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ARTICLE

Weak hydrogen bonds in adducts between freons: the rotational study of CH_2F_2-CH_2ClF

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The rotational spectra of 2 isotopologues of the molecular adduct CH_2F_2-CH_2ClF show that the two subunits are held together through two weak C-H$\cdots$F-C and one C-H$\cdots$Cl-C linkages, rather than through three weak C-H$\cdots$F-C connections. This suggests the weak Cl$\cdots$H interaction to be observed preferentially to a weak F$\cdots$H one. Structural information on these weak hydrogen bonds has been obtained. The dissociation energy has been estimated from centrifugal distortion to be 5.3 kJ$\cdot$mol^{-1}.

1 Introduction

Hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) have replaced chlorofluorocarbons (CFCs) as refrigerants, due to their small ozone depletion potentials.[1] Their different atmospheric chemistry, with respect to CFCs, is plausibly related to the possibility of forming weak hydrogen bonds (WHBs)[2] such as C-H$\cdots$X-C, with X = F, Cl.

These two types of WHBs, C-H$\cdots$F-C and C-H$\cdots$Cl, can be characterized by studying gas phase molecular complexes in which the two monomers (typically freons) are held together by these linkages, when no interactions due to solvent or solid state effects mask their genuine nature.

The C-H$\cdots$F-C intermolecular linkages have been described, indeed, through the rotational studies in supersonic expansions of several adducts displaying only this kind of interactions, such as the CH_2F_2 dimer,[3] CH_3F-CF_3H,[4] CH_2F_2-CH_2=CF_2 and CH_2F_2-CF_2=CHF,[5] and CH_2F_2-CH_2=CHF.[6] The H$\cdots$F bond length was found to be in the range 2.5 – 2.9 Å, and the interaction energy for each C-H$\cdots$F-C about 2 kJ/mol. Later on, the investigations of the rotational spectra of the trimer[7] and of the tetramer[8] of CH_2F_2 showed that the C-H$\cdots$F-C WHB leads to the formation of oligomers based on WHB networks. The number of WHBs increases from 3 in the dimer to 9 in the trimer and to 16 in the tetramer.

As to the C-H$\cdots$Cl-C linkage, only three microwave investigations are available describing this interaction.[9-11] In all of them, the C-H$\cdots$Cl-C WHBs occur in association with one or more C-H$\cdots$F-C WHBs. The three studies show that the C-H$\cdots$Cl-C WHB is preferred when it can be formed in the place of one C-H$\cdots$F-C WHB.

The study of 1:1 complex between CH_2ClF (Freon 31) and CH_2F_2 (Freon 32) will supply further data to verify if the C-H$\cdots$Cl-C

WHBs is effectively stronger than the C-H$\cdots$F-C one. Based on our expertise, we could expect three WHBs to link the two subunits, but would they be three C-H$\cdots$F-C or two C-H$\cdots$F-C and one C-H$\cdots$Cl-C linkages? The answer is given below.

2 Experimental Section

A gas mixture of 1% of both CH_2F_2 and CH_2ClF (commercial samples) in Helium at a stagnation pressure of 0.5 MPa was expanded through the solenoid pulsed valve (General valve, series 9, nozzle diameter 0.5 mm) into the Fabry–Perot cavity at $5\cdot10^{-2}\cdot$Pa. The microwave spectra of two isotopologues (^{35}Cl and ^{37}Cl) have been recorded using a COBRA-type[12] pulsed supersonic jet Fourier-transform microwave (FTMW) spectrometer[13], described elsewhere[14], working in the 6–18 GHz frequency region. Each rotational transition is instrumentally split into two component lines by Doppler effect (see Figure 1),[12] enhanced by the coaxial arrangement of the supersonic jet and resonator.

3 Results and Discussion

3.1 Theoretical calculations

Three different isomers with the two subunits linked together by three WHBs can exist for the CH_2F_2-CH_2ClF molecular adduct (see the upper part of Table 1).

Geometry optimizations of these three isomers have been performed with *ab initio* calculations at the MP2 level of theory and 6-311++G(d,p) triple-zeta- split-valence basis set by using Gaussian03 Quantum Chemistry Package.[15] We obtained their rotational and ^{35}Cl quadrupole coupling constants, and their dipole moment components.

We also calculated their relative energies (ΔE) and their relative ground state energies (ΔE_0, based on harmonic vibrational

frequency calculations). In addition, the dissociation energy (E_D) values have been calculated after evaluating the BSSE corrections.[16] Form I has clearly a C_1 symmetry. To establish the symmetries of forms II and III it turned out to be a bit complicated: the ΔE values indicate the C_s forms to be slightly less stable than the slightly distorted C_1 forms, but the more significant ΔE_{BSSE} and ΔE_0 values (which include the BSSE or the zero point energy corrections) give the opposite indication For this reason we calculated the energies of these forms imposing the C_s symmetry. All these data (including the symmetry) are listed in Table 1. One should note that small change in the orientation of CH_2ClF causes a switch of the relative orientations of the b- and c-axes.

Table 1 *Ab initio* shapes and spectroscopic parameters of the calculated molecular adducts of CH_2F_2-CH_2ClF.

	I	II	III
Symmetry	C_1	C_s	C_s
A/MHz	4443	6377	3944
B/MHz	1080	912	1155
C/MHz	975	886	1075
$1.5\chi_{aa}$/MHz	49.2	-101.9	45.4
$0.25(\chi_{bb}-\chi_{cc})$/MHz	-19.7	1.7	-25.9
χ_{bc}/MHz	29.2	0.0	0.0
χ_{ab}/MHz	16.1	0.0	3.8
χ_{ac}/MHz	1.9	2.5	0.0
μ_a/D	-1.91	-2.24	3.12
μ_b/D	-1.19	0.00	0.59
μ_c/D	0.02	-0.06	0.00
ΔE/cm^{-1}	0[a]	62	102
ΔE_{BSSE}/cm^{-1}	2	0[b]	67
ΔE_0/cm^{-1}	0[c]	36	54
E_D[d]/kJ mol^{-1}	5.3	5.6	5.1

[a]Absolute energy= -837.04473 E_h. [b]Absolute energy BSSE corrected= -837.041714 E_h. [c]Absolute zero point energy = -836.97838 E_h. [d]Dissociation energy

3.2 Rotational spectra

According to the theoretical calculations, the most stable species should be conformer I (from the ΔE_0 values) or conformer II (following ΔE_{BSSE}). Since μ_a is expected to be the larger dipole moment component in both cases, we searched for both conformers in the frequency regions where the 4←3 μ_a–type bands were expected (4 and 3 correspond to the upper and lower rotational quantum numbers, J' and J'', respectively). We found a relatively strong transition whose quadrupole pattern was matching that of the 4_{04}←3_{03} transition (each rotational state is indicated as J_{KaKc}) of the most abundant isotopologue (^{35}Cl) of conformer I. It was then easy to find several additional $K_a = 0$ transitions and, after a preliminary

fit, to extend the assignment of the μ_a–type spectrum up to $J = 9$ and $K_a = 3$. Then, 9 μ_b–type transitions were measured. Each transition appears as a quartet, the typical pattern due to quadrupole splitting of a nucleus with spin $I = 3/2$ as ^{35}Cl. As an example, the 4_{04}←3_{03} transition is shown in Figure 1; there, each quadrupole component appears further split into two components, due to the instrumental Doppler effect.

The same procedure was used to assign the spectrum of the ^{37}Cl isotopologue, with a similar hyperfine structure, but with a separation between the quadrupole component lines reduced by about the ratio between the nuclear electric quadrupole moments of the two chlorine isotopes, $R \approx Q(^{37}Cl)/Q(^{35}Cl) \approx -0.062/-0.079 = 0.788$.

The experimental transition frequencies (given as ESI[†]) have been fitted using Pickett's SPFIT program[17] within semirigid Watson's Hamiltonian (I^r representation, S-reduction).[18] The standard deviation is less than 2 kHz for both (^{35}Cl and ^{37}Cl) fits. No μ_c type transitions have been observed, in agreement with the zero or small calculated value of the corresponding dipole moment component.

Table 2 Experimental spectroscopic parameters of the two isotopologues of conformer I.

	CH_2F_2-$CH_2{}^{35}ClF$	CH_2F_2-$CH_2{}^{37}ClF$
A/MHz	4361.912(3)[a]	4295.106(4)
B/MHz	1053.0440(5)	1038.0981(5)
C/MHz	949.3755(3)	934.1084(3)
D_J/kHz	1.381(2)	1.378(4)
D_{JK}/kHz	9.30(1)	8.51(6)
D_K/kHz	16.8(6)	17.3(7)
d_1/kHz	-0.220(3)	-0.223(4)
d_2/kHz	-0.020(2)	-0.018(7)
$1.5\chi_{aa}$/MHz	52.78(1)	41.36(3)
$0.25(\chi_{bb}-\chi_{cc})$/MHz	-20.329(4)	-16.058(5)
χ_{bc}/MHz	31.6(1)	24.7(2)
χ_{ab}/MHz	11.4(9)	10(1)
χ_{ac}/MHz	-1.9[b]	-1.5[b]
N[c]	128	72
σ[d]/kHz	1.9	1.7

[a]Error in parentheses in units of the last digit. [b]Fixed at the *ab initio* value (See Table 1). [c]Number of measured hyperfine components in the fit. [d]Standard deviation of the fit

**Table 3** Effective structural parameters of conformer I of CH_2F_2-CH_2ClF

	r_0	r_e
R/Å	3.661(2)[a]	3.564
α/°	59.2(1)	58.8
β/°	82.8(1)	85.2

[a]Error in parentheses in units of the last digit
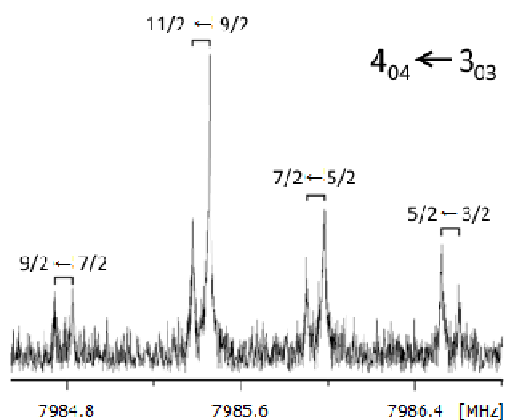
Fig.1. The $\Delta F = 1$ quadrupole hyperfine splitting components of the $4_{04} \leftarrow 3_{03}$ transition of the ^{35}Cl isotopologue, with values of F as indicated.

3.3 Structural information

In principle, structural information could be obtained from the values of the off-diagonal hyperfine coupling constants for the chlorine nucleus. However, since we had to fix the off-diagonal constant χ_{ac} to the *ab initio* value, we could not reach a good experimental value of the angular orientation of the C-Cl bond from these data. The experimental rotational constants, related to the vibrational ground state geometry (r_0), are smaller than their *ab initio* values, which refer to the hypothetical vibrationless (r_e) structure. Most of the discrepancies can be accounted for by a longer r_0 distance between the two subunits. However, since we have six available rotational constants, we could use them to perform a partial r_0-structure fit. We found, indeed, that fitting the C1C6 distance and the F3C1C6 and Cl7C6C1 angles (R, α and β of Fig. 2), we were able to reproduce the experimental rotational constants within 1 MHz.

The r_0 and r_e values of the three parameters are listed in Table 3. All the other parameters were fixed at their *ab initio* values. The effective value of R is 0.1 Å larger than the theoretical one.
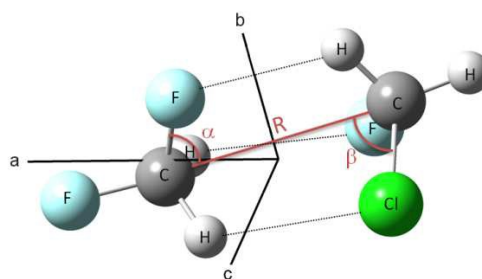
Fig. 2. Shape of conformer I. The principal axes and the fitted structural parameters are indicated.

From these data we derived the bond lengths of the three WHBs and the distance between the two carbon atoms of the two freon units. They are listed in Table 4, and there compared to the corresponding parameters of two related molecular complexes, CH_2F_2-CH_2Cl_2 and $(CH_2F_2)_2$.

Table 4 r_0 values of the three WHBs and of the C---C distance of CH_2F_2-CH_2ClF, CH_2F_2-CH_2Cl_2 and $(CH_2F_2)_2$.

	$r(F{\cdots}H)$/Å	$r(H{\cdots}Cl)$/Å	$r(C{-}{-}{-}C)$/Å	Ref.
$(CH_2F_2)_2$	2.628, 2.759	--	3.55(1)	3
CH_2F_2-CH_2ClF	2.633, 2.861	3.169	3.661	this work
CH_2F_2-CH_2Cl_2	2.489(2)	3.147(2)	3.755(1)	10

One can note that the C-C distance increases evenly in going from $(CH_2F_2)_2$, to CH_2F_2-CH_2ClF, and to CH_2F_2-CH_2Cl_2, by ~ 0.1 Å for each added Cl atom. This is in agreement with the larger atomic radius of Cl.

From the experimental constants of the two isotopologues it has been possible to calculate the r_s substitution coordinates[19] of the Cl atom. Their values (see Table 5) are very similar to the r_e and r_0 ones, confirming the conformational assignment.

Table 5 The Cl r_s-substitution coordinates are compared to the r_e and r_0 values

	r_s	r_e	r_0
a/Å	±1.870(1)[a]	-1.922	-1.898
b/Å	±0.965(2)	-0.929	-0.960
c/Å	±0.05(3)	-0.097	-0.095

[a]Error in parentheses in units of the last digit.

3.4 Dissociation energy

When the stretching motion leading to the dissociation of the complex occurs almost parallel to the *a*-axis, its force constant (k_s) can be estimated within the pseudo-diatomic approximation:[20]

$$k_s = 16\pi^4(\mu R_{CM})^2[4B^4+4C^4-(B-C)^2(B+C)^2]/(hD_J) \qquad (1)$$

where μ, R_{CM} and D_J are the reduced mass, the distance between the centres of mass estimated from r_0 structure (3.723 Å) and quartic centrifugal distortion constant D_J (reported in Table 2), respectively. The resulting value is k_s = 4.6 N·m^{-1}, corresponding to a harmonic stretching frequency of about 51 cm^{-1}. From the force constant, it is possible to evaluate the dissociation energy by assuming a Lennard-Jones potential function, according to:[21]

$$E_D = 1/72 \; k_s \, R_{CM}^2 \qquad (2)$$

We obtained E_D = 5.3 kJ·mol^{-1}, in very good agreement with the *ab initio* value. This value is in line with the dissociation energies evaluated in a similar way for $(CH_2F_2)_2$ (E_D = 6.6 kJ·mol^{-1})[3] and CH_2F_2-CH_2Cl_2 (E_D = 7.6 kJ·mol^{-1}).[10] Since Eq.s (1) and (2) contain several elements of approximation, uncertainties of up to 20% are expected for the E_D values. We can, however, state that an average interaction energy of about 2.2 kJ·mol^{-1} for each WHB comes out from these data.

4 Conclusions

This study confirms the results obtained with the rotational investigation of the CH_2F_2-CH_2Cl_2 adduct:[10] the C-H···Cl-C bridge is preferred with respect to the C-H···F-C weak hydrogen bond. In CH_2F_2-CH_2Cl_2 two isomers were calculated to be stable minima with the two subunits connected by three weak hydrogen bonds, but the one with one C-H···F-C and two C-H···Cl-C links resulted experimentally to be more stable than the one with one C-H···Cl-C and two C-H···F-C interactions.[10] In the present study, we found that isomer I, where the two subunits are linked to each other by one C-H···Cl-C and two C-H···F-C weak hydrogen bonds, rather than isomer II, with three C-H···F-C interactions, is the absolute minimum. So, in both complexes, the form with the highest possible number of C-H···Cl-C linkages, is the favorite one.

However, in the present case, also isomer III has the same set of weak hydrogen bonds of isomer I. We believe that, fluorine being more electron-withdrawing than chlorine, the hydrogens of CH_2F_2 are more suitable to act as proton donors, so favoring the formation of isomer I.

The average interaction energy of these weak hydrogen bonds is confirmed to be one order of magnitude smaller than that of classical hydrogen bonds.

We also obtained the structural parameters related to this kind of weak hydrogen bond.
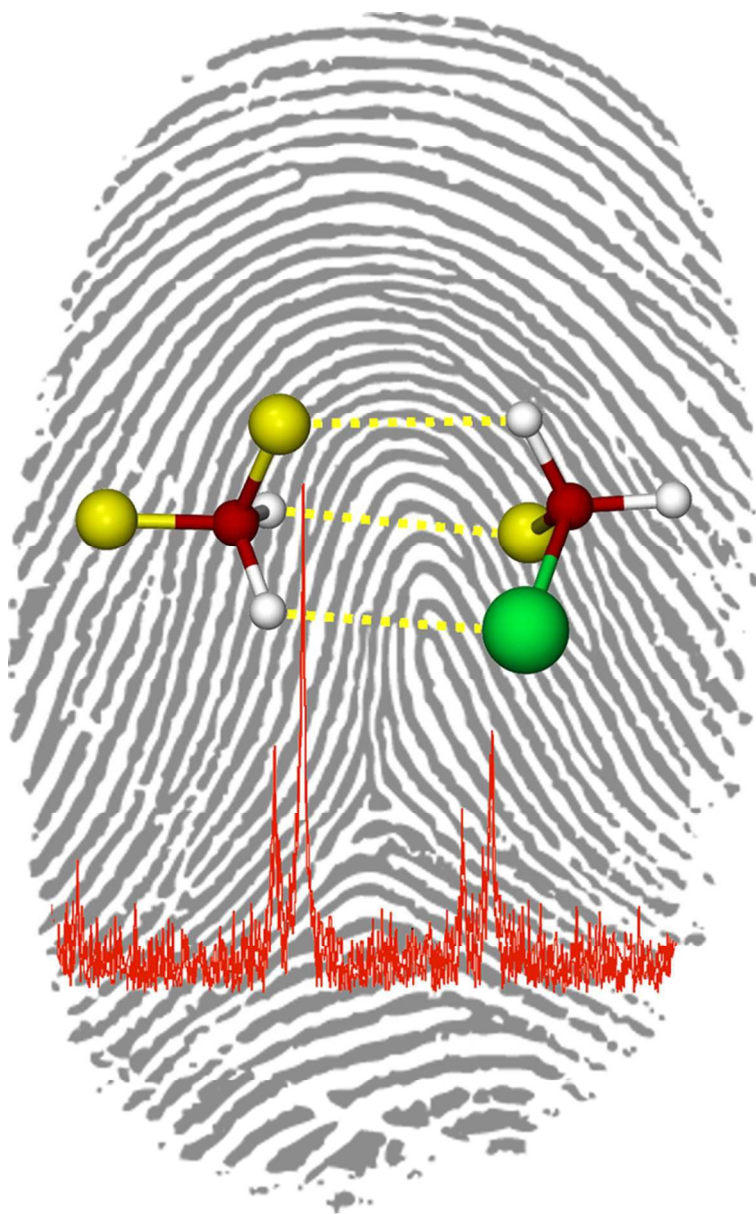
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Notes and references

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† Electronic Supplementary Information (ESI) available: [Tables of experimental transition frequencies and of the *ab initio* geometry]. See DOI: 10.1039/b000000x/

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