Infrared and ab Initio Study of the Relative Stability and Geometry of the 3-Fluoropropene−Hydrogen Chloride van der Waals Complexes

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The mid-infrared spectra (4000−400 cm^{-1}) of complexes between the cis and gauche conformers of 3-fluoropropene, CH_2═$CHCH_2F$, and HCl have been recorded in liquefied argon at temperatures ranging from 103 to 123 K. From this data, the complexation enthalpy for the complex with *cis*-3-fluoropropene was determined to be −9.6(3) kJ mol^{-1}, while that for the complex with gauche 3-fluoropropene was estimated, from the observed HCl stretching frequency, to be −10.4(5) kJ mol^{-1}. The stoichiometry of these complexes was determined from constant temperature, variable concentration experiments to be 1:1. A few weak bands in the spectra are assigned to higher order complexes. An ab initio study of the structures and vibrational frequencies of the complex was performed at the B3LYP/6-311++G(d,p) level. These calculations show that HCl can form a van der Waals bond with either the carbon−carbon double bond or the fluorine atom. Comparison of the experimental frequencies with the calculated ones shows that all observed complex bands were due to complex formation with the fluorine atom.

Introduction

Unsaturated alkyl halides can give rise to two different types of van der Waals complexes with an electrophile such as hydrogen chloride. This is the consequence of the presence of two different electron donor sites, the halide atom and the carbon−carbon double bond. With the halide atom, a so-called σ complex is formed; with the double bond a π complex is formed.[1] Based on a comparison of published complexation enthalpies for the hydrogen chloride complexes of methyl fluoride and ethene, it was predicted[1] that for vinyl fluoride the π complex should dominate. In the infrared spectra of cryosolutions of mixtures of vinyl fluoride and hydrogen chloride, however, only the σ complex could be identified,[1] which led the authors to conclude that the presence of the electronegative fluorine in the α position substantially degrades the donor capacity of the π bond.

The influence of the fluorine atom is largely reduced by moving it to the β position. Therefore, on the basis of the same comparison, it is not unrealistic to expect that in 3-fluoropropene, given the correct experimental conditions, not only the σ, but also the π, complex should be observable.

The spectra of 3-fluoropropene, 3-FP, have long been of interest to spectroscopists, and its spectral characteristics have been intensily investigated. The spectroscopic literature has recently been reviewed,[2] and the experimental evidence shows that the compound can occur as two different stable conformers in which the fluorine is either cis or gauche with respect to the double bond.[2] The fluid phase enthalpy difference between the conformers is relatively small, so that the conformers have comparable populations in cryosolution.[2]

The conformational characteristics complicate the study of the van der Waals complexes between 3-FP and HCl. For the cis conformer, a σ complex and a single π complex can be formed. The absence of symmetry in the gauche conformer means that not only a σ complex but also two different π complexes can in principle form. Thus, a total of five different species must be considered. In this study, we have investigated the infrared spectra of solutions of 3-FP and HCl or DCl in liquid argon, while the characteristics of the different 1:1 complexes have been predicted using DFT calculations. It will be shown that from the spectra the formation of not more than two 1:1 species can be ascertained. Their identification and relative stability will be discussed below.

Experimental Section

3-FP was obtained from Fluorochem (UK) with a stated purity of 98%. It was used without further purification. Small amounts of HCl were produced by hydrolyzing PCl_3 with H_2O and then purified through fractionation on a low-temperature, low-pressure column. Purity was tested by gas-phase infrared spectroscopy. The argon used in this study, obtained from L'Air Liquide, had a stated purity of 99.9999%.

The mid-infrared spectra were recorded in the region between 4000 and 400 cm^{-1} on Bruker IFS 66v and Bruker IFS 113v FT-IR spectrometers. These instruments were used in conjunction with a broad band MCT detector, Ge/KBr beam splitter, and globar source. The interferograms were averaged over 200 scans, Happ-Genzel apodized, and Fourier transformed using a zero-filling factor of 4 to give 0.5 cm^{-1} resolution spectra. The solutions were studied in a 7 cm cell equipped with ZnSe windows. A detailed description of the liquid rare gas setup has previously been given.[3]

Ab Initio Calculations. The density functional theory calculations were obtained using Gaussian 94.[4] For all calculations, Becke's three-parameter exchange functional[5] was used in combination with the Lee−Yang−Parr correlation functional,[6] while the 6-311++G(d,p) basis set was used throughout. To reduce the errors arising from the numerical integration, for all

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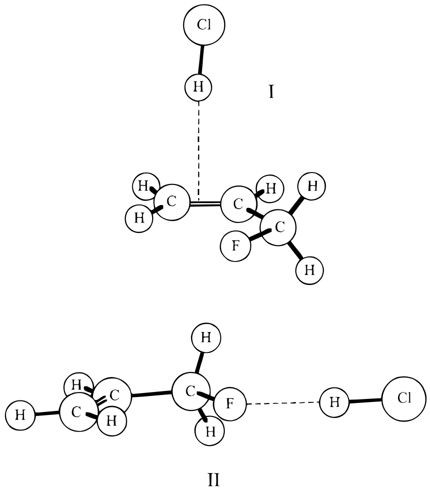

Figure 1. Ab initio structures of the 1:1 complexes of cis-3-fluoropropene with hydrogen chloride.

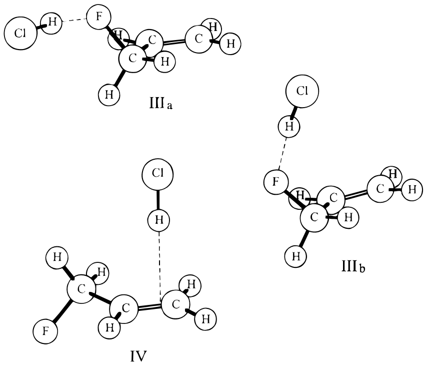

Figure 2. Ab initio structures of the 1:1 complexes of gauche-3-fluoropropene with hydrogen chloride.

calculations the fine grid option, corresponding to roughly 7000 grid points per atom, was used.

The complexation energies were calculated by subtracting the energies of monomers from those of the complexes, and these energies were corrected for basis set superposition error, BSSE, using the counterpoise method of Boys and Bernardi.[7] For the equilibrium geometries the vibrational frequencies and infrared intensities were calculated from a standard harmonic force field.

Equilibrium Geometry. Full geometry optimizations for the 1:1 complexes between allyl fluoride and hydrogen chloride were performed starting from a series of different initial geometries. These converged into five different complexes, which are shown in Figures 1 and 2. In all complexes, the hydrogen chloride interacts with the electron donor via its hydrogen atom, and it can be seen that for both conformers of 3-FP σ and π complexes are calculated to be stable. Relevant structural parameters of the complexes have been collected in Table 1.

In the π complex of the cis conformer, structure I of Figure 1, the hydrogen chloride is nearly perpendicular to the plane of the ethylenic fragment, which is as found for other π complexes.[8] The σ complex, structure II, attains its minimum energy when the HCl is in the plane of symmetry of cis-3-FP, which results in a complex with C_s symmetry.

For the gauche conformer, initial π complex geometries were selected in which the HCl was on either side of the alkene plane. When the HCl is on the side of this plane, which is opposite to the one with the fluorine atom, a π complex results, shown as structure IV in Figure 2. However, when the HCl is on the same side as the fluorine atom, the initial structures evolved into a complex in which the hydrogen interacts with the fluorine atom, thus giving rise to a σ complex. This complex is shown as structure IIIb in Figure 2. A second σ complex, structure IIIa, was found in which the HCl points away from the allyl group. The occurrence of two σ complexes in which HCl is bonded to the same fluorine atom raises the question of the potential barrier separating them. This barrier was investigated by performing calculations for different orientations of HCl with respect to the fluorine atom. The orientation was set via the Cl−H···F−C dihedral angle, and for each calculation this angle was fixed at the chosen value while all other structural parameters were relaxed. The converged energies as a function of the dihedral angle were taken to represent the potential energy for the internal rotation of HCl. This potential shows a single barrier of approximately 1 kJ mol^{-1} when the HCl is in the vicinity of the carbon−carbon double bond, but for the other cases the potential is very flat over a considerable range of values of the dihedral angle. Conformers IIIa and IIIb correspond to shallow dips of less than 0.1 kJ mol^{-1} in this nearly-flat region. Therefore, IIIa and IIIb should not be regarded as separate conformers. The actual σ complex presumably exhibits a large-amplitude torsional motion around the van der Waals bond and this complex will be referred to as complex III in the discussions below. It can be seen in Table 3 that the vibrational frequencies predicted for IIIa and IIIb are very similar. For comparison with the experimental data, therefore, for complex III we will use the average frequencies and shifts of IIIa and IIIb.

TABLE 1: B3LYP/6-311++G(d,p) Structural Parameters (Å), Uncorrected, and BSSE-Corrrected Complexation Energies (kJ/mol) for the 1:1 Complexes of 3-Fluoropropene with HCl

	cis			gauche			
	I	II	monomer	IIIa	IIIb	IV	monomer
$r_{C=C}$	1.3320	1.3284	1.3280	1.3303	1.3303	1.3328	1.3302
r_{C-C}	1.4953	1.4931	1.4952	1.4897	1.4900	1.4953	1.4929
r_{C-F}	1.3951	1.4113	1.3978	1.4271	1.4272	1.4063	1.4099
$R_{F-H(Cl)}$		1.9559		1.9321	1.9330		
$r_{\pi\cdots H(Cl)}$	2.4028					2.4534	
r_{H-Cl}	1.2978	1.2952		1.2964	1.2963	1.2957	
ΔE	−10.19	−15.65		−17.00	−16.98	−7.51	
E_{BSSE}	−2.06	−2.13		−2.15	−2.04	−2.01	
ΔE_{corr}	−8.13	−13.52		−14.85	−14.94	−5.50	

[a] The bond length in monomer HCl is 1.2869 Å.

The formation of a σ complex must be expected to be accompanied by a weakening of the C−F bond while in the π complexes mainly the C═C bond will be weakened. In all cases the H−Cl bond will be weaker in the complex than in the monomer. As a weakening of a bond is accompanied by an increase in its bond length, these expectations are borne out by the structural data in Table 1. Thus, in the σ complexes the C−F bond length is increased by 1.2% and 1.0% for the gauche and cis conformers, respectively, while for the π complexes this bond length decreases by 0.3% and 0.2%. In the latter complexes the C═C bond lengths increase by 0.2% and 0.3%, while the changes for the σ complexes are less than 0.01% and 0.03%, respectively.

The calculated complexation energies, given in Table 1, suggest that the σ complexes are significantly more stable than the π complexes, with the gauche σ more stable by some 10% than the cis σ. If we treat, in a crude approximation, the BSSE-corrected complexation energies as Gibbs energy differences at 100 K, a temperature typical for the experimental study, the populations for the gauche and cis π complexes relative to that

TABLE 2: B3LYP/6-311++G(d,p) Vibrational Frequencies (cm^{-1}) and IR Intensities (km mol^{-1}) for cis-3-Fluoropropene and Its 1:1 Complexes with HCl

		cis-$\mathrm{CH_2CHCH_2F{\cdot}HCl}$								
		complex I			complex II			cis-$\mathrm{CH_2CHCH_2F}$		
	approximate description	ν	int.	$\Delta\nu$	ν	int.	$\Delta\nu$	ν	int.	ν^a
A′	ν_1 $=\mathrm{CH_2}$ antisym stretch	3236.1	4.1	1.6	3233.6	1.9	−0.9	3234.5	5.0	3302
	ν_2 $=\mathrm{CH_2}$ sym stretch	3151.3	2.7	1.9	3147.0	2.6	−2.4	3149.4	3.7	3206
	ν_3 $=\mathrm{CH}$ stretch	3135.3	8.5	3.3	3134.1	5.7	2.1	3132.0	11.6	3192
	ν_4 $-\mathrm{CH_2}$ sym stretch	3033.7	24.6	12.6	3023.7	24.4	2.6	3021.1	34.7	3091
	ν_5 $\mathrm{C{=}C}$ stretch	1711.6	5.7	2.7	1698.3	11.3	−10.6	1708.9	5.8	1706
	ν_6 $-\mathrm{CH_2}$ deformation	1488.4	7.2	0.9	1488.0	8.0	0.5	1487.5	4.9	1520
	ν_7 $=\mathrm{CH_2}$ deformation	1449.1	6.8	5.8	1445.8	5.2	2.5	1443.3	5.6	1460
	ν_8 $-\mathrm{CH_2}$ wagging	1406.1	16.7	0.8	1406.1	9.9	0.8	1405.3	12.3	1436
	ν_9 $=\mathrm{CH}$ in-plane bending	1316.9	0.6	1.9	1317.0	0.5	2.0	1315.0	0.2	1313
	ν_{10} CF stretch	1102.8	39.5	−11.2	1117.9	43.7	3.7	1114.0	43.9	1145
	ν_{11} $=\mathrm{CH_2}$ wagging	964.2	50.3	6.7	969.9	67.2	12.4	957.5	51.8	1015
	ν_{12} $\mathrm{C{-}C}$ stretch	900.6	17.8	−2.0	901.8	2.9	−0.8	902.6	4.3	927
	ν_{13} $\mathrm{C{-}C{-}F}$ bending	608.3	13.7	3.6	609.5	6.9	4.8	604.7	7.6	611
	ν_{14} $\mathrm{C{=}C{-}C}$ bending	275.0	10.5	15.6	262.3	5.4	2.9	259.4	2.7	271
A″	ν_{15} $-\mathrm{CH_2}$ antisym stretch	3073.1	15.0	17.7	3058.6	17.9	3.2	3055.4	23.6	3143
	ν_{16} $-\mathrm{CH_2}$ twisting	1253.0	0.0	−2.7	1258.1	0.1	2.4	1255.7	0.1	1283
	ν_{17} $-\mathrm{CH_2}$ rocking	1035.2	11.6	−2.7	1045.3	22.3	7.4	1037.9	12.8	1050
	ν_{18} $=\mathrm{CH}$ out-of-plane bending	1014.5	10.6	0.1	1021.1	7.2	6.7	1014.4	9.5	1015
	ν_{19} $=\mathrm{CH_2}$ out-of-plane bending	982.5	90.3	−14.6	1001.2	57.8	14.1	997.1	59.5	888
	ν_{20} $=\mathrm{CH_2}$ twisting	560.3	13.9	1.7	580.3	14.5	21.7	558.6	12.9	546
	ν_{21} asym torsion	164.4	2.7	−1.7	184.2	5.0	18.1	166.1	3.9	149
	HCl stretch^b	2844.2	383	−275.9	2782.5	467	337.6			

[a] MP2/6-311++G(d,p) values from ref 2. [b] HCl monomer: 3120.1 cm^{-1}; 26.3 km mol^{-1}.

TABLE 3: B3LYP/6-311++G(d,p) Vibrational Frequencies (cm^{-1}) and IR Intensities (km mol^{-1}) for gauche-3-Fluoropropene and Its 1:1 Complexes with HCl

		gauche-$\mathrm{CH_2CHCH_2F{\cdot}HCl}$											
		complex IIIa			complex IIIb			complex IV			gauche-$\mathrm{CH_2CHCH_2F}$		
	approximate description	ν	int.	$\Delta\nu$	ν	int.	$\Delta\nu$	ν	int.	$\Delta\nu$	ν	int.	ν^a
A	ν_1 $=\mathrm{CH_2}$ antisym stretch	3219.4	8.9	3.9	3220.1	8.7	4.6	3215.7	6.4	0.2	3215.5	11.5	3285
	ν_2 $=\mathrm{CH}$ Stretch	3153.3	5.9	5.3	3153.2	6.0	5.2	3147.7	4.4	−0.3	3148.0	6.8	3212
	ν_3 $=\mathrm{CH_2}$ sym stretch	3131.8	7.7	2.9	3132.9	6.9	4.0	3128.5	4.8	−0.4	3128.9	9.3	3184
	ν_4 $-\mathrm{CH_2}$ antisym stretch	3111.2	11.3	23.0	3110.3	11.6	22.1	3091.9	16.3	3.7	3088.2	20.3	3165
	ν_5 $-\mathrm{CH_2}$ sym stretch	3053.8	22.2	18.2	3055.5	23.1	19.9	3038.5	24.9	2.9	3035.6	32.3	3102
	ν_6 $\mathrm{C{=}C}$ stretch	1705.9	0.4	0.0	1705.7	0.4	−0.2	1697.6	3.0	−8.3	1705.9	0.6	1701
	ν_7 $-\mathrm{CH_2}$ deformation	1500.3	5.0	2.2	1499.8	6.2	1.7	1498.7	4.5	0.6	1498.1	4.0	1522
	ν_8 $-\mathrm{CH_2}$ wagging	1458.4	19.9	0.1	1458.9	17.0	0.6	1460.3	16.4	2.0	1458.3	16.6	1475
	ν_9 $-\mathrm{CH_2}$ wagging	1385.1	18.4	0.8	1383.1	14.8	−1.2	1388.6	14.6	4.3	1384.3	14.7	1414
	ν_{10} $=\mathrm{CH}$ in-plane bending	1319.3	0.3	2.2	1318.2	0.1	1.1	1316.9	0.4	−0.2	1317.1	1.3	1315
	ν_{11} $-\mathrm{CH_2}$ twisting	1257.5	4.6	−1.6	1258.7	5.3	−0.4	1262.1	2.5	3.0	1259.1	3.9	1291
	ν_{12} $\mathrm{C{-}C}$ stretch	1177.7	2.3	0.8	1178.9	2.1	2.0	1175.5	2.2	−1.4	1176.9	2.3	1198
	ν_{13} CF stretch	961.8	173	−40.3	961.9	166	−40.6	1011.9	146	9.4	1002.5	139	1057
	ν_{14} $=\mathrm{CH}$ out-of-plane bending	1026.7	15.5	−2.4	1025.5	15.5	−3.6	1035.9	19.6	6.8	1029.1	14.6	1019
	ν_{15} $-\mathrm{CH_2}$ rocking	983.9	10.5	1.0	983.1	15.6	0.2	983.6	28.5	0.7	982.9	5.1	999
	ν_{16} $=\mathrm{CH_2}$ out-of-plane bending	979.1	31.5	9.2	979.4	25.8	9.5	977.5	53.1	7.6	969.9	7.5	937
	ν_{17} $=\mathrm{CH_2}$ wagging	919.5	63.5	−8.2	918.7	63.1	−9.0	927.9	6.1	0.2	927.7	62.6	918
	ν_{18} $=\mathrm{CH_2}$ twisting	659.9	11.4	2.7	658.2	8.1	1.0	665.9	10.4	8.7	657.2	7.9	656
	ν_{19} $\mathrm{C{-}C{-}F}$ bending	434.2	6.4	1.1	431.5	4.6	−1.6	436.1	3.8	3.0	433.1	2.8	435
	ν_{20} $\mathrm{C{=}C{-}C}$ bending	337.6	20.3	4.6	329.6	9.2	−3.4	342.9	15.2	9.9	333.0	8.5	339
	ν_{21} $\mathrm{C{-}C{-}F}$ bending	133.7	3.1	16.4	106.2	0.5	−11.1	117.1	0.5	−0.2	117.3	1.2	115
	HCl stretch^b	2826.9	458	−293.2	2828.9	392	−291.2	2813.4	390	−306.7			

[a] MP2/6-311++G(d,p) values from ref 2. [b] HCl monomer: 3120 cm^{-1}; 26.3 km mol^{-1}.

of the more stable complex III are calculated to be 0.001% and 0.015%, respectively. Hence, it is not very likely that in cryosolutions the π complexes will be detected simultaneously with the σ complexes. It will be seen below that this is confirmed by the experiments.

The vibrational frequencies and infrared intensities calculated for the 1:1 complexes are collected in Table 2 for the cis conformer and in Table 3 for the gauche conformer. In these tables the monomer 3-FP frequencies are also given, both at the DFT level as obtained here and at the previously published MP2 level.[2]

Vibrational Spectra. 3-*Fluoropropene*. The vibrational spectra of 3-FP have been discussed several times before.[2,9,10] These studies include a discussion of the infrared spectra of solutions in liquid rare gases (Ar, Kr, Xe), with the assignments based on a comparison with ab initio vibrational frequencies at the MP2 level.[2] For the present study the vibrational spectra (unscaled) have been calculated at the DFT level, using the same 6-311++G(d,p) basis set as in ref 2. For several modes these frequencies differ markedly from the MP2 values. This is best illustrated by the $=\mathrm{CH_2}$ out-of-plane bending in the cis conformer. The DFT frequency for this vibration is 997 cm^{-1}, while the unscaled and scaled MP2 values are 888 and 877 cm^{-1}, respectively.[2] As this vibration occurs in a region crowded with fundamentals, it is clear that assignments based on comparison with calculated frequencies will be affected by such a difference. Therefore, we have critically reassessed the previous assignments in light of the new calculations and in light of the complexation shifts observed in this study (vide infra), and it was judged necessary to refine the previous assignments in a number of cases.

The symmetric CH_2 stretch of the gauche conformer is assigned in ref 2 to a band at 2901 cm^{-1} in the spectrum of the LAr solution. This assignment is in disagreement with the MP2 and the DFT calculations, which predict this vibration at slightly higher frequencies than the corresponding mode in the cis conformer, assigned in ref 2 at 2941 cm^{-1}. Inspection of the spectra recorded at the lowest temperatures in LAr shows that the 2941 cm^{-1} band has an intense low-frequency shoulder at 2936 cm^{-1}, which is absent from the frequency tables in ref 2. In view of the ab initio calculations, we propose assigning the 2941 cm^{-1} band to $\nu_s(CH_2)$ in the gauche conformer, and the 2936 cm^{-1} to the same vibration in the cis conformer, while the 2901 cm^{-1} band, and the other nearby bands, are assigned as overtones, intensity-enhanced by Fermi resonance with the CH stretches. No attempts have been made to assign these overtones specifically.

In the liquid rare gas solutions the C═C stretch in the cis conformer was previously assigned at 1654 cm^{-1} and near 1630 cm^{-1} in the gauche conformer.[2] The DFT calculations predict these vibrations at 1708.9 and 1705.9 cm^{-1}, respectively. Thus, the calculated separation between the two is nearly an order of magnitude smaller than in the above assignment. At the lowest temperatures in LAr, the cis band shows a relatively weak low-frequency shoulder, shifted by approximately 2.5 cm^{-1} from the main maximum. We prefer to assign ν(C═C) in the gauche conformer to this shoulder, bringing the assignments in much closer agreement with the predictions. In rare gas solutions the cis conformer is slightly more stable than the gauche conformer.[2] Nevertheless, in the CH stretching region the gauche bands are slightly more intense, which can be explained by the statistical advantage of the gauche conformer. The shoulder assigned here to ν(C═C) in the gauche is much weaker than the cis band. This, however, is readily rationalized from the ab initio infrared intensities, which are 0.6 and 5.8 km mol^{-1} for the gauche and cis conformers, respectively.

A band at 1242 cm^{-1} in the spectra of the cryosolutions has previously[2] been assigned as the ═CH in-plane bending in the gauche conformer, while the same mode in the cis conformer, and the $-CH_2$ twisting in both conformers, were not assigned. The ═CH in-plane bending modes are calculated, with low intensities, at 1315 and 1317 cm^{-1} in cis and gauche, respectively, while the $-CH_2$ twisting is predicted at 1282 cm^{-1} in the cis with an intensity 0.2 km mol^{-1}, and at 1259.1 cm^{-1} in the gauche conformer with an intensity 3.9 km mol^{-1}. We, therefore, prefer to assign the 1242 cm^{-1} band as the $-CH_2$ twisting in the gauche conformer.

The C−C stretch in the gauche conformer was assigned in ref 2 at 1160 cm^{-1} in the vapor phase, and to a band at 1098 cm^{-1} in LAr. Such a solvent shift is rather unusual. Therefore, we prefer to assign this vibration to the weak band at 1164 cm^{-1}, which is absent from the frequency tables in ref 2. Besides being in much better agreement with the gas-phase frequency for this mode, it is also in excellent agreement with the DFT frequency at 1176.9 cm^{-1} for this vibration.

The DFT calculations predict that in the region around 1100 cm^{-1} only ν(CF) of the cis conformer occurs. We assign the more intense band at 1115 cm^{-1} to this vibration. This leaves the 1098 cm^{-1} band discussed above unassigned. It will be shown below that when 3-FP is complexed with HCl, the 1115/1098 cm^{-1} doublet gives rise to a complex doublet with a frequency separation similar to that of the monomer doublet. This is not unlike the behavior of a Fermi doublet upon complexation.[11] Therefore, we propose that the 1115/1098 cm^{-1} doublet is ν(CF) of the cis conformer in Fermi resonance with an overtone. A possibility is the first overtone of the 551 cm^{-1} band, assigned as the $═CH_2$ twisting of the cis conformer. The ═CH twisting coordinate has A″ symmetry, but the $v = 2$ vibrational level of this mode is totally symmetric, allowing Fermi resonance with the $v = 1$ level of ν(CF). The assignment proposed here must, however, be regarded as preliminary.

We propose assigning the bands observed in the cryosolutions at 936, 926, 918, and 903 cm^{-1} to the four fundamentals predicted by DFT in the region between 969.9 and 902.6 cm^{-1}, in the same order. This assignment is supported by the optimal agreement between experimental and calculated frequencies and is also supported by the observed complexation shifts in this region (vide infra), which are all in the direction predicted by the DFT calculations. It may be observed, though, that these assignments are not in full agreement with the ab initio intensities: the gauche band calculated at 969.9 cm^{-1}, with a DFT intensity of 8 km mol^{-1}, is assigned to the band at 936 cm^{-1}. The experimental intensity of the latter is slightly smaller than that of the 926 cm^{-1} band, assigned to a cis mode at 957.5 cm^{-1} with an intensity of 52 km mol^{-1}.

A consequence of the above assignments is that the $═CH_2$ out-of-plane deformation of the cis conformer and the ρCH_2 of the gauche conformer, previously assigned in the 950−900 cm^{-1} region,[2] must be located at higher frequencies, and that the 971 cm^{-1} band, previously assigned to the $═CH_2$ wagging in the cis conformer, must be attributed to another fundamental. We propose that the ═CH out-of-plane deformation and the $═CH_2$ out-of-plane deformation of the cis conformer are assigned in the order calculated, which is the same at the MP2 and DFT levels, to the bands at 993 cm^{-1} and 984 cm^{-1}, respectively. Furthermore, we assign the gauche $\rho(CH_2)$ with a predicted low intensity of 5 km mol^{-1} to the weak band at 971 cm^{-1}. Close scrutiny of the contour of the 993 cm^{-1} band shows that its high-frequency slope decreases less steeply than the low-frequency slope, which suggests that a weak band is hidden on the high-frequency side of the 993 cm^{-1} band. We assign this weak transition to the ═CH out-of-plane deformation of the gauche conformer.

The changes in the assignments of the bands in the 1175−900 cm^{-1} region proposed here lead to a better agreement between experiment and calculation. The assignments in ref 2 show an average deviation of 3.7% between experimental and MP2/6-311++G(d,p) frequencies, and of 2.5% with the fixed scaled frequencies, while the average deviation from the DFT frequencies is 3.1%. With the changes proposed here, the average deviation from the unscaled DFT frequencies decreases to 1.7%. We, therefore, conclude that the present assignments are an improvement over the previous ones.[2]

Complexes. Vibrational spectra of mixtures of 3-FP and HCl dissolved in LAr were recorded at temperatures ranging from 103 to 123 K. The mole fractions used varied between 1.5×10^{-5} and 1.3×10^{-4} for 3-FP, and between 3.5×10^{-5} and 5.3×10^{-4} for HCl. Numerous new bands due to the formation of complexes between the two species were observed. This is

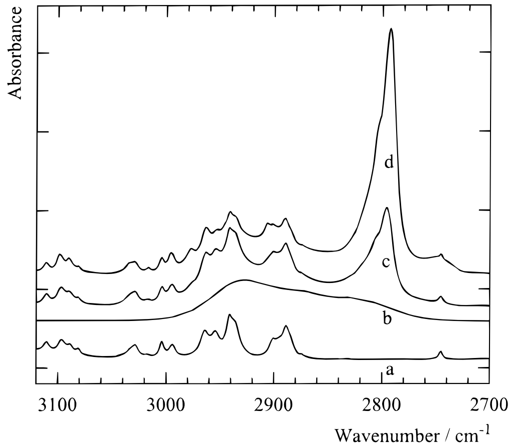

Figure 3. Infrared spectra in the CH and HCl stretching region of 3-fluoropropene and HCl in liquid argon: (a) monomer 3-fluoropropene; (b) monomer HCl; (c) mixture of 3-fluoropropene and HCl recorded at 120 K; (d) mixture of 3-fluoropropene and HCl recorded at 105 K. The mole fractions for the mixed solution were 7.5 × 10^{-5} for 3-FP and 2.0 × 10^{-4} for HCl. Similar concentrations were used to record the monomer spectra.

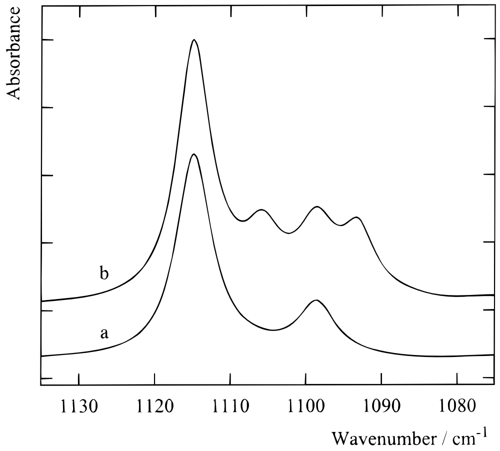

Figure 4. Infrared spectra in the cis ν(CF) stretching region, recorded at 103 K, of solutions in liquid argon of 3-fluoropropene (a) and of a mixture of 3-fluoropropene and HCl (b). The mole fractions for the mixed solution were 2.3 × 10^{-5} for 3-FP and 2.1 × 10^{-4} for HCl. A similar concentration of 3-FP was used to record the monomer spectrum.

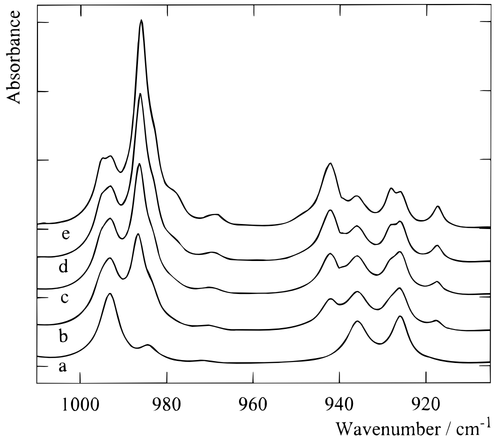

Figure 5. Infrared spectra in the 1010−910 cm^{-1} region of a solution in liquid argon of 3-fluoropropene recorded at 105 K (a), and of a mixture of 3-fluoropropene and HCl in liquid argon, recorded at 122 K (b), 117 K (c), 110 K (d), and 105 K (e). The mole fractions of 3-FP and HCl were 2.3 × 10^{-5} and 2.1 × 10^{-4}, respectively.

TABLE 4: Observed Vibrational Frequencies (cm^{-1}) and Complexations Shift (cm^{-1}) for the σ Complex of cis-3FP with HCl

approximate description	monomer[a]	complex	$\Delta\nu$ ab initio	$\Delta\nu$ observed
ν_7 =CH_2 deformation	1414	1416	+5.8	+2
ν_{10} −CF stretch	1115	1106	−11.2	−9
$2\nu_{20}$	1099	1093	-	−6
ν_{11} =CH_2 wagging	972	968	+6.7	−3
ν_{12} C−C stretch	903	901	−2.0	−2
ν_{13} C−C−F bending	604	602	+3.6	−2
ν_{18} =CH oop bending	993	995	+0.1	+2
ν_{19} =CH_2 oop bending	984	978	−14.6	−6
$2\nu_{19}$	1854	1858	-	+4
HCl stretch	2870	2804	−276	−67

[a] Observed values from ref 2.

TABLE 5: Observed Vibrational Frequencies (cm^{-1}), and Complexation Shifts (cm^{-1}) for the σ Complex of gauche-3FP with HCl

approximate description	monomer[a]	complex	$\Delta\nu$ ab initio	$\Delta\nu$ observed
ν_4 −CH_2 antisym stretch	2964	2977	+22.5	+13
ν_5 −CH_2 sym stretch	2946	2941	+19	+5
ν_9 −CH_2 wagging	1364	1363	−1	−1
ν_{11} −CH_2 twisting	1242	1241	−1	−1
ν_{12} C−C stretch	1164	1166	+1.4	+2
ν_{13} C−F stretch	1019	986	−40.5	−33
ν_{14} =CH oop bending	984	978.5	−3.0	−5.5
ν_{15} −CH_2 rocking	971	968	+0.6	−3
ν_{16} =CH_2 oop bending	936	942	+9.3	+6
n17 =CH_2 wagging	918	917	−8.6	−1
$2\nu_{16}$	1873	1884	-	+11
HCl stretch[b]	2870	2793	−293	−77

[a] Observed values from ref 2.

illustrated in Figures 3−5, and the observed frequencies have been collected in Tables 4 and 5.

In Figure 3 the CH and HCl stretching region of the monomer spectra (a, b) are compared with that of a mixture, recorded at 120 K (c) and 105 K (d). The prominent, temperature-dependent bands near 2800 cm^{-1} in spectra c and d are assigned as the HCl stretches of 1:1 complexes of 3-FP with HCl. They will be discussed later. Detailed comparison of spectra a, c, and d shows that a few of the CH stretches show shifts due to complex formation.

The two bands in the monomer spectrum (a) of Figure 4 have been assigned, as discussed above, as a Fermi doublet, with the high-frequency component due to ν(CF), and the low-frequency component resulting from the first overtone of the =CH_2 twisting of the cis conformer. The spectrum of the mixture serves to demonstrate that a doublet due to the complex, with frequency separation similar to that of the monomer doublet, has been observed. The spectra in Figure 4 can also be used to deduce the nature of the observed complex of the cis conformer. The ab initio frequencies in Table 2 show that ν(CF) in the π complex is predicted to be shifted by +3.9 cm^{-1} from the monomer band, while the shift for the σ complex should be −11.2 cm^{-1}. The higher frequency of the two complex bands in Figure 4 is shifted by −9 cm^{-1} from the monomer band. Taking into account possible influences from the Fermi resonance, this shift is in excellent agreement with that for the σ complex, and it follows that the observed complex doublet is due to this complex. No sign of a complex band can be seen on the high-frequency side of the monomer ν(CF) band, so it must be concluded that the concentration of the π complex, if formed, is much lower than that of the σ complex, below the detection limit of the present experiment.

In the spectra of the mixture shown in Figure 5, the most prominent complex band is that at 986 cm^{-1}. In view of its intensity it must be assigned as ν(CF) of the complex formed with the gauche conformer (the corresponding monomer band falls at 1020 cm^{-1}, outside the region shown). Its complexation shift of -34 cm^{-1} is in good agreement with the shift of -40.5 cm^{-1} predicted for the σ complex. This shows that for the gauche conformer the σ complex is also formed. Analogous to the behavior of the cis conformer, the ν(CF) complexation shift for the π complex of the gauche conformer is calculated to be $+9.4$ cm^{-1}. No complex band can be detected on the high-frequency side of the monomer ν(CF) band of this conformer, which shows that for the gauche conformer also the concentration of the π complex is below the detection limit.

The ν(C=C) region is of diagnostic value for examining π complex formation. Tables 2 and 3 show that for the π complexes red shifts of -8 to -10 cm^{-1} are predicted, while for the σ complexes either no shift or a very small blue shift is predicted. In the spectra of the mixtures in the ν(C=C) region no separate complex bands could be detected. This is compatible with the formation of σ complexes, but again signals that no observable concentrations of the π complexes were formed.

From Figure 5 it is further clear that for many fundamentals a corresponding complex band can be detected. In none of the cases, however, can their shifts be interpreted as proving the formation of a π complex. The very weak shoulder near 945 cm^{-1}, visible only at the lowest temperatures, is assigned to a 1:2 complex.

With the absence of π complexes in the solutions well established, we can now return to the HCl stretches of the complexes shown in Figure 3. We have demonstrated before that the HCl stretching band of HCl complexes shows some tailing toward high frequencies due to the presence of hot bands.[8] These hot bands, however, do not produce observable shoulders, while it is clear from Figure 3 that the main HCl complex band has a high-frequency shoulder. We, therefore, assign this splitting to the presence of cis and gauche conformers of the complex.

It is known that the DCl stretching bands of DCl complexes have somewhat smaller bandwidths, so that a conformational splitting must be detectable in the DCl stretching region as well. Spectra of 3-FP/DCl mixtures have been recorded, and the DCl stretching region of a 3-FP/DCl mixture is compared for two different temperatures with the spectrum of a solution containing only DCl in Figure 6. Especially at the lower temperature, the solution containing only DCl gives rise to detectable DCl oligomer bands[3] in the 2020−2050 cm^{-1} region. In the same region the DCl stretches in the complexes with 3-FP occur also. It is clear from Figure 6 that the latter are much more intense than the oligomer bands, so that their characteristics are clearly visible. The spectra in Figure 6 then show that the doublet structure of the DCl stretching band is very obvious. This is taken to support the assignment that the splitting is due to the formation of complexes containing different conformers of 3-FP.

For the HCl as well as the DCl stretches the weaker component of the doublet occurs on the high-frequency side. Because of the statistical advantage of the gauche conformer, the band due to the gauche complex should have the higher intensity if band intensities are equal. Moreover, its infrared intensity is predicted, as can be seen in Tables 2 and 3, to be significantly higher than that of the complex with the cis conformer. Thus, the spectra must be interpreted to show that the HCl stretch of the gauche complex occurs at lower frequencies than that of the cis complex. As the complexation shift of ν(HCl) is correlated with the complexation enthalpy,[12] it follows that the gauche complex is slightly more stable than the cis complex. This is in line with the ab initio results that the predicted complexation energy, both uncorrected and BSSE corrected, for the gauche conformer is larger by approximately 1.3 kJ mol^{-1}.

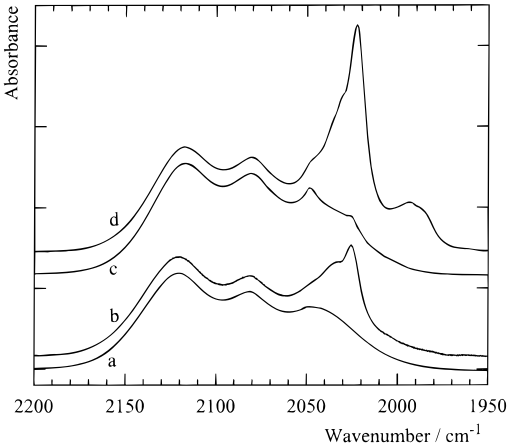

Figure 6. Infrared spectra in the DCl stretching region of solutions in liquid argon containing only DCl, recorded at 120 K (a) and at 105 K (c), and of a solution in liquid argon containing 3-fluoropropene and DCl, recorded at 120 K (b) and at 105 K (d). The mole fractions for the mixed solution were 1.5×10^{-5} for 3-FP and 2.1×10^{-4} for DCl. A similar concentration of DCl was used to record the monomer spectrum.

At higher concentrations of the monomers and at lower temperatures, weak bands on the low-frequency side of the HCl (DCl) stretches of the 1:1 complexes become more prominent, as is especially evident near 1990 cm^{-1} in Figure 6. These bands are attributed, as usual,[13] to complexes of 3-FP with two molecules of HCl. No attempts were made to analyze these bands in detail, but their position in the spectrum suggests that they are due to chain-type complexes in which the second HCl is hydrogen bonded to the chlorine atom of the first one.[13]

Stoichiometry. The stoichiometry of a complex in solution can be determined from a study of the relative intensities of the bands as a function of the concentration of the monomers.[3] This is because the intensity $I_{A_mB_n}$ of a band due to the complex is related to the intensities I_A and I_B of monomer bands by the equation

$$I_{A_mB_n} = C(I_A)^m(I_B)^n$$

in which C is a constant related to the equilibrium constant of the complexation reaction, and m and n are the number of molecules A and B, respectively, in the complex. This equation shows that for a concentration series the plot of $I_{A_mB_n}$ versus $(I_A)^x(I_B)^y$ yields a straight line only when $x = m$ and $y = n$.

For the present study, a series of solutions, containing mole fractions between 2.0×10^{-5} and 1.2×10^{-4} for 3-FP, and between 4.0×10^{-4} and 5.0×10^{-4} for HCl, was studied at 108 K. It is clear from the above discussion, and from Figures 3 and 5, that many fundamentals of 3-FP occur grouped together in overlapping multiplets. Although for the mixed 3-FP/HCl solutions the complex bands are readily identified, it can be seen in Figure 5 that the strong overlap in the multiplets makes reliable band fittings very difficult. This prevents the measurement of integrated intensities of the individual bands in most cases. The only multiplet amenable to accurate measurements is the one shown in Figure 4. It was discussed above that all transitions in this region must be associated with the cis

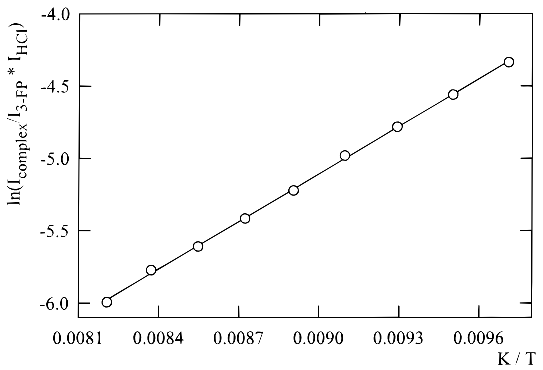

Figure 7. Van't Hoff plot for the determination of the complexation enthalpy of the 1:1 complex between *cis*-3-fluoropropene and HCl.

conformer, and, consequently, only the stoichiometry of the complex with cis 3-FP could be determined. The integrated intensity of the 1115 cm^{-1} band was used as I_A, and the integrated intensity of the 1106 cm^{-1} complex band was taken to be $I_{A_mB_n}$. The intensity of monomer HCl was deduced by subtraction techniques, described previously,[3] applied to the HCl stretching region. The data were used to make plots for values of x and y equal to 1 and 2. Only for $x = y = 1$ did the plot show a linear relationship, which confirms the 1:1 stoichiometry of the complex giving rise to the 1106 cm^{-1} band.

Although no quantitative evidence for the stoichiometry of the complex formed with gauche 3-FP could be obtained, it is clear from the spectra that the bands due to this complex show an intensity behavior qualitatively similar to those of the complex with the cis conformer, and it may therefore be safely assumed that also the gauche complex has 1:1 stoichiometry.

It was pointed out above that a small number of weak bands in the spectra had to be attributed to complexes with higher stoichiometry. Their weakness and, in some cases, complex structure, however, prevent the determination of the stoichiometry of the complexes involved.

Stability. From van't Hoff's isochore it can be shown that for a 1:1 complex the logarithm of the intensity ratio $\ln(I_{\text{complex}}/I_{3-\text{FP}}I_{\text{HCl}})$ varies linearly with $1/T$. The slope of the linear relation, after correction for the thermal expansion of the solvent,[14] equals $-\Delta H°/R$, and thus provides a method to measure the complexation enthalpy $\Delta H°$. Unfortunately, the complexity of the spectra made the determination of $\Delta H°$ for the complex with gauche 3-FP impossible. The complexation enthalpy for the complex with cis 3-FP was determined from a set of nine spectra recorded in the temperature interval between 103 and 123 K. As $I_{3-\text{FP}}$ the sum of the integrated intensities of the 1115 and 1098 cm^{-1} monomer bands obtained by least-squares band fitting was used, and I_{complex} was obtained by summing the integrated intensities of the 1106 and 1093 cm^{-1} complex bands. As described above, here the intensities for monomer HCl were obtained by subtraction techniques applied to the HCl stretching region. The van't Hoff plot constructed from the intensities, and the linear regression line through the experimental points, are shown in Figure 7. The slope of the linear regression, corrected as described before,[14] yields a complexation enthalpy of −9.6(3) kJ mol^{-1}.

As discussed above, as a consequence of the relative positions of the HCl stretches, the complex with the gauche conformer is more stable than the one with the cis conformer. A quantitative estimate of the stability difference can, in principle, be obtained from the relation between the complexation enthalpy and the HCl stretching frequency of the complex.[15] This relation was derived using data from complexes of HCl with alkyl chlorides, and its applicability to fluorides is not guaranteed at the outset. Application of the relation to the experimental HCl stretching frequency of $CH_3F{\cdot}HCl$[16] gives a $\Delta H°$ of −5.9(5) kJ mol^{-1}, while the value determined from a temperature study[16] is −380 cm^{-1} or −4.5 kJ mol^{-1}. This result is encouraging, but when the relation is applied to ν(HCl) of the present cis complex a $\Delta H°$ of −5.6(5) kJ mol^{-1} is found, in rather poor agreement with our experimental value of −9.6(3) kJ mol^{-1}. Therefore, it must be expected that the stability difference between cis and gauche complexes predicted with this relation will be only approximate. The ν(HCl) of the gauche complex is shifted by 10 cm^{-1} from that of the cis complex, which leads to a difference between the complexation enthalpies of 0.8 kJ mol^{-1}. The ab initio calculations predict the gauche complex to be more stable by 1.3 kJ mol^{-1}. In view of the approximate character of the difference in $\Delta H°$, and in view of of the different nature of the quantities compared, the agreement between these two values may be regarded as satisfactory.

The absolute value of the BSSE-corrected ab initio complexation energy of cis 3-FP·HCl exceeds the experimental $\Delta H°$ by 40%. This, however, is not unexpected, as both thermal contributions and solvent influences tend to result in a $\Delta H°$ which is significantly lower than the ab initio complexation energy.[17]

Conclusions

In this work we have analyzed the spectra of and carried out ab initio calculations for the complexes between 3-fluoropropene and hydrogen chloride. Close scrutiny of the spectra of monomer 3-fluoropropene has led to improved assignments for a number of fundamentals.

In the spectra of mixed solutions, bands due to complexes of both the cis and gauche 3-fluoropropene have been identified. Comparison of the positions of the complex bands with the frequencies predicted by ab initio has shown that for both conformers the σ complex is formed, where the hydrogen chloride interacts with the fluorine atom of 3-fluoropropene. No bands due to π complexes, in which the hydrogen chloride interacts with the carbon−carbon double bond, have been detected. This is consistent with the lower stability of the π complexes predicted by the ab initio calculations.

A concentration study has shown that the complex formed with the cis conformer has the 1:1 stoichiometry 3-fluoropropene·HCl. Based on qualitative intensity arguments, the same stoichiometry was assigned to the complex with the gauche conformer. A few very weak bands in the spectra of the mixed solutions were attributed to a complex with higher, most likely 1:2 stoichiometry. That no more bands of this species were observed is attributed to the very low concentration of this species in the solutions studied, combined with the strong overlap of its bands with those of the 1:1 complex.

The complexation enthalpy of the 1:1 complex with the cis conformer was found from a temperature study to be −9.6(3) kJ mol^{-1}, while that for the complex with the gauche conformer was estimated at −10.4(5) kJ mol^{-1}.

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