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Microwave Spectroscopy

Lone-Pair···π Interaction: A Rotational Study of the Chlorotrifluoroethylene–Water Adduct**

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The rotational spectrum of the chlorotrifluoroethylene–water adduct shows that water links to a fully halogenated alkene through a lone-pair (lp)···π interaction.

Water is ubiquitous in chemical, physical, and biological systems, and the knowledge of the ways it interacts with the various kind of molecules and biomolecules helps to understand solvation processes in aqueous environments and its effects on gas-phase reactions.[1]

The typology of the complexes that water forms with organic molecules has been described and classified in a recent article.[2] Using alcohols, ethers, amines, amides or N-containing aromatics, water is linked to the partner molecule with relatively strong (15–25 kJ mol^{-1}) O−H···O, O−H···N or N−H···O hydrogen bonds. With ethers,[3] aliphatic amines,[4] diazines,[5] alcohols,[2,6] water acts generally as a proton donor. However, when making an adduct with phenols[7] and with NH groups inserted in an aromatic ring,[8] water takes the role of a proton acceptor. With amides[9] and amino acids,[10] water forms a two-hydrogen-bond ring structure with the double role of proton donor and proton acceptor.

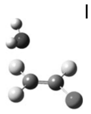
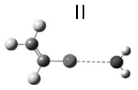
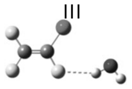
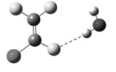
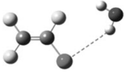
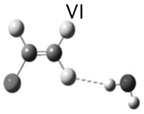
With hydrogen-containing freons, water forms weak (4–6 kJ mol^{-1}) OH···halogen hydrogen bonds, such as OH···F or OH···Cl.[11] When both Cl and F atoms are present in a freon molecule, sometimes the OH···Cl linkage is favorite,[11b] but the OH···F one is preferred in other cases.[11c] However, when a aliphatic freon molecule is perhalogenated, and no hydrogen atoms are present in the molecule, then a halogen bond (6–10 kJ mol^{-1}), rather than a hydrogen bond is formed.[12]

The geometries of the adducts of water with molecules containing a π-electron system, such as ethylene–water[13] and benzene–water[14] have been found to be stabilized by OH···π interactions, although with high dynamical effects.

No rotational investigations of an adduct of water with a molecule fully halogenated and with a π-electron system has been reported. For this reason, we decided to investigate the microwave spectrum of the adduct of water with chlorotrifluoroethylene (C_2ClF_3, freon-1113).

Before collecting the spectra, the full geometry optimization of the complex has been done with ab initio calculation at the MP2/6-311++G(d,p) level using the Gaussian03 program package.[15] Six plausible conformers were found. The relative energies and spectroscopic constants were obtained and collected in Table 1. To have a better estimate of the energy differences, all intermolecular binding energy values were counterpoise corrected for the basis set superposition error (BSSE).[16] The most stable conformer, rather than to be stabilized by a hydrogen bond or a halogen bond, is characterized by a lp···π interaction. Its ab initio geometry is given in the Supporting Information.

Table 1: MP2/6-311++G(d,p) shapes and spectroscopic parameters of the six more stable forms of the complex C_2ClF_3–H_2O.

	I	II	III
			
$A/B/C$ [MHz]	2356/1352/1234	3948/876/717	3327/1057/802
χ_{aa}/χ_{bb}-χ_{cc}/χ_{ab} [MHz]	−24.4/−49.9/54.6	−71.1/−4.2/19.6	9.1/−84.1/48.9
$\lvert\mu_a\rvert/\lvert\mu_b\rvert/\lvert\mu_c\rvert$ [D]	1.9/1.4/0.6	3.2/0.8/0.0	0.3/1.2/0.0
$\Delta E/\Delta E_{BSSE}$ [cm^{-1}]	0/0[a]	476/18	645/214
	IV	V	VI
			
$A/B/C$ [MHz]	2705/1145/804	3146/1027/774	3319/889/701
χ_{aa}/χ_{bb}-χ_{cc}/χ_{ab} [MHz]	−62.2/129.2/35.1	15.0/−90.7/43.2	11.8/−86.0/46.4
$\lvert\mu_a\rvert/\lvert\mu_b\rvert/\lvert\mu_c\rvert$ [D]	2.8/1.4/0.0	2.4/1.0/0.0	1.3/2.4/0.2
$\Delta E/\Delta E_{BSSE}$ [cm^{-1}]	667/261	773/355	903/373

[a] Absolute energies: −910.899334 and −910.895724 E_h, respectively.

The rotational spectrum of C_2ClF_3 has been reported previously.[17] Its spectrum appeared very intense and then the assignment of the rotational spectrum of C_2ClF_3–H_2O looked promising.

We searched first for the μ_a-type transition of species I, which were expected to be the most intense ones. The J 3←2 μ_a-band was assigned first, then many more μ_a- and μ_b-transitions have been measured. Only transitions correspond-

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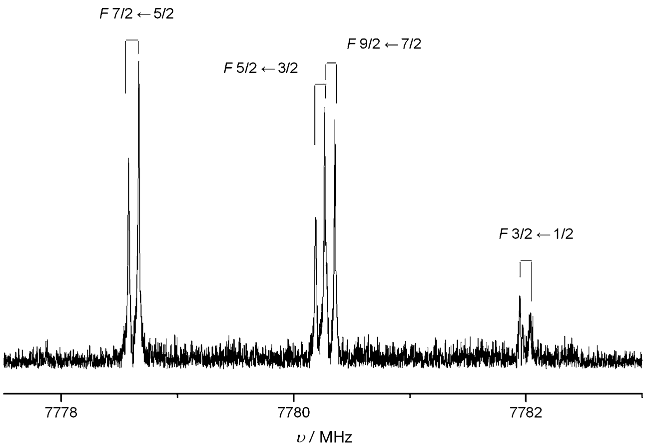

Figure 1. Recorded $3_{1,2}\leftarrow 2_{1,1}$ transition of the observed conformer of C_2ClF_3–H_2O showing the ^{35}Cl hyperfine structure. Each line exhibits the Doppler doubling.

ing to conformer I of Table 1 were observed and assigned. Each of them appeared as a multiplet of lines (see Figure 1) because of the nuclear quadrupole moment of the ^{35}Cl (or ^{37}Cl) nucleus.

The transition frequencies were fitted to the spectroscopic constants with Pickett's SPFIT computer program,[18] according to the following Hamiltonian given in Equation (1),

$$H = H_{\mathrm{R}} + H_{\mathrm{CD}} + H_{\mathrm{Q}} \qquad (1)$$

where H_{R} represents the rigid rotational parts of the Hamiltonian. The centrifugal distortion contributions (analyzed using the S reduction and I^r representation)[19] are represented by H_{CD}. H_{Q} is the operator associated with the ^{35}Cl (or ^{37}Cl) quadrupolar interaction. The obtained spectroscopic parameters are reported in the first column of Table 2.

After partial structural adjustments, the spectra of the ^{37}Cl, $H_2{}^{18}O$, D_2O, and DOH isotopologues were searched and assigned. They were fitted with the same procedures as described for the normal species, and the spectroscopic parameters are also shown in Table 2. All measured transitions are given in the Supporting Information.

The conformational assignment is straightforward: comparing the experimental values of the rotational and quadrupole coupling constants of Table 2 to the theoretical values of Table 1, one can see that the match is acceptable only for conformer I, which is dominated by a lp···π bonding.

No lines were identified in the spectrum attributable to the higher energy conformers. Besides to the high energy, this non-observation could be due to conformational relaxation, a process that takes easily place in supersonic expansions whithin interconformational barriers lower than $2kT$.[20]

It is presumable that water undergoes a nearly free rotation in the complex. Only one spectrum was observed, indeed, for the monodeuterated species, but the intensities of its rotational transitions are the double of those of the dihydrogenated and of the dideuterated species when the H/D ratio is about 1:1. This indicates that the spectra of the two monodeuterated species are not distinguishable, in accord with a nearly free internal rotation of water about its symmetry axis. In none of the isotopologues, splittings attributable to the torsional motion of water were observed. The transitions we measured were only belonging to the $m = 0$ torsional state.

According to what said above, the angular position of water cannot be precisely determined from the isotopic substitution. The large decreases of the rotational constants in going from the C_2ClF_3–H_2O to the C_2ClF_3–D_2O species (see Table 2) makes it possible, however, to establish that the hydrogen atoms are oriented far away from the C_2ClF_3 unit.

The r_s substitution coordinates[21] can be reliably determined, however, for the Cl and O atoms. The obtained values are shown in Table 3, and there compared to the values calculated with a partial r_0 geometry. In such a r_0 geometry, the parameters defining the position of the O atom have been modified from the ab initio values ($r_{\mathrm{O\cdots Cl}} = 2.8286$ Å, OC1C2 = 101.8°, OC1-C2Cl = 87.8°) to the empirically corrected values ($r_{\mathrm{O\cdots Cl}} = 2.947$ Å, OC1C2 = 100.5°, OC1-C2Cl = 88.4°) which best reproduce the rotational constants of the $C_2{}^{35}ClF_3$–H_2O, $C_2{}^{37}ClF_3$–H_2O, and C_2ClF_3–$H_2{}^{18}O$ isotopologues.

Table 2: Spectroscopic constants of all measured isotopologues of C_2ClF_3–H_2O.

	$C_2{}^{35}ClF_3$–H_2O	$C_2{}^{37}ClF_3$–H_2O	C_2ClF_3–$H_2{}^{18}O$	C_2ClF_3–D_2O	C_2ClF_3–DOH
A [MHz]	2265.0902(5)[a]	2254.829(2)	2218.789(1)	2182.9360(6)	2235.4866(6)
B [MHz]	1321.8363(4)	1298.3329(4)	1282.8122(4)	1263.5962(5)	1292.4213(4)
C [MHz]	1224.4208(2)	1201.2806(4)	1189.0918(4)	1171.0099(5)	1199.7660(4)
D_J [kHz]	3.103(6)	2.972(9)	3.146(6)	3.282(8)	3.473(7)
D_{JK} [kHz]	−6.46(3)	[−6.46][b]	−8.69(6)	−8.41(6)	−8.71(5)
D_K [kHz]	17.55(4)	[17.55]	21.4(1)	20.84(8)	22.58(7)
d_1 [kHz]	−0.482(5)	[−0.482]	−0.546(5)	−0.723(6)	−0.714(6)
d_2 [kHz]	−0.185(7)	[−0.185]	−0.164(8)	−0.216(8)	−0.248(6)
χ_{aa} [MHz]	−24.14(1)	−20.51(3)	−20.03(1)	−19.40(2)	−21.36(1)
χ_{bb}-χ_{cc} [MHz]	−51.28(1)	−38.95(1)	−52.51(1)	−53.60(2)	−52.32(1)
χ_{ab} [MHz]	54.8(4)	43(1)	46.6(6)	50.1(8)	49.8(4)
N[c]	86	44	80	72	92
σ [kHz][d]	3.1	2.5	3.4	3.9	4.1

[a] Uncertainties (in parentheses) are expressed in units of the last digit. [b] Fixed to the value obtained for normal species. [c] Number of transitions in the fit. [d] Standard deviation of the fit.

Table 3: r_s coordinates [Å] of the Cl and O atoms.

	a		*b*		*c*	
	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.
O	±2.177(1)[b]	2.135	±1.152(1)	−1.223	±1.079(1)	1.329
Cl	±1.870(1)	−1.874	±0.736(2)	−0.735	[0][b]	−0.014

[a] Uncertainties (in parentheses) are expressed in units of the last digit.
[b] Slightly imaginary value: set to zero.

One can note that the *c*-coordinate of the oxygen atom is not satisfactorily reproduced, probably due to the large amplitude bending motions of the full molecule of water with respect to C_2ClF_3.

The shape and atom numbering of the observed conformer are shown in Figure 2. The observed lp⋯π interaction can be explained in terms of an electron-withdrawing effect from the π-electronic system towards the halogen atoms (especially the F atoms) generating a positive potential above the carbon atom C1. This effect has been theoretically described, and the region of low electronic density is called "π-hole".[22]

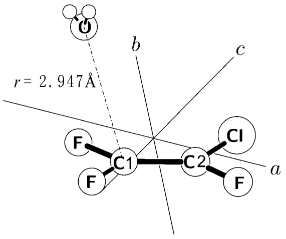

Figure 2. Conformation and principal axis of the observed species (conformer I) of C_2ClF_3–H_2O.

MP2/6-311++G(d,p) counterpoise-corrected ab initio calculations supplied for the dissociation energy of the complex a value of 6.6 kJ mol^{-1}, which can be considered, in a first approximation, the energy of the lp⋯π interaction.

This Fourier-transform microwave spectroscopy investigation of the rotational spectra of C_2ClF_3–H_2O and of its isotopologues allowed to point out irrefutably that its more stable configuration is established by a lp⋯π interaction. This is, to our knowledge, the first time that this interaction is observed and described through a rotational study in a molecular complex. Comparing our results to those obtained by rotational studies of ethylene–water,[13] benzene–water,[14] tetrafluoromethane–water, and chlorotrifluoromethane–water adducts,[12] we can state that this kind of interaction—in competition with hydrogen bonds and halogen bonds—takes place when water is interacting with perhalogenated alkenes.

A similar effect, the Bürgi–Dunitz *n*–π* interaction has been found to stabilize one or two conformers in amino acids. In the case of β-alanine, one conformer over the four observed ones (the highest in energy) is stabilized by such a linkage rather than an intramolecular hydrogen bond.[23] In the case of γ-aminobutyric acid (GABA), two conformers (including the most stable one) over nine present this intramolecular interaction.[24] Finally, the *n*–π* interaction is considered responsible for the thermal conversion of 5-aminovaleric acid to δ-valerolactam.[25]

This represents another interesting experimental evidence on the investigation of weak interaction, provided by rotational spectroscopy.

Experimental Section

Molecular clusters were generated in a supersonic expansion, under conditions optimized for the dimer formation. Details of the Fourier-transform MW[26] spectrometer (COBRA-type[27]), which covers the range of 6.5–18 GHz, have been described previously.[28]

A gas mixture of about 1 % of chlorotrifluoroethylene (commercial sample used without further purification) in He at a stagnation pressure of about 0.25 MPa was passed over a sample of H_2O and 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 a doublet because of 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.

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