Rotational Spectroscopy

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The Halogen Bond and Internal Dynamics in the Molecular Complex of CF_3Cl and H_2O**

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The pulsed supersonic-jet Fourier-transform microwave spectrum of the molecular complex of CF_3Cl (freon-13) and water is effectively that of a symmetric top and shows that its two units (CF_3Cl and H_2O) are held together by an O···Cl halogen bond.

Considerable attention has been dedicated during the last years to chlorofluorocarbons (CFCs). Much attention has been dedicated to their impact on the atmospheric processes, in relation to both the role in the reduction of ozone and in the greenhouse effect. Their complexation with atmospheric water affects their reactivity and it seems to accelerate, for example, the decomposition rate of freons in the atmosphere.[1] These complexes provide us the opportunity to study the effect of intermolecular bonding which can be interesting in connection with photochemical reaction dynamics.[2] In fact there is evidence that water molecules may have decisive influence on gas-phase reactions[3,4] and there are many unusual features associated with the kinetics and energetics of hydrated chemical systems.[5,6] Water molecules can stabilize the intermediates of such reactions but these effects are often difficult to distinguish. Experimental evidence can be accounted for by invoking pre-reactive complexes of haloderivatives with water.[7,8]

Water is a key solvent and provides the fundamental environment to the course of life. Water is often noncovalently bound to organic molecules or biomolecules and its internal dynamics in the formed complexes contribute to determine the properties of these systems.[9] Water plays an important role in (bio)organic reactions (molecular recognition), radiation absorption,[10] and in atmospheric dynamic processes, mainly because of its ability to form hydrogen bonds. Although generally water is considered more effective as a proton acceptor rather than as a proton donor, its amphiproticity is well-known in both solution and hydrated complexes investigated in the gas phase. Through hydrogen bonding, water possesses the ability to form complexes with itself or with other molecules and generally the complexity of the rotational spectrum of complexs of water with partner molecules is inversely proportional, in a first approximation, to the size of the molecular complex under investigation.

In freons, all data suggest O–H···X (X = F, Cl) to be a weak interaction but observation of the behavior of the freon–water complex shows that it is quite difficult to rationalize. The rotational spectrum of the complex CH_2F_2–H_2O complex outlined a weak O–H···F linkage with water as proton donor.[11] When the freon molecule contains both a F and a Cl atom, an interesting question arises: which of the hydrogen bonds, O–H···Cl or O–H···F, is stronger? The microwave (MW) study of the CH_2ClF–H_2O complex showed that only the O–H···Cl interaction was observed, so that the O–H···Cl interaction was proclaimed to be stronger.[12] But the analysis of the MW spectrum of 1-chloro-1-fluoroethane, a molecule with a structure similar to chlorofluoromethane, made possible the detection of an complex with a O–H···F hydrogen bond[13] and overturned the conclusions of Ref. [12]. Finally, in the CF_4···H_2O complex (CF_4 is also known as Freon-31), the favorable dipole–dipole interactions induced the formation of an anti H-bond with the oxygen atom situated in the CF_3 cavity.[14]

The anti-hydrogen bond, that is the trend to form halogen bonds, was first described, in conjunction with MW spectroscopy, by Klemperer and co-workers.[15] Simple dihalogen molecules, such as F_2 and ClF, reacted with water and by using a special experimental procedure (fast-mixing nozzles) formed their complexs with water, which are also characterized by halogen bond interactions.[16] In a recent perspective article Legon described the halogen bond as a noncovalent interaction, not so different from hydrogen bonding.[17] The existence of the halogen bond was already mentioned in 1863 as the earliest report of halogen bonding in a complex with an N···I interaction,[18] but it is probably less familiar and investigated than usual hydrogen bonding.

An intriguing question is how a water molecule will interact with multihalogenated molecules, containing different halogen atoms, such as CF_3Cl (Freon-13).

In the CF_3Cl–H_2O complex several configurations are possible and it appears difficult to state which one is the global minimum, that is, which one is the predominant interaction. Will the leading interaction in the complex be a

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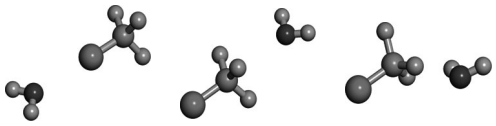
hydrogen bond? And, in such a case, which halogen atom, chlorine or fluorine, will be involved in the H bond? Or, if a halogen bond is preferred, will it be an O···F or an O···Cl bond? To answer these questions, we decided to investigate the high-resolution rotational spectrum of the $CF_3Cl–H_2O$ complex.

To support the assignment of the rotational spectrum, we performed some preliminary ab initio computations at the MP2/6-311++G(d,p) level.[19] Three stationary points were found and their images and spectroscopic parameters are reported in Table 1.

Table 1: Ab initio (MP2/6-311++G(d,p)) values of spectroscopic constants of the three more stable conformers of the $CF_3Cl–H_2O$ complex.

Parameter	I	II	III
Contact	O···Cl	O···F	O–H···F
A [MHz]	5638.6	5624.5	3499.9
B [MHz]	1105.1	1436.8	1216.0
C [MHz]	1102.6	1431.7	1071.6
μ_a [D]	3.34	−1.77	−0.86
μ_b [D]	−0.03	0.04	−1.42
μ_c [D]	0.00	−0.01	0.03
χ_{aa} [MHz]	−74.5	−72.3	20.4
χ_{bb} [MHz][a]	37.5	36.2	−57.6
E_0 [cm^{-1}]	0[b]	261	469
D_0 [kJ mol^{-1}][c]	11.1	7.9	5.4
D_{CP} [kJ mol^{-1}]	6.5	0.7	1.7



[a] μ_g and χ_{gg} (g = a,b,c) are the dipole-moment components and the ^{35}Cl quadrupole coupling constants, respectively, χ_{cc} is the completion to 0 of χ_{aa} and χ_{bb}. [b] E_0 is the ZPE corrected relative energy of each conformer. The absolute value of the MP2 energies is −872.960975 E_h. [c] D_0 and D_{CP} are the dissociation energies without and with counterpoise corrections, respectively.

Rather surprisingly, we could identify only a symmetric rotor spectrum, when all the predicted structures suggested asymmetric rotors. Some questions arise. Have we not explored the potential-energy surface correctly and had we missed any structure? Was the theory wrong and was there a conformer, predicted to be an asymmetric rotor, that was effectively a symmetric rotor?

We found, indeed, compact sets of transitions evenly spaced by a quantity that is very close to the theoretical $B+C$ value (B and C are rotational constants) of the conformer predicted to be most stable. Following this conformational assignment, we predicted and easily assigned the rotational spectra of the isotopologues $CF_3{}^{37}Cl–H_2O$, $CF_3{}^{35}Cl–H_2{}^{18}O$, $CF_3{}^{35}Cl–OHD$, and $CF_3{}^{35}Cl–D_2O$. Although we readily observed the rotational spectra, the data-fitting procedure was complicated mainly because of the overlap of various K-component lines (K is the quantum number of the projection of the rotational angular momentum along the axis of symmetry of the complex) of the corresponding hyperfine ^{35}Cl (or ^{37}Cl) quadrupole coupling structures. However, it was possible to obtain good fit functions by using Pickett's SPFIT program.[20]

As a consequence of the symmetric-top characteristic of the spectra, only one quadrupole coupling constants, χ_{aa}, was determined.

For the $CF_3{}^{35}Cl–H_2O$ and $CF_3{}^{37}Cl–H_2O$ complexs we measured transitions, originating from $m=\pm1$ and $K=0$ states (m and K are quantum numbers), and fitted functions to the data. For $K=1$ we observed transitions, but we did not fit functions to the data because, similar to other cases, the data are affected by the odd powers of the angular momenta.[14,21,22]

The relaxation process upon supersonic expansions of the metastable ($m=\pm1$) state to the ground ($m=0$) state is outlined[23] to be nuclear-spin-forbidden for the "symmetric" species $CF_3Cl–H_2O$, $CF_3Cl–D_2O$, and $CF_3Cl–H_2{}^{18}O$. However, we measured the spectrum of $m=\pm1$ for the most abundant species. The experimental spectroscopic constants are reported in Table 2 for all isotopologues.

A part of the spectrum corresponding to the J: 4←3 transition of the $CF_3{}^{35}Cl–H_2O$ main isotopic species is shown in Figure 1 and all the line frequencies are available in the Supporting Information.

Freon-13 ($CF_3Cl–H_2O$) is an interesting quantum mechanical system. A symmetric-top molecule (CF_3Cl) is bound to an asymmetric planar-top molecule (H_2O) and therefore, the combined system should be an asymmetric top. However, the large-amplitude motions of water render the complex an effective symmetric top. This symmetric-top appearance of the rotational spectra of molecules that are predicted to be asymmetric-top complexes has been previously observed in $CF_4···H_2O$[7] and in benzene–water complexes.[21,24,25] In the structural analysis we describe the complex in the vibrationally averaged structure using at least the four coordinates shown in Figure 2.

Table 2: Experimental spectroscopic constants of the observed conformers of the $CF_3Cl–H_2O$ complex.

$m=0$	$CF_3{}^{35}Cl–H_2O$	$CF_3{}^{37}Cl–H_2O$	$CF_3Cl–D_2O$	$CF_3Cl–HOD$	$CF_3Cl–H_2{}^{18}O$
B [MHz]	1094.0577(3)[a]	1091.5176(3)	1014.4074(1)	1052.3865(6)	1031.5384(7)
χ_{aa} [MHz]	−78.42(7)	−61.82(6)	−78.35(1)	−78.40(6)	−78.46(7)
D_J [kHz]	0.653 (5)	0.636(4)	0.578(2)	0.62(1)	0.55(2)
D_{JK} [kHz]	10.33(5)	10.11(5)	9.921(8)	10.45(5)	103.7(2)
σ [kHz][b]	2	5	1	1	7
N[c]	36	35	39	24	25
$m=\pm1$					
B [MHz]	1093.6729(5)	1091.1357(8)			
χ_{aa} [MHz]	−78.39(1)	−61.87(8)			
D_J [kHz]	0.450(1)	0.44(1)			
σ [kHz]	1	1			
N	16	10			

[a] Error in parentheses in units of the last digit. [b] Root mean square deviation of the fit. [c] Number of lines in the fit.

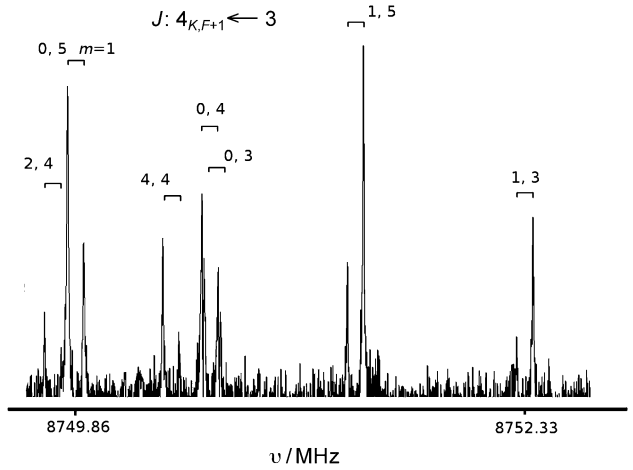


Figure 1. Part of the rotational spectra of the CF_3Cl–H_2O complex which shows symmetric-top behavior and hyperfine interaction of Cl originating from both $m=0$ and $m=\pm1$ states. Each line displays the Doppler doubling effect.

There, R_{cm} is the distance between the two centers of mass of the two subunits. The two angles, Ψ and θ, measure the bending amplitudes of the two constituent molecules. The angle Φ describes the rotation of the two subunits with respect to each other. To estimate the potential curve for every structural parameter, an ab initio grid was calculated in steps of 2° over the full range of angles (and in steps of 1° close to the minima). While the dihedral angles were keep fixed at every step, the rest of geometric parameters were re-optimized for each point along the path. The results are plotted in Figure 3.

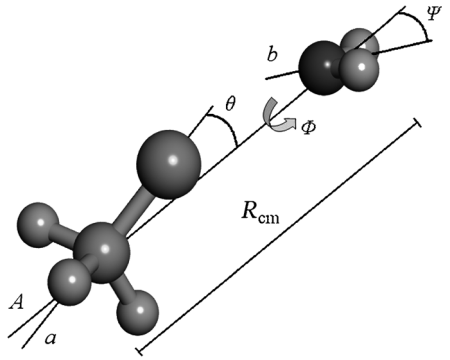


Figure 2. Molecular system with the coordinates used to discuss the molecular structure and internal dynamics.

The obtained barriers can support some assertions: 1) the relative bending motion of CF_3Cl is at a single minimum, with the corresponding coordinate θ confined close to 0°, that is, the C–Cl···O atoms are in a linear arrangement; 2) the bending of the water molecule with respect to CF_3Cl has two equivalent minima, $\Psi_e=\pm27°$ pointing to an asymmetric rotor with an interconversion barrier of about 14 cm^{-1}. This potential is similar to that reported for other systems;[24,26] 3) the V_6 potential (described by the Φ angle) is very flat, around 1 cm^{-1}. Such a flat potential-energy function and the relatively light mass of the hydrogen atoms indicate that the

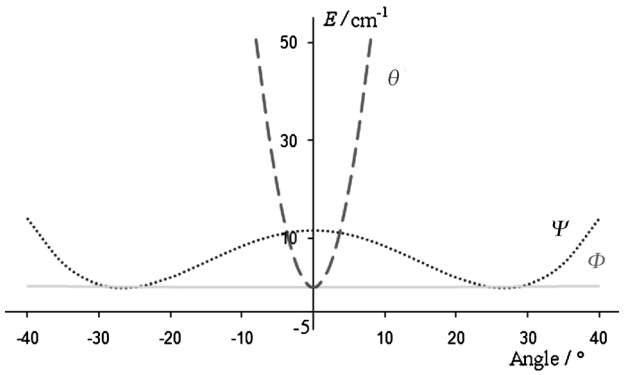


Figure 3. Ab initio potential-energy surface profiles along θ, ψ, and Φ angles which are defined in Figure 2.

water molecule is completely delocalized with respect to the C_3-symmetric axis, allowing a free rotation. This is the key factor which makes the system an effectively symmetric top, with the water molecule rotating around CF_3Cl. Correspondingly, only the rotational constant B can be determined (for all isotopologues) from the MW spectrum. According to a rather approximate model, we can assume the symmetry axes of CF_3Cl and water to lie along the a axis and their structure to not be altered upon formation of the complex, and then calculate the substitution coordinate of each substituted atom.[27] The parameter r (the distance between the Cl and O atoms) was estimated to be 3.028(3) Å versus 2.982 Å obtained by ab initio calculation. Moreover, because of the nearly free rotation of the subunits, we could assume that the C_{2v} symmetry of water is not perturbed upon full deuteration. The Chutjian method for multiple isotopic substitutions[28] provides the coordinate of the hydrogen atoms $|a|=$ 4.280(5) Å, close to the calculated parameters (+4.273 Å). All r_s structural parameters are reported in Table 3.

Table 3: Relevant structural parameters of experimental and calculated substitution coordinates of the CF_3Cl–H_2O complex.

		Cl	O	H
$\|a\|$ [Å]	obs	0.740(2)	3.768(3)	4.280(8)
	calcd	0.757	3.738	4.273

The stretching force constant (k_s) is estimated from the distortion constants (D_J) because the halogen-bond-stretching motion lies almost parallel to the a axis. For submolecules with large moments of inertia, Equation (1) is used,[29] where

$$k_s = 128\pi^4 (\mu R_{cm})^2 B_0^4/(h D_J) \quad (1)$$

μ, R_{cm}, and D_J are the diatomic reduced mass, the distance between the centers of mass and the first-order centrifugal distortion constant, respectively. A k_s value of 4.96 $N\,m^{-1}$, which corresponds to a stretching frequency of 74 cm^{-1}, was obtained. By assuming a Lennard–Jones potential function and using the approximated Equation (2)[30] the dissociation

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

energy (E_D) was found to be 7.7 kJ mol^{-1}. This value is in quite good agreement with the calculated value, once basis set superposition error (BSSE) corrections (see Table 1) are included. Moreover, this value is similar to the dissociation energies determined for the related molecular complexes between CFCs and water, as shown in Table 4.

Table 4: Dissociation energies (E_D) for monohydrated CFCs.

Complex	Interaction	E_D [kJ mol^{-1}]	Ref.
CH_2F_2–H_2O	O–H···F	7.5	[11]
CH_2ClF–H_2O	O–H···Cl	8.5	[12]
CH_3CHClF–H_2O	O–H···F	5.4	[13]
CF_4–H_2O	O···F	5.0	[14]
CF_3Cl–H_2O	O···Cl	7.7	this work

All of the complexes are weakly bound with interactions corresponding to dissociation energy values smaller than the E_D values characteristic of classical (O–H···O, O–H···N, O–H···S, and N–H···O) hydrogen bonds. However in the last two cases much remains to be learnt about the role of water. During the formation of a halogen bond, CF_3Cl is an electron acceptor. The strength of the O···F interaction is intermediate with respect to the O···Cl and O-H···F interactions.

The electron-withdrawing group $-CF_3$ modifies the electrostatic potential and a positively charged region, centered in the direction of the C–Cl bond, is created. The so-called "σ hole"[17,31] interacts favorably with the electron-rich part of a molecule, that is, the halogen bond. The σ hole is due to the special symmetry of CF_3Cl whereas it is inhibited by the T_d symmetry of CF_4. Therefore, in the CF_4–H_2O complex dipole–dipole interactions are dominant.

Experimental Section

A commercial sample of chlorotrifluoromethane was purchased from Aldrich and used without further purification. The spectra of the deuterated and $H_2{}^{18}O$ isotopologues were observed for enriched heavy-water samples.

The rotational spectra in the frequency region of 6–18.5 GHz were measured using a COBRA-type[32] pulsed supersonic-jet Fourier-transform microwave (FT-MW) spectrometer[33] described elsewhere[34] and updated with the FTMW++ set of programs.[35] A gas mixture of approximately 2% of chlorotrifluoromethane in helium was passed over the water sample and expanded through the solenoid valve (General Valve, Series 9, nozzle diameter 0.5 mm) into the Fabry–Pérot cavity. The backing pressure was kept at 0.3 MPa.

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