\nu_7 + \nu_{11}$
1609	vvs	1610	ν_4	C=C stretch
1586	w			C=C stretch, $\text{H}_2\text{C}=^{13}\text{CHCl}$
1582	w			C=C stretch, $\text{H}_2^{13}\text{C}=\text{CHCl}$
1558	w	1559		$\nu_8 + \nu_{11}$
1513	m	1513		$\nu_9 + \nu_{11}$
1429	vww			$2\nu_{10}$
1418	vww			$2\nu'_{10}$
1384	vw,sh			
1367	s	1371	ν_5	CH_2 deformation
1279	vs	1280	ν_6	C=C—H in plane deformation
1233	vw	1233		$2\nu_{11}$
1029	vs	1031	ν_7	CH_2 rocking
941	vvs	942	ν_8	C=C—H out of plane deformation
895	vvs	897	ν_9	CH_2 wagging
718	vs	722	ν_{10}	C— ^{35}Cl stretch
712	s,sh	716	ν'_{10}	C— ^{37}Cl stretch
619	s	620	ν_{11}	CH_2 twist
398	w	398	ν_{12}	C=C—Cl in plane deformation

^a Abbreviations: vvs, very, very strong; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; ^b Taken from ref. 12.

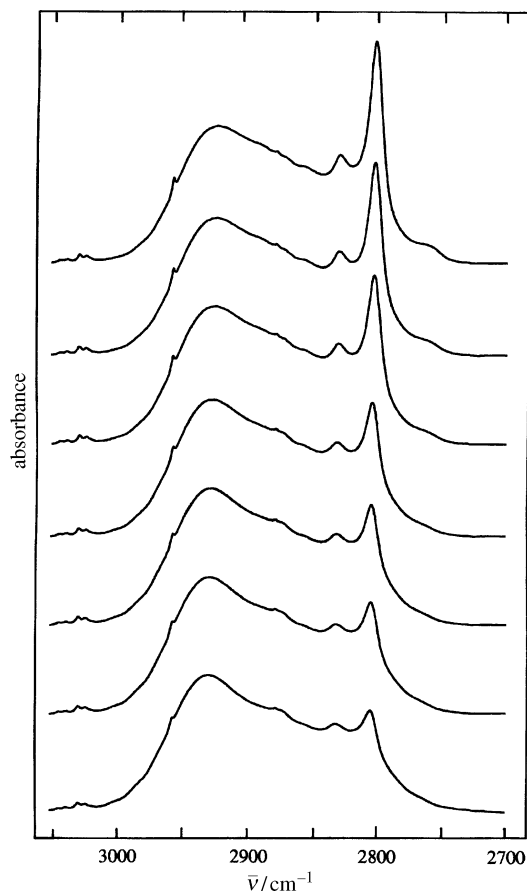


Fig. 3 $\nu_{\text{H-Cl}}$ region for a $\text{CH}_2=\text{CHCl-HCl}$ mixture dissolved in liquefied argon. From top to bottom, the temperatures of the solutions were 100.1, 102.3, 104.6, 109.0, 111.6, 114.1 and 116.3 K.

the most likely candidate is the species having 1 : 2 stoichiometry. This assignment of the 2758 cm^{-1} band will be justified below.

The red shift of the H-Cl -stretching fundamental for the σ - and π -bonded complex was calculated, above, to be 60 and 61 cm^{-1} , respectively. Both values, apart from being extremely similar, are somewhat smaller than the experimental shift of 69.0 cm^{-1} . Therefore, as for $\text{CH}_2\text{CHF}\cdot\text{HCl}$,³ it appears impossible to assign the complex present in the solutions from the shift of the H-Cl stretching.

In the spectra of argon matrices containing both vinyl chloride and HCl complexation, splittings have been observed for both the $\nu_{\text{C-Cl}}$ and the ω_{CH_2} fundamentals.^{1,2} In the spectra of solutions of vinyl chloride and a large excess of HCl two weak bands, assigned to the $\text{C-}^{35}\text{Cl}$ and $\text{C-}^{37}\text{Cl}$ stretches in $\text{CH}_2=\text{CHCl}\cdot\text{HCl}$, appear at 710 and 705 cm^{-1} .

As discussed above, in the σ -complexes the C-Cl stretch is calculated to be red shifted by *ca.* 8 cm^{-1} . In contrast, when a π -complex is formed, this fundamental is predicted to be blue shifted by *ca.* 2.5 cm^{-1} . The experimental observation of the bands at 710 and 705 cm^{-1} , on the low-frequency side of the monomer $\nu_{\text{C-Cl}}$, then proves that a σ -complex is formed in solution.

For alkyl chloride- HCl complexes,^{4,5} the C-Cl stretches were found to occur between the frequencies for the monomeric species and those for the crystalline phase. It is clear from the above that the same sequence is observed for the vinyl chloride species, which can be seen as supplementary evidence that the HCl molecule in the 1 : 1 complex is indeed hydrogen bonded to the chlorine atom.

In the spectra of vinyl chloride- HCl mixtures trapped in solid matrices,^{1,2} a blue shift of some 7 cm^{-1} was observed for the CH_2 wagging. At high HCl concentration in LAr solutions

on the high-frequency side of the CH_2 wagging at 895 cm^{-1} , a weak shoulder appears at *ca.* 902 cm^{-1} . The shift of this band is close to that predicted for the σ -complexes, and, therefore, we assign this shoulder to the σ -complex.

Vinyl bromide. The bands observed in the mid-IR spectrum of vinyl bromide dissolved in liquid argon at 122 K , and their assignment, based on vapour-phase spectra,¹² are summarized in Table 6. Upon decreasing the temperature of the solution the intensity of all bands decreases rapidly, signalling a strong decrease in the solubility of vinyl bromide.

In the region of $\nu_{\text{C=C}}$, near 1600 cm^{-1} , a strong Fermi doublet is observed, with maxima at 1602 and 1599 cm^{-1} . These bands are assigned to the $\nu_{\text{C=C}}$ and the combination of the C=C-Br and the C=C-H in-plane deformation modes, respectively. The weak bands in the same region, at 1579 and 1573 cm^{-1} , are assigned to the $\text{CH}_2=^{13}\text{CHBr}$ and $^{13}\text{CH}_2=\text{CHBr}$ isotopomers, respectively.

Because of the limited solubility of vinyl bromide, its complexes with HCl can only be observed by using higher concentrations of HCl . The presence of HCl oligomeric species⁶ in such solutions hampers the interpretation of the spectra. In Fig. 4, the ν_{HCl} region of a solution containing $0.5 \times 10^{-3}\text{ M}$ vinyl bromide and $3.5 \times 10^{-3}\text{ M}$ HCl , recorded at several temperatures between 100.3 and 111.9 K , is shown. Several weak bands appear near 2800 cm^{-1} upon decreasing the temperature of the solution.

In Fig. 5, the contribution of complexed species to the HCl -stretching region have been isolated. This figure was obtained by subtracting a rescaled spectrum of a dilute solution of HCl from the spectrum of a more concentrated mixed solution. Next to the bands due to HCl oligomeric species, marked as D (dimer), Tr (trimer) and Te (tetramer), a weak band due to $\text{CH}_2=\text{CHBr}\cdot\text{HCl}$ can be observed at 2782 cm^{-1} .

Even at higher concentrations of HCl , no complexation splittings of fundamentals localised in the vinyl group were observed in the spectra of vinyl bromide- HCl mixtures.

Table 6 Observed^a frequencies (cm^{-1}) and assignments for vinyl bromide

liq. argon	rel. int. ^a	gas ^b	ν_i	approximate description
3115	w	3115	ν_1	CH_2 antisym. stretch
3082	m	3087	ν_2	C-H stretch
3024	m	3027	ν_3	CH_2 sym. stretch
2739	vw			$2\nu_5$
1874	w	1877		$2\nu_8$
1838	m	1841		$\nu_8 + \nu_9$
1803	m	1806		$2\nu_9$
1612	w,sh			$\nu_7 + \nu_{10}$
1602	vs	1610	ν_4	C=C stretch
1599	vs		$\nu_6 + \nu_{12}$	Fermi resonance
1579	vw			C=C stretch, $\text{H}_2\text{C}=^{13}\text{CHBr}$
1573	vw			C=C stretch, $\text{H}_2\text{ }^{13}\text{C}=\text{CHBr}$
1524	vw	1524		$\nu_8 + \nu_{11}$
1483	w	1484		$\nu_9 + \nu_{11}$
1384	vww			
1371	m	1372	ν_5	CH_2 deformation
1351	m	1353		$\nu_6 + \nu_{12}$
1256	vs	1258	ν_6	C=C-H in plane deformation
1164	vww			$2\nu_{11}$
1006	s	1007	ν_7	CH_2 rocking
941	vs	942	ν_8	C=C-H out of plane deformation
900	vs	902	ν_9	CH_2 wagging
609	s	611	ν_{10}	C-Br stretch
583	s	582	ν_{11}	CH_2 twist
344	w	345	ν_{12}	C=C-Br in plane deformation

^a Abbreviations: vvs, very, very strong; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. ^b Taken from ref. 12.

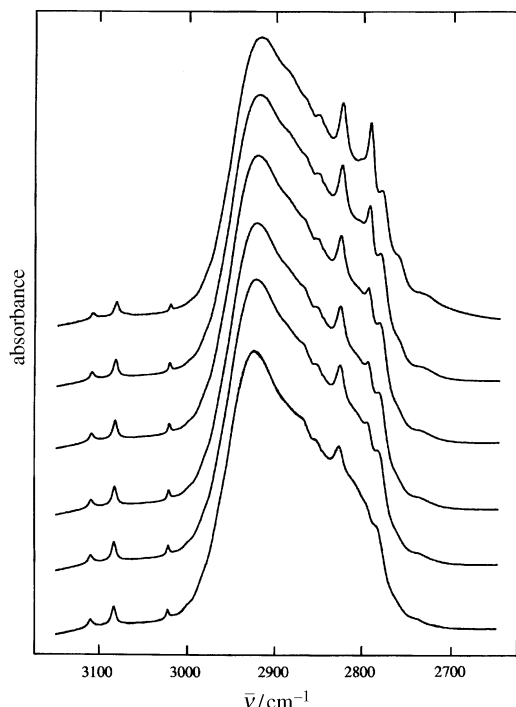


Fig. 4 $\nu_{\text{H-Cl}}$ region for a $\text{CH}_2=\text{CHBr-HCl}$ mixture dissolved in liquefied argon. From top to bottom, the temperatures of the solutions were 100.3, 102.4, 104.7, 106.3, 109.5 and 111.9 K.

Allyl chloride. The behaviour of monomer allyl chloride in liquefied noble gases has been described in detail elsewhere,¹⁴ and these data were used to interpret the spectra obtained here. Next to the absorption bands of the individual components, in the spectrum of a mixture of allyl chloride and HCl in liquid argon a new band appears at 2758 cm^{-1} . This suggests that a van der Waals complex is also formed between allyl chloride and HCl. Note that only one complex band of $\text{CH}_2=\text{CHCH}_2\text{Cl}\cdot\text{HCl}$ is observed in the $\nu_{\text{H-Cl}}$ region, while both the *cis*- and the *gauche*-conformers of allyl chloride are present in solution. Clearly, the conformation of the allyl group does not have an observable influence on the strength

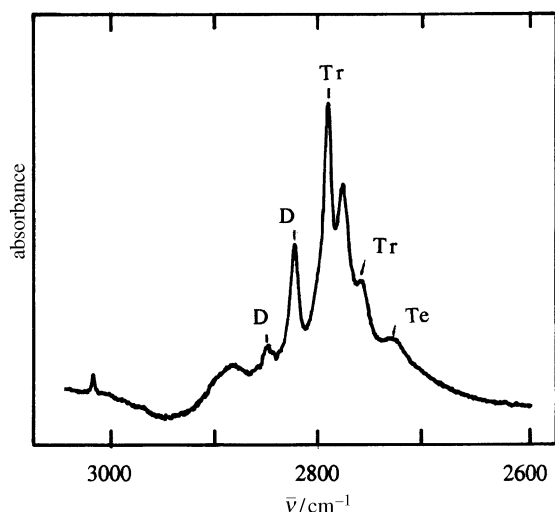


Fig. 5 Contribution of the complexed species for a solution of $0.5 \times 10^{-3}\text{ M}$ vinyl bromide and $3.5 \times 10^{-3}\text{ M}$ HCl, recorded at 100.3 K. The bands marked with D, Tr and Te are due to $(\text{HCl})_2$, $(\text{HCl})_3$ and $(\text{HCl})_4$, respectively. The broad feature near 2845 cm^{-1} is an artefact, caused by a small temperature difference in the spectra used in the subtraction. The weak, sharp band at 3020 cm^{-1} is due to monomer vinyl chloride.

of the hydrogen bond. This is analogous to the behaviour observed for the *n*-propyl chloride \cdot HCl complex.⁵

The $\nu_{\text{C-Cl}}$ region of allyl chloride is shown in detail in Fig. 6a. Only one isotopic doublet, with maxima at 748 and 745 cm^{-1} , can be observed in the $\nu_{\text{C-Cl}}$ region, showing that both conformers have identical C—Cl-stretching frequencies. Next to these bands, a broad band occurs at 732 cm^{-1} . This band is assigned to crystalline particles suspended in the solution, which is confirmed by the observation of other bands due to crystalline allyl chloride in the spectra.

In Fig. 6b, the spectrum of a mixed solution is given. In the latter, the band at 732 cm^{-1} has disappeared. Instead, a doublet with maxima at 738 and 735 cm^{-1} appears. On the other hand, no new bands are observed in the $\nu_{\text{C=C}}$ region. In analogy with the vinyl chloride complex, the position of the complex bands at 738 and 735 cm^{-1} suggests that the HCl molecule complexes *via* the chlorine atom and not *via* the carbon-carbon double bond.

Stoichiometry of the observed species

The stoichiometry of the vinyl chloride complexes was confirmed from a concentration study, following a procedure described previously.³ To this end, IR spectra of several solutions containing different concentrations of vinyl chloride, varying from 0.2×10^{-3} to $6.8 \times 10^{-3}\text{ M}$, and of HCl, varying from 0.4×10^{-3} to $1.0 \times 10^{-2}\text{ M}$, were recorded at a constant temperature of $104.0 \pm 0.3\text{ K}$.

The analysis requires the integrated intensities of a band of all species involved in the equilibrium. Unfortunately, the broad band due to monomer HCl strongly overlaps with the ν_{HCl} bands of the complexes. Therefore, I_{HCl} was obtained as follows: at the same temperature at which the solution of the vinyl chloride-HCl mixture was investigated, the spectrum of a solution containing only HCl was also recorded. The intensity of the HCl band of this solution was rescaled so as to reproduce accurately, in the region above 2800 cm^{-1} , the monomer HCl contribution in the spectrum of the vinyl chloride-HCl mixture. The numerically integrated intensity of the rescaled band was then used as the integrated intensity of the HCl monomer, I_{HCl} .

In Fig. 7, this procedure is illustrated for a solution, record-

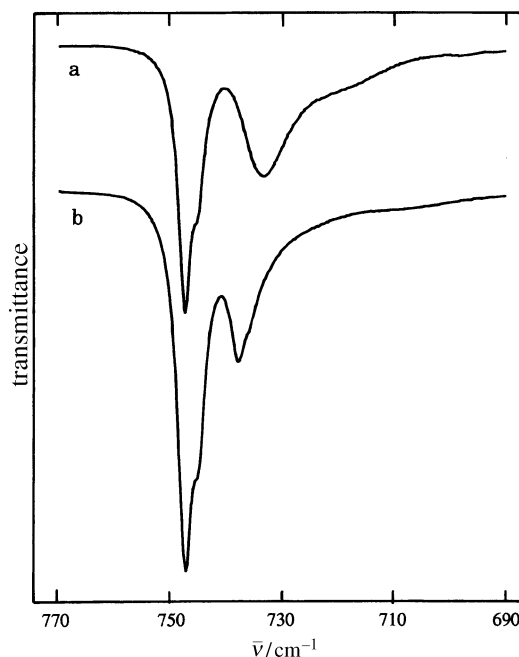


Fig. 6 $\nu_{\text{C-Cl}}$ region of the spectra of: a, allyl chloride dissolved in liquefied argon at 122 K; and b, allyl chloride-HCl mixture dissolved in liquefied argon at 122 K

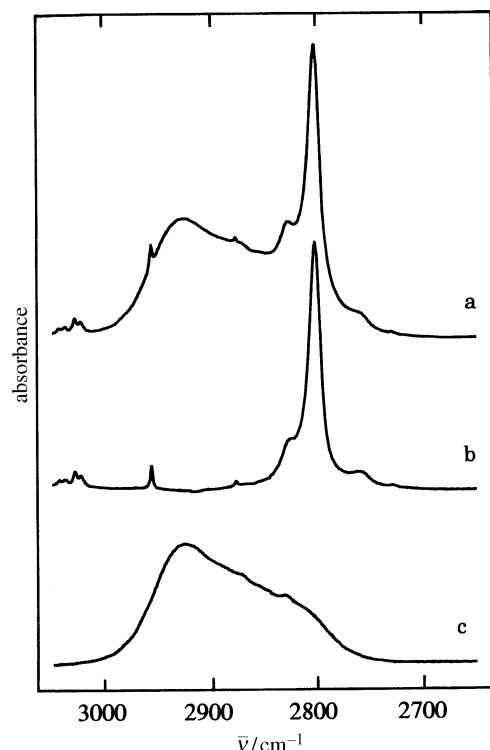


Fig. 7 Experimental spectrum of a solution in liquefied argon of: a, a vinyl chloride–HCl mixture at 98 K; c, of solution of HCl; and b, the difference between a and c

ed at 98 K. The upper trace gives the spectrum as recorded from the solution; the lower trace is the rescaled spectrum obtained from a solution containing only HCl. The middle trace is the result of subtraction of the rescaled HCl spectrum from that of the mixed solution. In this spectrum, the bands due to complexes appear at 2830, 2800 and 2758 cm^{-1} . Their intensities were obtained from a least-squares band fitting of this region, using Gauss–Lorentz sum profiles. This yielded the intensity of both the 2830 and 2800 cm^{-1} band. The agreement between the calculated and the experimental spectrum in the region near the band at 2758 cm^{-1} was not completely satisfactory. The reason for this is, presumably, the presence in this region of weak spectral features due to HCl oligomers, incorrectly accounted for in the subtraction process. In addition, the band may be slightly asymmetric due to the presence of excited-state transitions not accounted for in the calculations. Therefore, as the intensity of the 2758 cm^{-1} band, the absorbance at the band maximum was preferred over the integrated intensity obtained from band fitting. As all spectra used in the concentration study were recorded at the same temperature, this approximation was regarded as acceptable.

For modes localised in the vinyl chloride moiety, the complex bands in general overlap strongly with the monomer modes, making an accurate determination of $I_{\text{CH}_2=\text{CHCl}}$ rather difficult. In fact, the C–Cl stretch is the only fundamental that exhibits a relatively large splitting. Unfortunately, because of the large IR intensity of the monomer bands, the problems with the non-linearity of the MCT detector prevented this mode being used for the determination of $I_{\text{CH}_2=\text{CHCl}}$. For the solutions studied, the intensities of the complex C–Cl stretches are small compared with those of the monomer modes, showing that only a minor fraction of the vinyl chloride molecules is complexed. Thus, the contribution of the complex to a band assigned accidentally degenerate to monomer and complex, can be neglected. Therefore, as monomer intensity $I_{\text{CH}_2=\text{CHCl}}$, the numerically integrated intensity of the 1368/1278 cm^{-1} doublet was used, without

correcting for the presence of complex bands.

To determine the stoichiometry of the complexes studied, the intensity of both the 2800 and the 2758 cm^{-1} band were plotted against the intensity products $I_{\text{C}_2\text{H}_3\text{Cl}}I_{\text{HCl}}$, $I_{\text{C}_2\text{H}_3\text{Cl}}(I_{\text{HCl}})^2$ and $(I_{\text{C}_2\text{H}_3\text{Cl}})^2I_{\text{HCl}}$. For the 2800 cm^{-1} band, a linear relationship was obtained only for the plot against the products $I_{\text{C}_2\text{H}_3\text{Cl}}I_{\text{HCl}}$ and for the 2758 cm^{-1} band such a relationship was found for the plot using $I_{\text{C}_2\text{H}_3\text{Cl}}(I_{\text{HCl}})^2$. Therefore, the 2800 and the 2758 cm^{-1} bands must be due to a 1 : 1 complex and a 1 : 2 complex, respectively. This is confirmed by the χ^2 values for the least-squares straight lines calculated for each of the plots, which are collected in Table 7.

The stoichiometry of the complexes with vinyl bromide and allyl chloride was not explicitly established. However, because the mixtures of HCl with these Lewis bases were investigated under experimental conditions completely similar to those for vinyl chloride, it may be safely assumed that the complexes observed also have a 1 : 1 stoichiometry.

Stability of the complexes

For $\text{CH}_2=\text{CHCl} \cdot \text{HCl}$ and $\text{CH}_2=\text{CHCl} \cdot (\text{HCl})_2$, the relative stability of the complex, expressed as a complexation enthalpy, ΔH^0 , was determined from a temperature study. Also, for $\text{CH}_2=\text{CHBr} \cdot \text{HCl}$ and $\text{CH}_2=\text{CHCH}_2\text{Cl} \cdot \text{HCl}$, temperature studies were attempted. Because of the low solubility of these species, however, no reliable value for their complexation enthalpy could be obtained.

Using the Van't Hoff relation, and making the usual assumptions,³ it is easily shown that $\ln\{I_{\text{CH}_2=\text{CHCl} \cdot (\text{HCl})_x}/I_{\text{CH}_2=\text{CHCl}}(I_{\text{HCl}})^x\}$ must be linearly related to $1/T$, and that the slope of the relation equals $-\Delta H_0/R$. The intensities required for this analysis were obtained in the same way as described in the previous paragraph.

In a first set of measurements, the spectra of a solution containing $ca. 1.5 \times 10^{-3}$ M vinyl chloride and 2.0×10^{-3} M HCl were recorded at several temperatures, between 95 and 115 K. Using the intensities of the HCl and $\text{CH}_2=\text{CHCl} \cdot \text{HCl}$ bands, obtained by analysing the ν_{HCl} region, and the intensity of the bands at 1368 and 1278 cm^{-1} , a Van't Hoff plot was constructed. From this plot, shown in Fig. 8(a), and accounting for density variations in the solutions,¹⁵ the complexation enthalpy was calculated to be -6.6 ± 0.1 kJ mol $^{-1}$.

To estimate the influence of the approximations introduced in the analysis, a second temperature study was carried out. Here, spectra of a solution containing $ca. 4.5 \times 10^{-3}$ M $\text{CH}_2=\text{CHCl}$ and 2.0×10^{-3} M HCl were recorded between 107 and 119 K. The absorbances of the 1368 and 1278 cm^{-1} bands were too high to allow accurate determination of integrated intensities; instead, the numerically integrated intensities of the overtones at 1874, 1833 and 1794 cm^{-1} were used. The Van't Hoff plot, obtained using these, and using the intensities of ν_{HCl} for monomer and complexed HCl, is shown in Fig. 8(b). From this plot, the complexation enthalpy was calculated to be -6.4 ± 0.2 kJ mol $^{-1}$. This second value is in excellent agreement with the first. Therefore, we propose to take the average value, -6.5 ± 0.2 kJ mol $^{-1}$, as the complexation enthalpy of the 1 : 1 complex.

To establish the relative stability of $\text{CH}_2=\text{CHCl} \cdot (\text{HCl})_2$, the IR spectra of a liquefied argon solution containing $ca.$

Table 7 χ^2 values, for the stoichiometry analysis of the complexes between vinyl fluoride and hydrogen chloride

abscissa	complex band	
	2800 cm^{-1}	2758 cm^{-1}
$(I_{\text{C}_2\text{H}_3\text{Cl}})^2I_{\text{HCl}}$	2.528	0.678
$I_{\text{C}_2\text{H}_3\text{Cl}}I_{\text{HCl}}$	0.854	1.113
$I_{\text{C}_2\text{H}_3\text{Cl}}(I_{\text{HCl}})^2$	12.573	0.264

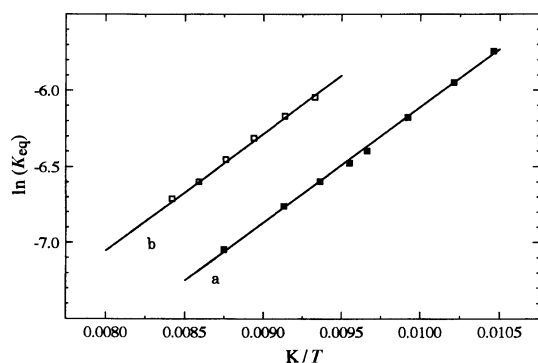


Fig. 8 Van't Hoff plots for vinyl chloride-HCl mixtures obtained by using: a, the intensity of the 1368 and 1278 cm^{-1} bands; and b, the intensity of the 1874, 1833 and 1794 cm^{-1} bands of vinyl chloride

2.0×10^{-3} M vinyl chloride and 4.0×10^{-3} M HCl were recorded between 106 and 117 K. As discussed above, an accurate determination of the integrated intensity of the 1 : 2 band at 2758 cm^{-1} is difficult, and, therefore, the absorbance of the band maximum of this band was used. The resulting Van't Hoff plot is shown in Fig. 9. From this, the complexation energy of the 1 : 2 bonded complex was calculated to be -10.60 ± 0.3 kJ mol $^{-1}$.

Discussion

The 1 : 1 complex bands observed for $\text{CH}_2\text{CHCl} \cdot \text{HCl}$ have frequencies compatible with the *ab initio* predictions for the σ -complex. From this we conclude that, in the cryosolutions, the σ -complex is formed. The spectra were carefully inspected in the regions where diagnostic π -complex bands are predicted to occur, but none have been found. This leads to the conclusion that, in the solutions studied, the concentration of the π -complex was below the detection limit.

For vinyl bromide, complex bands localised in the Lewis base were not observed and, consequently, the nature of the complex cannot be deduced. For allyl chloride, the appearance of the complex C-Cl stretches on the low-frequency side of the monomer bands is, in analogy with the vinyl chloride complex, taken as evidence for the formation of a σ -complex. For this Lewis base, a thorough search for bands assignable to a π -complex was also negative.

In conclusion, it is clear that, only for vinyl and allyl chloride are the σ -complexes with HCl detected. For vinyl chloride, for which the *ab initio* calculations indicate a similar strength for σ - and π -complexes, just as for vinyl fluoride,³ this is somewhat surprising. A possible explanation can be deduced from the *ab initio* calculations. For both σ -complexes, the potential hindering internal rotation of the H-Cl moiety is very shallow, with a very small barrier separating the two conformers. In such a potential, crowding

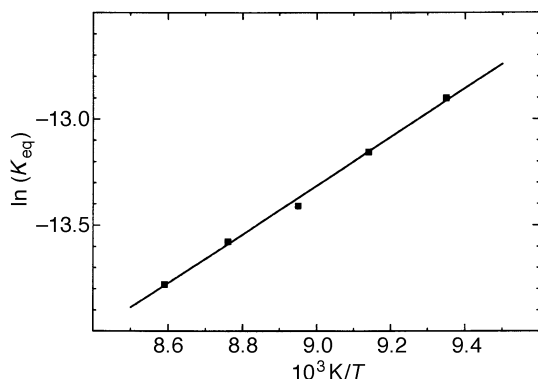


Fig. 9 Van't Hoff plot for the 1 : 2 complex between vinyl chloride and HCl

of torsional levels slightly above the barrier occurs.¹⁶ These levels have sufficiently low energies to be substantially thermally populated. In contrast, because the dissociation energy of the π -complexes is much higher than the **1a/1b** barrier, the vibrational levels in the potential governing the stretching of the van der Waals bond in this complex are more regularly separated, and only a limited number of them are thermally accessed. Consequently, the σ -complex shows an important statistical advantage, leading to the observed dominance of the σ -complexes. Furthermore, it is possible that differences in solvation contribute to the dominance of the σ -complex. However, the dipole moments of **1a**, **1b** and **11** are very similar and, thus, such differences must be due to the interaction of the solvent with the higher multipoles of the solutes. Therefore, these differences may be expected to be relatively small.

It is interesting to compare the complexation enthalpies for the HCl complex of vinyl fluoride, -6.2 ± 0.2 kJ mol $^{-1}$, and vinyl chloride, -6.5 ± 0.2 kJ mol $^{-1}$, with those of the HCl complexes of CH_3F , -4.6 ± 0.4 kJ mol $^{-1}$, and CH_3Cl , -7.8 ± 0.4 kJ mol $^{-1}$. It is clear that, for the fluorides, the vinyl complex is significantly more stable than the methyl complex, which shows that the vinyl group acts as an electron donor. However, the chlorides show the opposite trend. Moreover, the increased stability from fluoride to chloride, caused by the lower electronegativity of the chlorine atom, is much less pronounced for the vinyl halide complexes. This can be explained from the resonance description of vinyl chloride. It is generally accepted that, for the latter, the $^-\text{CH}_2-\text{CH}=\text{Cl}^+$ mesomer is important.¹⁷ The chlorine atom in this mesomer is a poor Lewis base, and this will cause the proton affinity of the chlorine atom to be smaller than in the alkyl halides.

It is tempting to interpret the 1 : 2 complex as one in which the first HCl molecule forms a σ -complex and the second a π -complex. However, the position of the HCl stretching assigned to this complex is very similar to that observed for the 1 : 2 complexes with alkyl halides,^{4,5} in which no π -complex is possible. Therefore, we prefer the interpretation that the 1 : 2 complex has a chain structure in which the second HCl is attached to the chlorine atom of the first, similar to the 1 : 2 complexes with vinyl fluoride.³

ΔH^0 for the 1 : 2 complex is 4.1 ± 0.4 kJ mol $^{-1}$ higher than that for the 1 : 1 complex. This value compares favourably with the complexation enthalpy of the HCl dimer in cryosolution,⁶ -3.8 ± 0.3 kJ mol $^{-1}$, in which a similar bond is formed. This lends support to the proposed structure of the 1 : 2 complex. If the slightly larger ΔH^0 for the second step in the formation of the 1 : 2 complex, compared with that for the HCl dimerization, is statistically significant, it reflects a weak cooperative effect,¹⁸ which causes the first hydrogen bond to be strengthened by the second and *vice versa*.

It was noted above that, even at the lowest temperatures, the greater part of dissolved molecules are not involved in complexes. However, in the spectra of mixed solutions, relatively strong bands due to the H-Cl-stretching mode in the 1 : 1 complex are observed. This shows that, for the complexes, the intensity of the HCl stretch is substantially higher than in monomer HCl. This important increase is confirmed by the *ab initio* calculations: the data in Table 4 show a predicted increase by a factor of 6.5 and by 6.9 for conformers **a** and **b** of the σ -complex, respectively. This intensity enhancement is a well known effect and has been explained in terms of the reduced ability, in the complex, of the electrons in the H-Cl bond to follow the H-Cl-stretching motion.^{19,20}

W.A.H. thanks the Fund for Scientific Research (FWO, Belgium) for an appointment as Postdoctoral Fellow. The FWO is also thanked for financial help toward the spectroscopic equipment used in this study. Financial support by the Flemish Community, through the Special Research Fund (BOF) is gratefully acknowledged.

References

- 1 L. Andrews, G. L. Johnson and B. J. Kelsall, *J. Am. Chem. Soc.*, 1982, **104**, 6180.
- 2 W. O. George, P. K. Hirani, E. N. Lewis, W. F. Maddams and D. A. Williams, *J. Mol. Struct.*, 1986, **141**, 227.
- 3 W. A. Herrebout and B. J. van der Veken, *J. Phys. Chem.*, 1996, **100**, 15695.
- 4 W. A. Herrebout and B. J. van der Veken, *J. Phys. Chem.*, 1993, **97**, 10622.
- 5 W. A. Herrebout and B. J. van der Veken, *J. Phys. Chem.*, 1994, **98**, 2836.
- 6 B. J. van der Veken and F. R. De Munck, *J. Chem. Phys.*, 1992, **97**, 3060.
- 7 P. Hoboza and R. Zahradnik, *Int. J. Quant. Chem.*, 1992, **42**, 581.
- 8 GAUSSIAN 92, Revision E3, M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1992.
- 9 H. B. Schlegel, *J. Comput. Chem.*, 1982, **3**, 214.
- 10 S. B. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553.
- 11 S. Scheiner, in *Theoretical Treatment of Large Molecules and Their Interactions*, ed. Z. B. Maksic and D. B. Boyd, Springer-Verlag, Berlin, 1991, and references therein.
- 12 W. A. Herrebout, B. J. van der Veken and J. R. Durig, *THEOCHEM*, 1995, **332**, 231.
- 13 C. W. Gullikson and J. Rud. Nilssen, *J. Mol. Spectrosc.*, 1957, **1**, 158, and references therein.
- 14 J. R. Durig, D. T. Durig, B. J. van der Veken, F. R. De Munck and W. A. Herrebout, in preparation.
- 15 B. J. van der Veken, *J. Phys. Chem.*, 1996, **100**, 17436.
- 16 N. S. True, *Chem. Phys. Lett.*, 1983, **101**, 326.
- 17 A. Streitwieser and C. H. Heathcock, *Introduction to Organic Chemistry*, Macmillan, New York, 3rd edn., 1985.
- 18 G. Maes and J. Smets, *J. Phys. Chem.*, 1993, **97**, 1818.
- 19 W. A. Herrebout, G. P. Everaert, B. J. van der Veken and M. O. Bulanin, *J. Chem. Phys.*, submitted.
- 20 M. M. Szczesniak, I. J. Kurnig and S. Scheiner, *J. Chem. Phys.*, 1988, **89**, 3131.

Paper 7/02484C; Received 11th April, 1997