Non covalent interactions stabilizing the chiral dimer of CH 2 ClF: A rotational study

Non covalent interactions stabilizing the chiral dimer of CH2ClF: a rotational study.

L.B. Favero, A. Maris, S. Melandri, P. Ottaviani, W. Caminati.

Physical Chemistry Chemical Physics 21 (2019) 3695-3700.

PCCP

Cite this: *Phys. Chem. Chem. Phys.*, 2019, 21, 3695

Non covalent interactions stabilizing the chiral dimer of CH_2ClF: a rotational study†

Laura B. Favero,[a] Assimo Maris,[b] Sonia Melandri,[b] Paolo Ottaviani[b] and Walther Caminati*[b]

Received 9th October 2018,
Accepted 27th December 2018

DOI: 10.1039/c8cp06288a

rsc.li/pccp

We report the rotational spectra of three isotopologues of the dimer of chlorofluoromethane, namely $CH_2{}^{35}ClF–CH_2{}^{35}ClF$, $CH_2{}^{35}ClF–CH_2{}^{37}ClF$ and $CH_2{}^{37}ClF–CH_2{}^{35}ClF$. The assigned (most stable) conformer is chiral (C_1 symmetry) and displays a network of two C–H•••Cl–C and one C–H•••F–C weak hydrogen bonds, combined with a Cl•••F halogen bond. The hyperfine structures due to the quadrupolar effects of the two non-equivalent ^{35}Cl (or ^{37}Cl) atoms have been fully resolved, leading to an accurate determination of two sets of diagonal and of some mixed quadrupole coupling constants. Information on the rs positions of the two Cl atoms and on the structural parameters of the hydrogen bonds has been obtained. The dissociation energy of the complex has been estimated as 5.9 kJ mol^{-1}.

Introduction

According to the IUPAC definition of a hydrogen bond, a weak hydrogen bond (WHB) is still the subject of some controversies about its classification as a hydrogen bond.[1] It is, however, considered as a molecular interaction playing an important role in chemistry, and a vast literature is dedicated to this topic.[2]

WHBs such as C–H•••O, C–H•••N and C–H•••F–C play an important role in biological, atmospheric and supramolecular chemistry.[3] Studies on such WHBs have been mainly performed using X-ray diffraction[4] and IR spectroscopy in rare gas solutions.[5] This kind of experimental information on WHBs, from solid state or solution investigations, is influenced by other intermolecular interactions which take place in condensed phases. In contrast, investigations on this kind of molecular system performed with high resolution spectroscopic techniques, especially pulsed jet Fourier transform microwave (FTMW) spectroscopy, provide precise data in an environment free from the interference of solvation and crystal lattice effects.[6]

Information obtained with this technique on the C–H•••O WHB has come from the study of the dimer of dimethylether,[7] or of the adducts of some ethers, ketones or aldehydes with some hydrogenated fluoro-Freons, together with the C–H•••F linkages.[8] The C–H•••N interaction has been described in the rotational studies of the complexes of pyridine with mono-, di- and tri-fluoromethane.[9]

Halogenated hydrocarbons have sites which can act as weak proton donors or weak proton acceptors, leading to easy formation of their oligomers or hetero adducts, with the subunits held together by a network of WHBs. The aliphatic hydrogen atoms have, indeed, been found to act as proton donors, thanks to the electron withdrawing effect of the halogen atoms. Difluoromethane (CH_2F_2) can be regarded as the prototype for this kind of ambivalent molecule. Its oligomers, $(CH_2F_2)_n$, with n = 2–4, have been recently characterized by FTMW. The rotational investigations of the dimer,[10] trimer[11] and tetramer[12] of CH_2F_2 pointed out the existence of 3, 9, and 16 C–H•••F–C WHBs, respectively. In the hetero adduct $CH_3F–CHF_3$, the two subunits are linked together by three weak C–H•••F–C WHBs, while the two subunits rotate through low V_3 barriers around their symmetry axes.[13]

Only a few adducts between Freon molecules containing halogen atoms other than fluorine have been investigated by rotational spectroscopy, $CH_2ClF•••FHC{=}CH_2$ and $CH_2ClF•••CH_2F_2$, which presents a combination of C–H•••F–C and C–H•••Cl–C WHBs,[14] and CH_2F_2 with CH_2Cl_2, characterized by two equivalent C–H•••Cl–C and one C–H•••F–C WHBs.[15] No complexes between Freons with two different heavy halogen atoms (Cl, Br, and I) have been investigated. This is because, unlike the F atom, for which the nuclear spin quantum number is I = 1/2, the other halogens have I = 3/2 or 5/2 and this results in very complicated quadrupole hyperfine structures of the rotational spectra of the halogenated multi-molecular systems. The analysis of the spectrum and the achievement of a correct fit are quite challenging when the two heavy halogen atoms in the complex are not equivalent to each other. From a spectroscopic point of view, the interpretation of the

[a] *Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), Sezione di Bologna CNR, via Gobetti 101, I-40129 Bologna, Italy*
[b] *Dipartimento di Chimica "G. Ciamician" dell'Università, Via Selmi 2, I-40126 Bologna, Italy. E-mail: walther.caminati@unibo.it*

†Electronic supplementary informati (ESI) available: Completion of ref. 20 and tables listing transition frequen es and *ab initio* geometries. See DOI: 10.1039/c8cp06288a

rotational spectrum of a system with multiple quadrupolar nuclei can be a very challenging task. For example, the rotational spectra of even simple molecules with two heavy halogen atoms have been reported only in a limited number of cases. Herein, we investigate the rotational spectrum of the dimer of CH_2ClF (Freon 31), $(CH_2ClF)_2$, with the aim of determining the orientation of the subunits in the complex and ascertaining which non-covalent interactions are more favorable.

Experimental section

Molecular clusters were generated under supersonic expansion, under conditions optimized for the formation of adducts. Details of a Fourier transform microwave spectrometer[16] (COBRA-type[17]), which covers the range of 6.5–18 GHz, have been described previously.[18]

A gas mixture of *ca.* 1% of CH_2ClF (commercial samples used without any further purification) in He at a stagnation pressure of 0.5 MPa was expanded through a solenoid valve (General Valve, Series 9, nozzle diameter 0.5 mm) into the Fabry–Pérot cavity. The spectral line positions were determined after Fourier transformation of the time-domain signal with 8k data points, recorded with 100 ns sample intervals. Each rotational transition appears as doublets due to the Doppler Effect. The line position is calculated as the arithmetic mean of the frequencies of the Doppler components. The estimated accuracy of the frequency measurements is better than 3 kHz. Lines separated by more than 7 kHz are resolvable.

Theoretical calculation

Two conformers (I and II), both stabilized by three WHBs, are, by chemical intuition and analogous to similar observed complexes, expected to be the most stable forms of the title complex. Their cage-like structures are shown in Table 1, together with the corresponding calculated spectroscopic parameters, useful for the investigation of the microwave spectrum. The corresponding geometries were optimized both at the MP2/6-311++G(d,p) and MP2/aug-cc-pVTZ levels of calculation,

Table 1 Theoretical shapes and spectroscopic parameters of the two most stable conformers of $(CH_2ClF)_2$: (a) MP2/aug-cc-pVTZ, (b) MP2(BSSE)/ aug-cc-pVTZ, (c) MP2/6-311++G(d,p), (d) MP2(BSSE)/6-311++G(d,p)

	I (a)	I (b)	I (c)	I (d)	II (a)	II (b)	II (c)	II (d)
Rotational constants/MHz								
A	2992	3019	3040	3096	4116	4076	4360	4292
B	918	885	885	781	765	748	751	672
C	893	868	856	773	713	691	699	631
First order centrifugal distortion constants/kHz								
D_J	0.80	0.86	1.04	1.41	0.48	0.81	0.58	0.88
D_{JK}	2.74	2.88	2.62	0.77	3.27–3.03		2.07–2.32	
D_K	1.21	1.86	3.82	12.8	16.0	57.5	25.1	85.8
d_1	0.00–0.01	0.02–0.03	0.03–0.13	0.05–0.12				
d_2	−0.04–0.04–0.05		0.00		0.00–0.01		0.00–0.05	
Electric dipole moment components/D								
m_a	−2.2–2.3	2.6–2.5	1.9–1.8	1.7–1.6	–			
m_b	−1.2–1.1	−1.3–1.1	−0.1	0.9			0.0	0.7
m_c	0.4	0.3	0.5	0.7	0.3	0.0	0.1	0.1
Quadrupole coupling constants of the L[a] chlorine atom/MHz								
w_{aa}	33.3	33.4	33.4	30.9	33.6	34.0	34.5	33.9
$w_{bb} - w_{cc}$	−71.0–71.7	58.4–60.7	72.3–83.6	−72.2	–	−80.1		
w_{ab}	5.2	5.2	9.4	1.7–4.9	2.1–8.9	−13.2		
w_{ac}	−5.6	−5.5	−8.7	−1.1	1.3		2.7–0.1	−1.1
w_{bc}	32.6	32.2	40.4	41.9–31.7	24.2–34.2	−28.8		
Quadrupole coupling constants of the R[a] chlorine atom/MHz								
w_{aa}	29.6	29.5	31.4	32.8	−63.3	−57.2	−66.5	−63.3
$w_{bb} - w_{cc}$	13.1	15.7	−7.5	0.0	3.8	−1.7	4.2	1.9
w_{ab}	−2.7	−3.2	−1.3	−8.6	−13.5	27.8	−13.0	22.1
w_{ac}	0.4	−0.6	1.8	13.3	7.2	−3.1	−0.5	−2.2
w_{bc}	−49.2	−49.1	−51.2	−49.4	−1.1	0.6–1.7	0.3	
Equilibrium and zero point relative energies and dissociation energies/kJ mol^{-1}								
ΔE_e	0[b]	0[c]	0.70	0.72	1.12	0.97	0[d]	0[e]
ΔE_0	0[f]	0[g]	0.47	0.60	1.14	1.01	0[h]	0[i]
D_e	17.0	14.0	17.0	8.7	16.3	13.0	17.7	9.4
D_0	15.0	11.8	14.6	6.9	13.8	10.8	15.0	7.5

[a] L and R indicate the chlorine atom in the left or right part of the complex, as it appears in the drawings at the top of the table. [b] Absolute energy: −1197.333373 E_h. [c] Absolute energy: −1197.332076 E_h. [d] Absolute energy: −1197.014584 E_h. [e] Absolute energy: −1197.011692 E_h. [f] Absolute energy: −1197.269344 E_h. [g] Absolute energy: −1197.268141 E_h. [h] Absolute energy: −1196.950212 E_h. [i] Absolute energy: −1196.947343 E_h.

and the subsequent evaluation of the Hessian matrix confirmed that the found stationary points are minima.

In order to account for basis set superposition effects (BSSE), the same kind of computation was also performed using the counterpoise correction procedure.[19] All calculations were performed by using the Gaussian09 suite of programs.[20]

The two isomers are very close in energy, but the MP2/ aug-cc-pVTZ method indicates isomer I to be more stable (0.7 kJ mol^{-1}), while the opposite is obtained with MP2/ 6-311++G(d,p) calculations (−1 kJ mol^{-1}).

Considering the conformational space of $(CH_2ClF)_2$, besides the structures stabilized by three WHBs, additional structures stabilized by two halogen–hydrogen intermolecular bonds can be hypothesized. Seven non-equivalent arrangements are possible, as shown in Fig. 1. Their characterization was attempted by free geometry optimization. All runs converged to isomerIorII, suggesting that structures stabilized by two WHBs either lie on very shallow minima or are not minima at all. It can also be hypothesized that these forms are transition states or intermediate forms in the pathway connecting conformersIandII, but unfortunately, our attempts to characterize such a kind of pathway, looking for the corresponding transition states, were unsuccessful.

Rotational spectra

The presence of several abundant isotopologues ($^{35}Cl/^{35}Cl$, $^{35}Cl/^{37}Cl$, $^{37}Cl/^{35}Cl$, and $^{37}Cl/^{37}Cl$, ratio 9/3/3/1) and of the two non-equivalent quadrupolar nuclei (^{35}Cl and ^{37}Cl) with a nuclear spin I= 3/2 and a relatively large nuclear electric quadrupole moment (Q) makes the spectrum quite dense and complicates the assignment.

The two isomers have very similar energies, and for both the m_a dipole moment component is calculated to be the largest one. For this reason we scanned frequency regions where m_a R-type bands of both conformers were expected to fall. We could easily observe one set of this kind of band, identifying at the beginning the intense K= 0, 1 transitions of the parent species. Each of them was split into several quadrupole component lines, as illustrated in Fig. 2 for the $9_{18} \leftarrow 8_{17}$ transition.

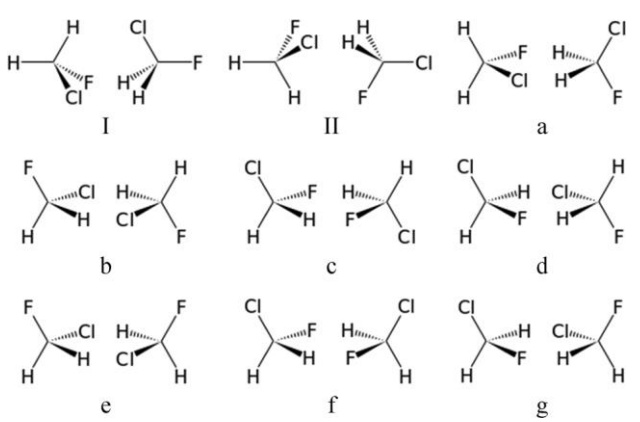

Fig. 1Sketches of the possible geometries of $(CH_2ClF)_2$ with two or three intermolecular contact points.

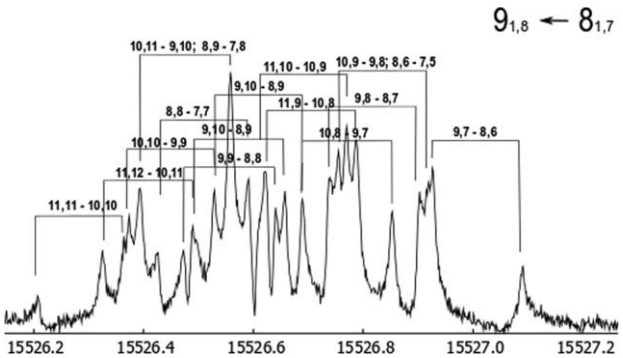

Fig. 2Recorded $9_{1,8} \leftarrow 8_{1,7}$ transition of the observed conformer of $(CH_2ClF)_2$, showing the hyperfine structure due to the quadrupolar effects of the two — nonequivalent — ^{35}Cl nuclei. Each line exhibits the Doppler doubling and is labeled as $F_1^{00}F^{00} \leftarrow F_1^{0}F^{0}$, where $F_1 = J + I_1$, $F = F_1 + I_2$ and I_1 and I_2 are the quantum numbers of the two nuclear spins. F_1 and F are half-integer values, but rounded to the upper integer in the figure.

After the first assignments, many additional m_a-type transitions, with J_{upper} and K_a up to 10 and 3, respectively, have been measured. Then, some hundred MHz below each transition of the parent species, two weaker transitions were observed, belonging to the $^{35}Cl/^{37}Cl$ and $^{37}Cl/^{35}Cl$ isotopically mixed isotopologues.

The intensities of these transitions were about 1/3 of those of the parent species, in consistency with the natural relative abundance of the two Cl isotopes and the existence of two non equivalent $^{35}Cl/^{37}Cl$ isotopologues.

All measured line frequencies were fitted with Pickett's SPFIT program[21] by direct diagonalization of the Hamiltonian consisting of Watson's ''S'' reduced semirigid-rotor Hamiltonian[22] in the I^r representation, implemented by the hyperfine Hamiltonian:

$$H = H_R + H_{CD} + H_Q \quad (1)$$

H_R represents the rigid-rotor Hamiltonian and the centrifugal distortion contributions are represented by H_{CD}, while H_Q is the operator associated with the quadrupolar interaction of the ^{35}Cl (or ^{37}Cl) nuclei with the overall rotation. The coupling scheme $F_1 = J + I(Cl_1)$, $F = F_1 + I(Cl_2)$ has been adopted. The obtained spectroscopic constants are reported in Table 2.

The two mixed isotopologues $^{35}Cl/^{37}Cl$ are distinguished from each other by the labels (L) and (R), which indicate the chlorine atom in the left (L) or right (R) part of the complex, as it appears in the drawings reported in Table 1.

We did not succeed in measuring the transitions of the $^{37}Cl/^{37}Cl$ isotopologue since its abundance is only ≈10% of that of the parent species.

The comparison of the experimental spectroscopic parameters with the theoretical values for the two conformations of Tables 1 and 2 leads to a straightforward assignment of the observed spectrum to conformer I, the one stabilized by two C–H• • •Cl–C and one C–H• ••F–C WHBs.

We could not observe lines belonging to conformer II, despite the very small complexation energy difference. This could be due to the conformational relaxation to the most stable conformer upon supersonic expansion. It has, indeed,

Table 2 Experimental rotational parameters of the observed isomer of $(CH_2ClF)_2$

	$^{35}Cl/^{35}Cl$	$^{35}Cl(L)/^{37}Cl(R)$	$^{37}Cl(L)/^{35}Cl(R)$
A/MHz	3014.53(2)[a]	2971.419(1)	2981.2(1)
B/MHz	867.7519(1)	859.3929(1)	854.4724(2)
C/MHz	848.5595(2)	840.3234(2)	834.4918(2)
D_J/kHz[b]	0.8967(4)	0.8885(4)	0.8864(4)
D_{JK}/kHz	4.68(2)	4.61(3)	4.42(3)
d_1/Hz	−0.0154(5)	−0.0063(5)	−0.0191(6)
d_2/Hz	−0.0447(5)	−0.042(1)	−0.041(2)
w_{aa}(L)/MHz	35.85(2)	35.83(2)	28.16(3)
w_{bb} + w_{cc}(L)/MHz	77.29(6)	63.23(5)	66.95(8)
w_{bc}(L)[c]/MHz	34.28(6)	40.85(2)	23.1(1)
w_{aa}(R)/MHz	31.64(2)	24.93(1)	31.66(3)
w_{bb} − w_{cc}(R)/MHz	2.82(8)	−13.25(6)	15.19(8)
w_{bc}(R)[c]/MHz	−52.71(6)	−41.07(2)	−52.2(1)
s[d]/kHz	3	3	3
N[e]	333	268	266

[a] Error in parentheses in units of the last digit. [b] D_K is not determined by the fit. [c] The non diagonal quadrupole coupling constants w_{ab} and w_{ac} are not determined by the fit. [d] RMS error of the fit. [e] Number of component lines in the fit.

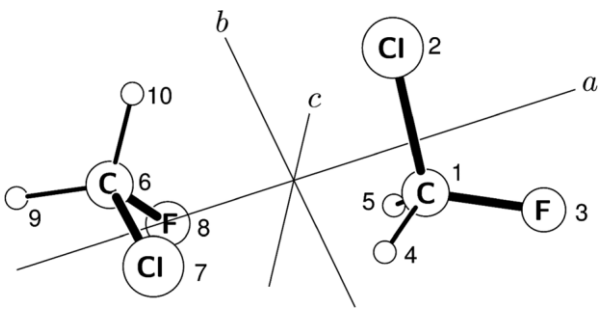

Fig. 3 Sketch, atom numbering, and principal axes of the observed conformer of $(CH_2ClF)_2$.

been shown that this kind of relaxation takes place easily when the interconversion barrier is smaller than $2kT$.[23]

Structural information

The C_1 configuration of the observed conformer of $(CH_2ClF)_2$ is shown in Fig. 3.

In Tables 1 and 3, Cl7 and Cl2 have been labeled as Cl(L) and Cl(R), respectively.

From the rotational constants of the two isotopologues, it is possible to calculate the substitution, r_s, coordinates[24] of the

Table 3 Substitution (r_s), r_0 and *ab initio* (r_e, MP2-(BSSE)/aug-cc-pVTZ) coordinates of the chlorine atoms in the observed isomer of $(CH_2ClF)_2$

		a/Å	b/Å	c/Å
Cl(L)	r_0	−2.097(5)[a]	0.852(9)	−0.50(1)
	r_s	±2.087(1)	±0.846(2)	±0.502(3)
	r_e	−2.171	0.760	−0.558
Cl(R)	r_0	1.524(6)	−0.77(1)	−0.822(8)
	r_s	±1.514(1)	±0.782(2)	±0.798(2)
	r_e	1.530	−0.871	−0.713

[a] Error in parentheses is in units of the last digits.

Table 4 Partial r_0 and r_e (MP2(BSSE)/aug-cc-pVTZ) structures of the observed isomer of $(CH_2ClF)_2$

	r_0	r_e
Fitted parameters		
R_{Cl_1H}/Å	3.014(8)[a]	3.003
$Cl_7H_4C_1$/°	131.2(2)	130.7
Cl_7H_4–C_1F_3/°	166.9(8)	164.6
$C_6Cl_7H_4$/°	87.4(6)	85.0
F_8C_6–Cl_7H_4/°	36(2)	42
Derived parameters		
$R_{F_8H_5}$/Å	2.713(8)	2.712
$R_{Cl_2H_{10}}$/Å	3.216(8)	2.963

[a] Uncertainties (in parentheses) are expressed in units of the last digit.

two Cl atoms in the principal axes of the parent species. A partial r_0 structure was obtained by adjusting five structural parameters, while keeping the remaining parameters fixed to their *ab initio* values, in order to reproduce the nine experimental rotational constants. The obtained parameters are reported in Table 4 and compared to the *ab initio* values.

From this partial r_0 structure, the lengths of the three WHBs have been derived and reported in Table 4. The full *ab initio* geometry is available in the ESI.†

Dissociation energy

Within the pseudo-diatomic approximation, the dissociation energy of the molecular adduct can be evaluated from the estimation of the force constant (k_s) relative to the stretching motion connecting the centres of mass of the two subunits, if such motion takes place almost parallel to the a-axis, so that:[25]

$$k_s = 16\pi^4(mR_{CM})^2[4B^4 + 4C^4 - (B-C)^2(B+C)^2]/(hD_J), \quad (2)$$

where m is the pseudo-diatomic reduced mass and R_{CM} (=3.74 Å) is the distance between the centres of mass of the two subunits. B, C and D_J are the experimental spectroscopic constants reported in Table 2. We obtained the value k_s = 5.1 N m^{-1}, for which the corresponding stretching frequency, in the harmonic approximation, is 50 cm^{-1}.

Assuming a Lennard-Jones type potential the dissociation energy (E_D) can be estimated as:[26]

$$E_D = 1/72\, k_s R_{CM}^2 \quad (3)$$

Table 5 Theoretical bond energy values (QTAIM) and intermolecular distances (MP2-(BSSE)/aug-cc-pVTZ) in $(CH_2ClF)_2$. L and R indicate the atoms in the left or right part of the complexes, as it appears in the drawings at the top of Table 1

Rotamer	L•••R	E_{bond}/kJ mol^{-1}	d/Å
I	Cl•••H	3.6	3.00
I	H•••Cl	4.5	2.96
I	F•••H	5.2	2.71
I	F•••Cl	3.8	3.49
II	Cl•••H	3.2	3.06
II	H•••F	7.0	2.52
II	F•••H	4.9	2.82
II	Cl•••F	—	3.58

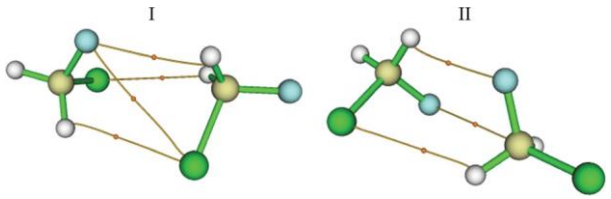

Fig. 4Non covalent interactions in the two more stable isomers of $(CH_2ClF)_2$, according to the QTAIM theory.

We have estimated E_D = 5.9 kJ mol^{-1}, which is similar to the values obtained for CH_2ClF•••CH_2F_2 (E_D = 5.3 kJ mol^{-1}),[14] $(CH_2F_2)_2$ (E_D =6.6 kJ mol^{-1})[10] and CH_2Cl_2•••CH_2F_2 (E_D = 7.6 kJ mol^{-1})[15] within the uncertainty of 20% that is expected for the E_D values. So, this value is comparable with the results of the MP2(BSSE)/6-311++G(d,p) method (see Table 1).

Atoms in molecule analysis

After the assignment of the spectrum, we believed the presence of two C–H•••Cl–C and one C–H•••F–C WHBs in the observed isomer to be indicative of a higher strength of the former one. However, following the suggestions of one referee, we applied to our system the quantum theory of atoms in molecules (QTAIM),[27] obtaining interesting results. This theory allows correlation of the topological properties of electron density function, $\rho(r)$, with elements of molecular structures: the localization of maxima $\rho(r)$ values enables the identification of atomic positions, whereas chemical bonds are defined as saddle points between the maxima. These saddle points, called Bond Critical Points (BCP), represent the minimum along the bonding direction and the maximum in all others.

Since both covalent and non-covalent bonds can be identified, using the Multiwfn software,[28] we applied QTAIM to the *ab initio* $\rho(r)$ values achieved at the MP2(BSSE)/aug-cc-pVTZ level of calculation, for both rotamers. With regard to rotamer I, four BCPs were obtained: one for each of the hydrogen–halogen interactions and one between the fluorine and chlorine atoms. Three BCPs were found for rotamer II, corresponding to two hydrogen–halogen interactions and a carbon–fluorine interaction. All these are shown graphically in Fig. 4.

A rough estimation of the bond energy E_{bond} is given by one half of the potential energy density $V(r)$ at the corresponding BCP: $E_{bond} = 1/2\,V(r_{BCP})$.[29] The values achieved for rotamers I and II are reported in Table 5 with the theoretical bond distances. The Cl•••H bonds appear weaker than the F•••H ones, thus rotamer II should be more stable than rotamer I, but the presence of an additional halogen–halogen interaction stabilizes rotamer I more than rotamer II.

In our previous investigations of dimers of Freons, we noted that the strength of halogen bonds was overwhelming compared to that of WHBs when one of the constituting Freons was fully halogenated. This happens in $CClF_3$•••CH_3F, where the linking interaction is a Cl•••F halogen bond.[30] However, it seems that the QTAIM method can point out when halogen bonds begin to contribute to the stability of a Freon dimer upon increasing the halogenation degree of the constituting Freons.

Conclusions

The microwave spectrum of $(CH_2ClF)_2$ represents an unprecedented investigation of an intermolecular complex with two non equivalent Cl atoms by rotational spectroscopy. This cluster consists, indeed, of the combination of two molecules of the same monomer, the different orientations of which make the two – heavy quadrupolar nuclei (^{35}Cl and ^{37}Cl, with high nuclear spin quantum numbers and large electric nuclear quadrupole moments) – non equivalent to each other. The consequent complex hyperfine structure of each transition has been successfully analyzed and interpreted in terms of ten quadrupole coupling parameters.

The complex does not have any element of molecular symmetry, thus it is a chiral species. Although one should expect the same concentration for the two enantiomers, it could be interesting to measure experimentally their relative concentration, since the formation of the complex upon supersonic expansion is a complicated process, and it could favor the formation of an even slightly more stable form. A considerable increase of the population of slightly more stable isotopologues of molecular complexes upon supersonic expansion has been often observed, for example in molecular complexes involving neon. In the case of the trimer pyridine–Ne_2, it turns out that under the jet conditions the ground-state population of the Py–^{22}Ne^{22}Ne isotopologue increases by a factor of $\cong$20 with respect to that of the normal (Py–^{20}Ne^{20}Ne) species.[31] In this example, the mass increase for the heavier isotopologue results in a lower zero-point energy. Then, the enrichment of slightly more stable species can be explained by the thermal quasi-equilibrium reached as a result of repeated dissociation and re-formation of adducts in the low-temperature molecular expansion.

The detection of conformer I, where the two subunits are linked to each other by two C–H•••Cl–C and one C–H•••F–C WHBs, rather than conformer II, with two C–H•••F–C and one C–H•••Cl–C interactions, suggests that C–H•••Cl–C is a linkage slightly stronger than C–H•••F–C for the investigated dimer. This confirms what was already determined in the case of CH_2Cl_2•••CH_2F_2,[15] but not for the adduct 1-chloro-1-fluoroethylene-acetylene.[32] The effects of C–X•••H bond angles or C–X bond lengths, which differ in the various adducts, could play a role in this preference. Moreover we found that besides hydrogen–halogen interactions, also halogen–halogen stabilizing interactions have to be considered to explain these apparently conflicting results. Indeed, a Cl•••F contact can take place both in CH_2Cl_2•••CH_2F_2 and CH_2FCl•••CH_2FCl species, whereas it is not feasible in $CHFClCH_2$•••HCCH.

With a pseudo diatomic approximation, which considers the two subunits to be rigid in the angular coordinates, the dissociation energy of this complex has been estimated, E_D = 5.9 kJ mol^{-1}. This value is similar to those obtained with the same method for a similar dimer involving Freons. It is not very different from the lowest theoretical value of Table 1 (6.9 kJ mol^{-1}, MP2(BSSE)/6-311++G(d,p)).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We gratefully acknowledge the financial support of the Italian MIUR (PRIN, project 2010ERFKXL_001) and the University of Bologna (RFO).

Notes and references

1 E. Arunan, G. R. Desiraju, R. A. Klein, J. Sadlej, S. Scheiner, I. Alkorta, D. C. Clary, R. H. Crabtree, J. J. Dannenberg, P. Hobza1, H. G. Kjaergaard, A. C. Legon, B. Mennucci and D. J. Nesbitt, *Pure Appl. Chem.*, 2011,8, 1619.

2 See for example: W. Caminati and J.-U. Grabow, Advance- ments in Microwave Spectroscopy, in *Frontiers and Advances in Molecular Spectroscopy*, ed. J. Laane, Elsevier, Amsterdam, 2018, ch. 17, pp. 569–598.

3 See, for example, (*a*) J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1988,27, 89; (*b*) J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990,29, 1304.

4 See, for example, T. Steiner, *Angew. Chem., Int. Ed.*, 2002,41, 48–76.

5 See, for example, S. N. Delanoye, W. A. Herrebout and B. J. Van der Veken, *J. Am. Chem. Soc.*, 2002,124, 11854.

6 See, for example, W. Caminati and J.-U. Grabow, Microwave spectroscopy: Molecular systems, in *Frontiers of molecular spectroscopy*, ed. J. Laane, Elsevier, *Amsterdam*, 2008, ch. 15, pp. 455–552.

7 Y. Tatamitani, B. Liu, J. Shimada, T. Ogata, P. Ottaviani, A. Maris, W. Caminati and J. L. Alonso, *J. Am. Chem. Soc.*, 2002,124, 2739.

8 See for example: (*a*) J. L. Alonso, S. Antolínez, S. Blanco, A. Lesarri, J. C. López and W. Caminati, *J. Am. Chem. Soc.*, 2004,126, 3244; (*b*) Q. Gou, G. Feng, L. Evangelisti, M. Vallejo López, A. Lesarri, E. J. Cocinero and W. Caminati, *Phys. Chem. Chem. Phys.*, 2013,15, 6714; (*c*) S. Blanco, J. C. López, A. Lesarri, W. Caminati and J. L. Alonso, *ChemPhysChem*, 2004,5, 1779; (*d*) L. B. Favero, B. M. Giuliano, S. Melandri, A. Maris, P. Ottaviani, B. Velino and W. Caminati, *J. Phys. Chem. A*, 2005,109, 7402; (*e*) P. Ottaviani, W. Caminati, L. B. Favero, S. Blanco, J. C. López and J. L. Alonso, *Chem. – Eur. J.*, 2006,12, 915.

9 (*a*) L. B. Favero, B. M. Giuliano, A. Maris, S. Melandri, P. Ottaviani, B. Velino and W. Caminati, *Chem. – Eur. J.*, 2010,16, 1761; (*b*) M. Vallejo-Lo´pez, L. Spada, Q. Gou, A. Lesarri, E. J. Cocinero and W. Caminati, *Chem. Phys. Lett.*, 2014,591, 216; (*c*) L. Spada, Q. Gou, M. Vallejo-Lo´pez, A. Lesarri, E. J. Cocinero and W. Caminati, *Phys. Chem. Chem. Phys.*, 2014,16, 2149.

10 (*a*) W. Caminati, S. Melandri, P. Moreschini and P. G. Favero, *Angew. Chem., Int. Ed.*, 1999,38, 2924; (*b*) S. Blanco, J. C. López, A. Lesarri and J. L. Alonso, *J. Mol. Struct.*, 2002, 612, 255.

11 S. Blanco, S. Melandri, P. Ottaviani and W. Caminati, *J. Am. Chem. Soc.*, 2007,129, 2700.

12 G. Feng, L. Evangelisti, I. Cacelli, L. Carbonaro, G. Prampolini and W. Caminati, *Chem. Commun.*, 2014,50, 171.

13 W. Caminati, J. C. López, J. L. Alonso and J.-U. Grabow, *Angew. Chem., Int. Ed.*, 2005,44, 3840.

14 (*a*) C. L. Christenholz, D. A. Obenchain, S. A. Peebles and R. A. Peebles, *J. Mol. Spectrosc.*, 2012,280, 61; (*b*) L. Spada, Q. Gou, S. Tang and W. Caminati, *New J. Chem.*, 2015,39, 2296.

15 Q. Gou, L. Spada, M. Vallejo-López, Z. Kisiel and W. Caminati, *Chem. – Asian J.*, 2014,9, 1032.

16 T. J. Balle and W. H. Flygare, *Rev. Sci. Instrum.*, 1981,52, 33.

17 J.-U. Grabow, W. Stahl and H. Dreizler, *Rev. Sci. Instrum.*, 1996,67, 4072.

18 W. Caminati, A. Millemaggi, J. L. Alonso, A. Lesarri, J. C. Lopez and S. Mata, *Chem. Phys. Lett.*, 2004,392, 1.

19 S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970,19, 553.

20 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci and G. A. Petersson, *et al.*, *Gaussian09 Revision D.01*, Gaussian Inc., Wallingford, CT, 2013.

21 H. M. Pickett, *J. Mol. Spectrosc.*, 1991,148, 371.

22 J. K. G. Watson, in *Vibrational Spectra and structure*, ed. J. R. Durig, Elsevier, New York/Amsterdam, 1977, vol. 6, pp. 1–89.

23 See for example: R. S. Ruoff, T. D. Klots, T. Emilson and H. S. Gutowski, *J. Chem. Phys.*, 1990,93, 3142.

24 J. Kraichman, *Am. J. Phys.*, 1953,21, 17–25.

25 D. J. Millen, *Can. J. Chem.*, 1985,63, 1477.

26 S. E. Novick, S. J. Harris, K. C. Janda and W. Klemperer, *Can. J. Phys.*, 1975,53, 2007.

27 R. F. W. Bader, *Atoms in Molecules: a Quantum Theory*, Clarendon Press, Oxford, 1990.

28 T. Lu and F. Chen, *Comput. Chem.*, 2012,33, 580–592.

29 E. Espinosa, E. Molins and C. Lecomte, *Chem. Phys. Lett.*, 1998,285, 170–173.

30 Q. Gou, L. Spada, E. J. Cocinero and W. Caminati, *J. Phys. Chem. Lett.*, 2014,5, 1591–1595.

31 L. Evangelisti, L. B. Favero, B. M. Giuliano, S. Tang, S. Melandri and W. Caminati, *J. Phys. Chem. A*, 2009,113, 14227.

32 H. O. Leung, M. D. Marshall and D. D. Grimes, *J. Chem. Phys.*, 2011,134, 034303.

