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PAPER

On the weak O–H···halogen hydrogen bond: a rotational study of CH₃CHClF···H₂O[†]

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We measured the molecular beam Fourier transform microwave spectra of six isotopologues of the 1:1 adduct of CH₃CHClF with water. Water prefers to form an O–H···F rather than an O–H···Cl hydrogen bond. This is just the contrary of what was observed in the chlorofluoromethane–water adduct, where an O–H···Cl link was formed (W. Caminati, S. Melandri, A. Maris and P. Ottaviani, *Angew. Chem., Int. Ed.*, 2006, **45**, 2438). The water molecule is linked with an O–H···F bridge to the fluorine atom, with $r(\text{F}\cdots\text{H}_w) = 2.14 \text{ \AA}$, and with two C–H···O contacts to the alkyl hydrogens with $r(\text{C}_1\text{--H}_1\cdots\text{O}_w) = 2.75 \text{ \AA}$ and $r(\text{C}_2\text{--H}_2\cdots\text{O}_w) = 2.84 \text{ \AA}$, respectively. Besides the rotational constants, the quadrupole coupling constants of the chlorine atom have been determined. In addition, information on the internal dynamics has been obtained.

Introduction

Intra or intermolecular linkages or contacts such as C–H···O, C–H···F, C–H···S, C–H···π are generally classified as weak hydrogen bonds (WHB) and represent a major topic in hydrogen-bond research.¹ While “classical” hydrogen bonds like O–H···O, O–H···N, O–H···S, and N–H···O are characterized (for neutral species) by interaction energies in the range 15–25 kJ mol^{−1}, the WHB interactions lie within a few kJ mol^{−1} and approach those of van der Waals forces. However, they have the same directional properties and electron density transfer similar to those of “classical” hydrogen bonds.² A recent IUPAC meeting promotes a redefinition of “hydrogen bonding”,³ and it has been even suggested to consider these interactions as only being contacts, reflecting the fact that hydrogen atoms are generally in the external part of a molecular system.

Studies on such WHB have been mainly performed by X-ray diffraction⁴ and IR spectroscopy in rare gas solutions.⁵ Also rotational spectroscopy combined with supersonic

expansions has been recently applied in order to study structural and energetic features of these weak interactions. The gas-phase investigations are free from solvent or crystal effects and can give more details on specific or local WHB interactions.⁶ C–H···F,⁷ C–H···O,⁸ C–H···S,⁹ C–H···π,¹⁰ and C–H···N¹¹ linkages have been recently structurally and energetically characterized with this technique.

Here we present a rotational study of another kind of WHB, the O–H···Hal interaction (Hal = halogen). With reference to MW investigations, if we take into account a series of 1,3 substituted propanes, we can see that the rotational spectrum of 1,3-propanediol is formed by the signatures of five conformers, all of them being stabilized by O–H···O H-bonds,¹² while in 3-fluoro-propan-1-ol, two conformers do not have any internal H-bond, and just one, the second in order of stability, is characterized by an internal O–H···F H-bond.¹³ In the case of 3-chloro-propan-1-ol, two conformers have been observed, both without an internal H-bond.¹⁴ All these data suggest O–H···Hal (Hal = F, Cl) to be a weak interaction. This is confirmed by the investigations of adducts of water with freons. While in CH₂F₂–H₂O the two constituent molecules are held together by a weak (bonding energy, $E_B = 7.5 \text{ kJ mol}^{-1}$) O–H···F bond,¹⁵ in CF₄–H₂O a halogen bond F···O is observed.¹⁶

Naturally the interesting question arises: which of the O–H···Hal WHB is stronger? For example, what are the key interactions that make the O–H···Cl linkage stronger or weaker than the O–H···F one? A few years ago, following the MW study of the CH₂ClF–H₂O complex, where only the form with an O–H···Cl interaction was observed ($E_B = 8.5 \text{ kJ mol}^{-1}$), we suggested this one to be stronger.¹⁷

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[†] Electronic supplementary information (ESI) available: Table of MP2/6-311++G** principal axes coordinates of the three conformers of CFE–W. Table of transitions of all the observed isotopomers. See DOI: 10.1039/c1cp20751b

1-Chloro-1-fluoroethane (Freon 151, from now CFE), has a structure similar as chlorofluoromethane, but with a hydrogen atom substituted by a methyl group. The microwave spectrum of CFE has been first studied by Thomas *et al.*¹⁸ with a conventional Stark modulation spectroscopy and by Hinze *et al.*¹⁹ with Fourier transform microwave spectroscopy, but this kind of information for the complex of CFE with water is not reported. The information of intermolecular interaction between CFE and water will be helpful in understanding the behavior of CFE in atmosphere. Moreover, experimental results can prove which kind of interaction is preferred in the complex. Based on these reasons, we studied the rotational spectra of several isotopologues of the complex of CFE with water (CFE-W) by pulsed jet molecular-beam Fourier transform microwave spectroscopy. The obtained results are described below.

Experimental section

Commercial samples of CFE, deuterated water (98% enriched, Aldrich), and oxygen 18 water (98% enriched, CIL) were used without further purification. The rotational spectra in the 6–18.5 GHz frequency region were measured on a COBRA-type²⁰ pulsed supersonic-jet Fourier-transform microwave (FTMW) spectrometer, described elsewhere,²¹ now operated with the FTMW++ set of programs.²²

A gas mixture of 2% CFE in Helium at a total pressure of 3 bar was streamed over water at room temperature, and expanded through the solenoid valve (General Valve, Series 9, nozzle diameter 0.5 mm) into the Fabry–Pérot-type cavity. Each rotational transition displays a Doppler splitting that originates from the supersonic jet expanding coaxially along the resonator axes. The rest frequency was calculated as the arithmetic mean of the frequencies of the two Doppler components. The estimated accuracy of the frequency measurements is better than 3 kHz, resolution is better than 7 kHz.

Theoretical calculations

Before collecting the rotational spectra, full geometry optimization of the complexes were performed at the MP2/6-311++G** level theory with Gaussian 03 program.²³

Three stable conformers were found. Their shapes are shown in Fig. 1, in order of stability. Their relative energies (ΔE), rotational and quadrupole coupling constants, and dipole moment components are reported in Table 1. Conformer I and conformer III display an O–H...F interaction, whereas conformer II displays an O–H...Cl interaction.

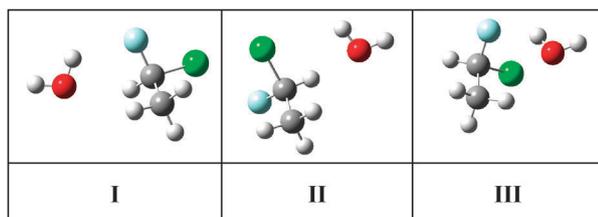


Fig. 1 The three most plausible structures of the complex of water with CFE.

Table 1 MP2/6-311++G** spectroscopic parameters of the plausible conformers of CFE–H₂O

	I	II	III
A/MHz	6541.6	3866.1	4131.3
B/MHz	1650.8	2230.3	1993.9
C/MHz	1503.1	1734.0	1802.9
χ_{aa}/MHz	−61.9	28.0	11.6
$(\chi_{bb}-\chi_{cc})/\text{MHz}$	−3.2	−85.9	−71.5
$ \mu_a /\text{D}$	2.0	3.2	0.8
$ \mu_b /\text{D}$	0.2	0.5	0.6
$ \mu_c /\text{D}$	0.3	0.2	0.2
$\Delta E/\text{cm}^{-1}$	0 ^a	58	156
$\Delta E'/\text{cm}^{-1}$	0 ^b	123	188

^a Absolute energy: −713.992438 E_h. ^b Counterpoise corrected energy, absolute value is −713.990157 E_h.

The three forms of the complex are almost isoenergetic, their energies being within 160 cm^{−1}. The corresponding theoretical structures are given in the ESI.†

A counterpoise correction²⁴ to the MP2/6-311++G** calculated energies (E') was performed. The results showed the global minimum remains the same and the relative energies of other conformers are in the same sequence but with the energy gaps slightly increasing.

Rotational spectra

According to the *ab initio* results, the first search for rotational transitions was focused on the μ_a -type transitions of conformers I and II. The first observed lines were assigned to $J = 3 \leftarrow 2$ band, $K_a = 0, 1$ transitions of conformer I, based on the considerably different expected quadrupole hyperfine structures between the two conformers. Only the rotational spectrum of conformer I was found and assigned. Each line was split into several components due to the nuclear quadrupole coupling of the ³⁵Cl nucleus and appeared as a doublet because of the Doppler effect.

None of the observed transitions was split for internal rotation effects of the water moiety, suggesting that water should be quite “rigid” within the complex. Fig. 2 shows the quadrupole hyperfine structure of the $3_{0,3} \leftarrow 2_{0,2}$ transition.

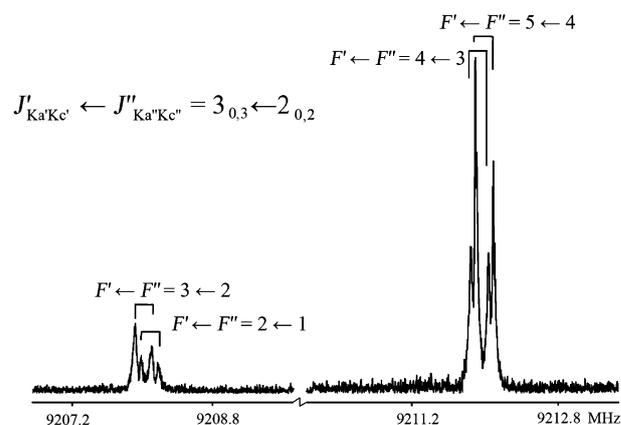


Fig. 2 Recorded $3_{0,3} \leftarrow 2_{0,2}$ transition of the observed conformer of CFE–H₂O showing the ³⁵Cl hyperfine structure. Each line exhibits the Doppler doubling.

Table 2 Spectroscopic constants of three isotopomers of CFE–W (S-reduction, I^r representation)

	Normal	³⁷ Cl(CFE–H ₂ O)	CFE–H ₂ ¹⁸ O
<i>A</i> /MHz	6515.5 (1) ^a	6496.6 (5)	6477.8 (1)
<i>B</i> /MHz	1609.0827 (3)	1575.4871 (2)	1521.1690 (2)
<i>C</i> /MHz	1465.4267 (3)	1437.5705 (2)	1393.4850 (2)
<i>χ</i> _{aa} /MHz	–63.467 (8)	–50.19 (1)	–94.71 (3)
(<i>χ</i> _{bb} – <i>χ</i> _{cc})/MHz	–4.054 (9)	–3.12 (9)	–1.03 (1)
<i>χ</i> _{ab} /MHz	–23.1 (3)	–21.6 (5)	–22.8 (6)
<i>D</i> _J /kHz ^b	1.954 (3)	1.843 (8)	1.827 (3)
<i>D</i> _{JK} /kHz	16.91 (5)	17.55 (5)	16.9 (0)
<i>d</i> ₁ /Hz	5 (3)	[5] ^c	[5] ^c
<i>d</i> ₂ /Hz	22 (2)	[22] ^c	[22] ^c
<i>N</i> ^d	54	41	29
<i>σ</i> /kHz ^e	2.6	4.4	2.0

^a Errors in parenthesis are expressed in units of the last digit. ^b The omitted quartic centrifugal distortion constant, *D*_K, is undetermined from the fit and has been fixed to zero. ^c Values in brackets have been fixed to the values of the “normal” (*i.e.* most abundant) species. ^d Number of fitted lines. ^e Standard deviation of the fit.

The measured lines were used to determine the spectroscopic constants collected in Table 2. The fits were performed using Pickett’s SPFIT program,²⁵ according to the Hamiltonian:

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

where *H*_R represents the rigid rotational part of the Hamiltonian, *H*_{CD} represents the centrifugal distortion contributions analyzed using the S reduction in the I^r representation,²⁶ and *H*_Q represents the interaction of ³⁵Cl (or ³⁷Cl) nucleus quadrupole moment with the overall rotation.²⁷

After the assignment of the spectrum of the normal species, the structure was adjusted successively to reflect the experimental rotational constants. Then we searched for and assigned the spectra of the ³⁷Cl, HOD, DOH, DOD and H₂¹⁸O isotopologues. These spectra were fitted with the same procedure described above for the normal one. The intensities of the rotational transitions of the CFE···DOH species were about 50% stronger than those of the CFE···HOD isotopologue, most likely because of zero-vibrational energy contributions. The derived spectroscopic parameters are collected in the second and third

Table 3 Spectroscopic constants of three H₂O deuterated species of CFE–W (S-reduction, I^r representation)

	CFE–DOH	CFE–HOD	CFE–DOD
<i>A</i> /MHz	6500.4 (1) ^a	6483.1 (5)	6460.7 (3)
<i>B</i> /MHz	1576.9202 (2)	1538.1134 (3)	1509.3648 (3)
<i>C</i> /MHz	1435.0612 (2)	1406.6168 (3)	1379.3846 (3)
<i>χ</i> _{aa} /MHz	–63.26 (2)	–63.060 (4)	–63.08 (2)
(<i>χ</i> _{bb} – <i>χ</i> _{cc})/MHz	–3.97 (1)	–3.78 (1)	–4.13 (1)
<i>χ</i> _{ab} /MHz	–28.4 (5)	–27.0 (6)	–24.3 (5)
<i>D</i> _J /kHz ^b	1.856 (3)	1.867 (4)	1.655 (4)
<i>D</i> _{JK} /kHz	16.5 (1)	18.4 (2)	15.7 (2)
<i>N</i> ^c	37	26	28
<i>σ</i> /kHz ^d	6.3	7.0	4.6

^a Errors in parentheses are expressed in units of the last digit. ^b The omitted quartic centrifugal distortion constants, *D*_K, *d*₁, *d*₂ are undetermined from the fit and have been fixed to zero. ^c Number of fitted lines. ^d Standard deviation of the fit.

Table 4 *r*_s coordinates of the isotopically substituted atoms of CFE–W

	<i>a</i> /Å		<i>b</i> /Å		<i>c</i> /Å	
	exptl	calc.	exptl	calc.	exptl	calc.
Cl	1.832 (9) ^a	1.823	0.235 (3)	0.233	0.251 (7)	0.270
H _{W,Hbond}	2.604 (6)	2.604	0.748 (2)	0.759	0.610 (2)	0.199
H _{W,Free}	3.781 (4)	3.814	0.408 (3)	0.520	0.495 (3)	0.679
O	3.003 (5)	2.945	0.168 (8)	0.168	0.466 (3)	0.478

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

Table 5 Partial *r*₀ geometry of CFE–W

Fitted parameters	Derived parameters		
<i>r</i> (O···F)/Å	2.910 (9)	<i>r</i> /Å	2.140
<i>α</i> (O···F–C)/°	87.4 (1)	<i>α</i> /°	136.2
<i>d</i> (O···F–C–Cl)/°	156.7 (2)	<i>β</i> /°	98.7
<i>α</i> (H′–O···F)/°	31 (4)	<i>r</i> (O···H ¹ C)/Å	2.753
<i>d</i> (H′–O···F–C)/°	–212 (8)	<i>r</i> (O···H ² C)/Å	2.842
<i>d</i> (H–O–H′···F)/°	–149 (5)	<i>R</i> _{CM} /Å	3.756

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

data columns in Table 2 for the ³⁷Cl and H₂¹⁸O, and in Table 3 for the deuterated species.

All measured transitions are available in the ESI.†

Conformation and structure

The values of rotational and Cl quadrupole coupling constants are in very good agreement with those calculated for species I, so that the conformational assignment is straightforward.

In addition, the *r*_s substitution coordinates²⁸ of the isotopically substituted atoms, Cl, O, and H atoms of water, reported in Table 4, are in good accord with the *ab initio* values. The only remarkable discrepancy is the |*c*| coordinate of the water hydrogen involved in the hydrogen bond, a quite frequent effect, related to the shrinkage of the H-bond upon H → D isotopic substitution.

Partial *r*₀ structures were calculated from the six sets of experimental rotational constants, either with the geometry of water²⁹ and CFE³⁰ fixed to the structure of the isolated molecules, or starting from the *ab initio* geometry. These latter values of *r*(O···F), ∠(O···F–C), ∠(O···F–C–Cl), ∠(H′–O···F), ∠(H′–O···F–C) and ∠(H–O–H′···F) are calculated and reported in Table 5.

The alternative H-bond parameters *r*, *α*, *β*, *r*(O···H¹) and *r*(O···H²) and *R*_{CM} given in Fig. 3, have been derived from the fitted parameters and reported in the right part of Table 5.

Here, the distance *R*_{CM} is the separation between the centers of mass of the two constituent molecules (3.756 Å).

Dissociation energy

The three translational motions and the three rotational degrees of freedom of the isolated water molecule are replaced by six low-energy vibrations upon formation of the complex. One of them can be thought, in a first approximation, as the stretching between the two centers of mass of the two forming molecules. When this stretching motion takes place along the

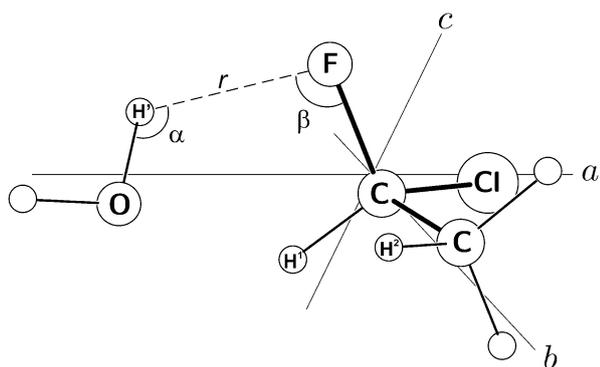


Fig. 3 Some structural parameters used through the text are indicated in the sketch of the observed conformer of CFE–W.

Table 6 Dissociation energies (E_B) for some molecular complexes with water linked to the partner molecule through an O–H···Hal WHB

Complex	O–H···Hal	$E_B/\text{kJ mol}^{-1}$	Ref.
CH ₂ F ₂ –W	O–H···F	7.5	15
CH ₂ ClF–W	O–H···Cl	8.5	17
CH ₃ CHClF–W	O–H···F	5.4	This work

inertial a -axis of the complex, it is possible to roughly evaluate the dissociation energy with the approximate pseudo-diatomic molecule model. Within this approximation, the stretching force constant (k_s) can be estimated by considering the complex as made of two rigid parts, and using the following equation³¹

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

where μ is the pseudo-diatomic reduced mass, D_I is the centrifugal distortion constant and R_{CM} is the distance between the centers of mass of the monomers. The value $k_s = 4.60 \text{ N m}^{-1}$ was obtained, which corresponds to a harmonic stretching frequency of 73 cm^{-1} .

By assuming a Lennard-Jones-type potential the dissociation energy has been estimated by applying the approximate formula:³²

$$E_B = 1/72k_sR_{CM}^2, \quad (3)$$

from which the value $E_B = 5.4 \text{ kJ mol}^{-1}$ was obtained.

This value is similar to the dissociation energies determined for the related molecular complexes with an O–H···Hal linkage, difluoromethane–water¹⁵ and chlorofluoromethane–water.¹⁷ Their values are reported in Table 6.

All these dissociation energy values are smaller than typical E_B values underlying classical (O–H···O, O–H···N, O–H···S, and N–H···O) hydrogen bonds.

Conclusions

We established the absolute minimum conformation and structure of the 1 : 1 adduct of CFE and water, by investigating the rotational spectra of several isotopic species. A few years ago we stated, according to the MW spectrum of

CH₂ClF–H₂O, that the O–H···Cl hydrogen bond is stronger than the O–H···F one. Now, the MW spectrum of CFE–W seems to indicate the contrary. The two interactions have very similar energies and it is the contribution of other effects, such as the stabilizing presence of secondary C–H···O contacts and/or even small local dipole–dipole interactions, which steer and self-align the moieties into their preferred absolute configuration.

The dissociation energy of CFE–H₂O has been estimated to be 5.4 kJ mol^{-1} , a value similar to that of other complexes with a O–H···Hal linkage. This value suggests classification of this kind of interaction as a WHB. In CH₂F₂–H₂O and in CH₂ClF–H₂O the water unit was undergoing a feasible internal rotation around its symmetry axis, reflected by two tunneling component lines for each rotational transition. Rather unexpectedly, such a tunneling effect was not observed in CFE–H₂O: so water appears to be more weakly bound to the partner molecule, but its internal rotation is more hindered than in the two other cases. Probably, the secondary H-bonds between O and H1C and H2C (see Fig. 3) with O···H1C and O···H2C distances of only $\sim 2.7\text{--}2.8 \text{ \AA}$ (see Table 5) render the internal rotation of water more hindered than in other cases.

Despite the *ab initio* calculations suggesting two additional configurations of similar stability with energies only slightly higher than that of the observed one, we could not observe their rotational lines. This is rationalized by the fact that the different conformers are separated by only low interconversion barriers that allow for efficient relaxation into the global minimum. It has been shown, indeed, that for barriers smaller than $2kT$ (*ca.* 420 cm^{-1} in our case), such a relaxation takes place.³³ In addition, it is likely that the two molecular subunits experience repeated formation and dissociation in the jet expansion.³⁴ Also this would lead to a strong preference for the most stable conformer in a jet expansion.

In our complex, two different halogens are involved with different diameters (and thus also size of the free electron pair) and different polarizabilities. Then the geometry of the organic frame sets constraints on the kind of directivity (which is supposed to be the characteristic feature of an H-bond compared to vdW or other mainly electrostatically driven interactions) that can be obtained if two interactions are present. What we learned in this situation is already phrased nicely in the title of the themed issue: ‘Weak Hydrogen Bonds—Strong effects?’. Our results would fit also a title like ‘Weak concurring Hydrogen bonds—Directing effects!’. Finally, we think that the spectroscopic findings in a situation that takes place at such a small energy scale represent evidence much stronger than quantum-chemical predictions at every available level.

Acknowledgements

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