Halogen–Halogen Links and Internal Dynamics in Adducts of Freons

4 AUTHORS, INCLUDING:

Qian Gou
Chongqing University
41 PUBLICATIONS **160** CITATIONS

SEE PROFILE

Lorenzo Spada
University of Bologna
18 PUBLICATIONS **31** CITATIONS

SEE PROFILE

Emilio José Cocinero
Universidad del País Vasco / Euskal Herriko …
111 PUBLICATIONS **1,184** CITATIONS

SEE PROFILE

# Halogen−Halogen Links and Internal Dynamics in Adducts of Freons

Qian Gou,[†] Lorenzo Spada,[†] Emilio J. Cocinero,[‡] and Walther Caminati*,[†]

[†]Dipartimento di Chimica, "G. Ciamician" dell'Università, Via Selmi 2, I-40126 Bologna, Italy

[‡]Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV-EHU), Apartado 644, E-48940 Bilbao, Spain

S *Supporting Information*

ABSTRACT: The pulsed jet Fourier transform microwave spectrum of the 1:1 complex between CF_3Cl and CH_3F shows that the two moieties are linked by a $Cl\cdots F$ halogen bond ($R_{Cl\cdots F}$ = 2.995 Å). The two symmetric tops CF_3 and CH_3 undergo free or almost free internal rotations, which alter the "rigid" value of the rotational constant A by almost 1 order of magnitude.

$R(Cl\cdots F)$ = 2.995 Å
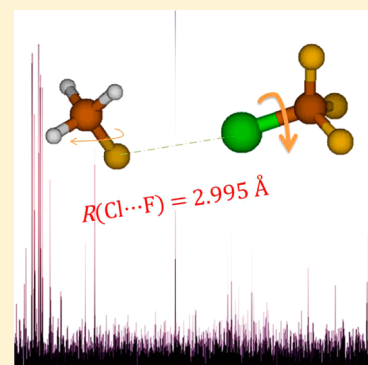
SECTION: Spectroscopy, Photochemistry, and Excited States

Considerable attention has been devoted in recent years to chlorofluorocarbons (CFCs) and to their impact on the atmospheric processes, in relation to both the role in ozone reduction and the greenhouse effect. The complexation of CFCs with atmospheric water and pollutants of the atmosphere affects their reactivity, and it seems to accelerate, for example, the decomposition rate of freons in the atmosphere.[1]

Precise information on the shapes, stabilities, structures, and internal dynamics of the complexes of CFCs with water and of their dimers or oligomers can be obtained from their investigations in isolation, free from solvent effects or solid-state linkages. The most popular techniques for these purposes are vibrational spectroscopy in cryogenic solutions[2] or rotational spectroscopy.[3,4]

Generally CFCs containing hydrogen form adducts with other molecules through weak hydrogen bonds (WHBs). Their C−H groups could indeed act as proton donors, a property enhanced by the electron withdrawing of the halogen atoms, and interact with the electron-rich regions of the partner molecules.[5,6] In addition, in adducts or oligomers of CFCs containing hydrogen, the monomer units are held together by networks of WHBs.[7−10] When CFCs do not contain hydrogen, the positive electrostatic region ("σ-hole")[4,11] can interact electrostatically with negative sites of another or of the same molecular entity, giving rise, according to IUPAC, to the so-called halogen bond (HaB).[12] However, it has been observed that when a CFC does not contain hydrogen and has a π electron system, a lone pair···π interaction (Bürgi−Dunitz) is favored.[13]

It has been found with rotational spectroscopy, for example, that CF_4 forms a trifurcated HaB with water ($CF_3\cdots O$)[14] and

with pyridine ($CF_3\cdots N$),[15] while strong dynamic effects considerably alter the values of the "rigid rotor limit" rotational constants. In addition, CF_4−H_2O, which is expected to be a classical asymmetric top, is found to be a quantum mechanical symmetric top. A good prototype molecule for investigating the HaB has been found to be CF_3Cl, whose Cl atom forms very easily HaBs. CF_3Cl forms, indeed, a C−Cl···O HaB with H_2O[16] and dimethyl ether[17] and a C−Cl···N HaB with NH_3,[18] in preference to the most common hydrogen bond. Also in the cases of CF_3Cl−H_2O and CF_3Cl−NH_3, strong dynamic effects have been observed; water and ammonia undergo effective free rotations with respect to the CF_3Cl, making the complex CF_3Cl−H_2O an effective symmetric top despite being an asymmetric rotor from theoretical calculations. In the case of CF_3Cl−dimethyl ether, the free internal rotation of the CF_3 group causes an unexpectedly large value of the rotational constant A.

After having characterized the C−Cl···O and the C−Cl···N HaBs using CF_3Cl as the "halogen donor", we decided to describe the C−Cl···F halogen−halogen bond by studying the rotational spectrum of CF_3Cl−FCH_3, which is the molecular adduct formed by Freon-13 and Freon-41. This 1:1 complex has been recently investigated using Fourier transform infrared and Raman spectroscopy in liquid krypton.[19] The authors discussed the existence of the C−Cl···F HaB, mainly based on their ab initio calculations. Surprisingly, the angles of HaBs predicted by ab initio methods are 169.9 and 109.4° for ∠C−

Cl···F and ∠C−F···Cl, respectively, far from the 180° ideal angles for HaB according to IUPAC. "The angle R−X···Y tends to be linear (180°)". The halogen atom X tends to align with the direction of the axis of the n-lone pair on Y or the π-bond electron pair in Y−Z". We believe that precise experimental information on the structure and internal dynamics can be supplied by the rotational spectrum. Below, we report the obtained results.

A MP2/aug-cc-pVDZ(-PP) ab initio investigation of $CF_3Cl-FCH_3$ is reported in ref 19. The authors present only one conformation and do not report any spectroscopic constant useful for the rotational spectroscopy investigation. For this reason, we performed our own calculations. We preliminarily explored the conformational space of the complex by molecular mechanics, using the conformational search algorithms implemented in MacroModel 9.2 within the MMFFs force field.[20] We found about 100 different geometries within an energy window of about 13 kJ mol^{-1}, which, at the MP2/6-311++G(d,p) level,[21] converged to the four most stable conformers (relative energies ΔE < 2 kJ mol^{-1}). All four conformers are characterized by C-X···F (X = F or Cl) HaBs.

In addition, the C−H···F WHBs contribute to the stabilities of conformers I and II. Vibrational frequency calculations at the same level of theory proved conformers I, II, and III to be real minima, while a negative frequency was found for conformer IV. However, when taking account of the basis set superposition error (BSSE) corrections,[22] conformer IV becomes, surprisingly, the one with the lowest energy. Shapes, relative energies, BSSE dissociation energies (E_D), calculated rotational constants, dipole moment components, and ^{35}Cl quadrupole coupling constants of the four conformers are summarized in Table 1.

Table 1. MP2/6-311++G(d,p) Shapes and Spectroscopic Parameters of the Four Most Stable Conformers of CF$_3$Cl−CH$_3$F

	I	II	III	IV
ΔE/kJ mol^{-1}	0.0[a]	0.9	1.0	1.3
ΔE_0/kJ mol^{-1}	0.0[b]	1.2	0.7	0.5
ΔE_{BSSE}/kJ mol^{-1}	2.7	3.6	0.3	0.0[c]
E_D/kJ mol^{-1}	1.8	0.8	4.2	4.5
A/MHz	3028	4708	4788	5512
B/MHz	1256	976	691	611
C/MHz	1058	948	678	611
μ_a/D	-0.9	0.2	-1.6	-3.2
μ_b/D	-0.1	-1.2	-1.8	0.0
μ_c/D	1.2	1.4	1.0	0.0
χ_{aa}/MHz	37.4	-69.9	-70.2	-74.3
$(\chi_{bb}-\chi_{cc})$/MHz	-109.9	-0.7	-4.2	0.0
χ_{ab}/MHz	-10.2	-18.2	20.3	0.0
χ_{ac}/MHz	0.1	-0.5	-0.4	0.0
χ_{bc}/MHz	1.7	-0.1	0.0	0.0

[a]Absolute energy E = −936.076714 E_h.   [b]Absolute energy E_0 = −936.113783 E_h.   [c]Absolute energy E_{BSSE} = −936.130914 E_h.

Following extensive spectral searches for the various conformers, we could identify, based on their ^{35}Cl quadrupole pattern, the $6_{06} \leftarrow 5_{05}$, $7_{07} \leftarrow 6_{06}$, and $8_{08} \leftarrow 7_{07}$ rotational transitions of conformer III. After that, we had some difficulties with the assignment of the corresponding $K_{-1} = 1$ transitions. We could finally identify these six transitions, again from the ^{35}Cl quadrupole pattern, which is shown in Figure 1 for the 6_{15}
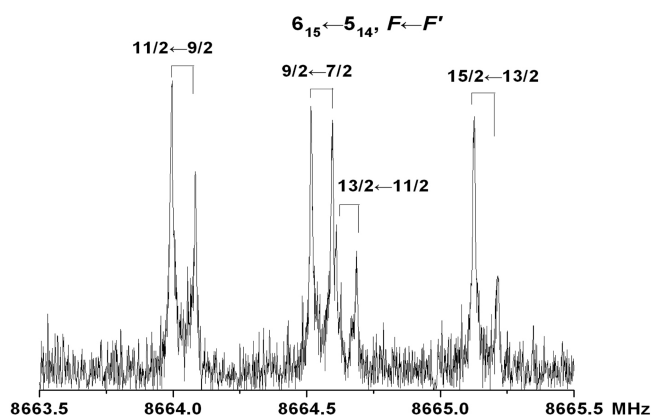

Figure 1. ^{35}Cl quadrupole hyperfine structure of the $6_{15} \leftarrow 5_{14}$ transition of CF$_3$^{35}Cl−CH$_3$F. Each line appears as a doublet due to the Doppler effect.

$\leftarrow 5_{14}$ transition. However, their insertion in the fitting produced an unexpectedly high value of the rotational constant A. We will see in a following section that this effect is due to the almost free internal rotations of the CF$_3$ and CH$_3$ tops.

It was then possible to assign the $K_{-1} = 0, 1$ transitions for all of the J values from 5 to 12. The observed transition lines were fitted using Pickett's SPFIT program,[23] according to the following Hamiltonian

$$H = H_R + H_{CD} + H_Q \tag{1}$$

where H_R represents the rigid rotational parts of the Hamiltonian. The centrifugal distortion contributions (analyzed using the S reduction and I^r representation)[24] 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 summarized in the first column of Table 2.

As one can see, the rotational constants B and C as well as the quadrupole coupling constants match best the corresponding theoretical values of conformer III. On the other hand, as previously outlined, the rotational constant A is 4−5 times larger than the theoretical value.

Furthermore, we could then assign the rotational spectrum of the ^{37}Cl isotopologue in natural abundance. Its rotational transitions are just a few MHz lower in frequency than those of the parent species. This is in agreement with the fact that the Cl atom lies very close to the center of mass of the adduct. The assignment of the spectrum was facilitated by two factors, (i) the ^{37}Cl quadrupole splittings, which are about 80% of those of the ^{35}Cl isotopologue (according to the ratio of the electric nuclear quadrupole moments Q), and (ii) the intensity of the lines, which is about one-third of that of the parent species. The obtained spectroscopic constants are listed in the second column of Table 2.

Finally, we measured the rotational spectra of two more isotopologues (^{35}Cl and ^{37}Cl) in which CH$_3$F is replaced by CD$_3$F. The results of the fittings are reported in the two right-hand columns of Table 2. The rotational constants A for both deuterated isotopologues are much smaller than those of the CH$_3$F species.

All measured transition frequencies are available in the Supporting Information.

In the observed conformer (see Figure 2, where the inertial principal axis system and the atom numbering are also shown), the angles ∠C1Cl2F6 and ∠Cl2F6C7 have the ab initio values

Table 2. Experimental Spectroscopic Constants of CF₃Cl−CH₃F

	CF₃³⁵Cl−CH₃F	CF₃³⁷Cl−CH₃F	CF₃³⁵Cl−CD₃F	CF₃³⁷Cl−CD₃F
A/MHz	21826(28)[a]	21573(64)	17264(35)	17079(39)
B/MHz	728.2164(3)	728.1154(2)	685.7804(4)	685.7554(4)
C/MHz	702.9987(3)	702.7130(3)	658.9718(4)	658.7455(4)
D_J/kHz	0.9363(8)	0.929(3)	0.961(1)	0.956(2)
D_{JK}/MHz	−0.2376(2)	−0.2360(3)	−0.1483(3)	−0.1469(4)
d_1/kHz	−0.1052(6)	[−0.1052][b]	−0.1279(9)	[−0.1279][b]
χ_{aa}/MHz	−73.3(1)	−58.1(2)	−72.3(2)	−57.1(2)
$\chi_{bb}-\chi_{cc}$/MHz	−5.2(3)	−4.3(4)	−6.4(4)	−5.2(4)
χ_{ab}/MHz	29.0(7)	22(1)	26(1)	18.7(9)
N^c	80	52	64	56
σ^d/kHz	2.9	1.7	1.9	2.4

[a]The error in parentheses is expressed in units of the last digit. [b]Fixed at the value of the ³⁵Cl isotopologue. [c]Number of transitions in the fit. [d]Standard deviation of the fit.
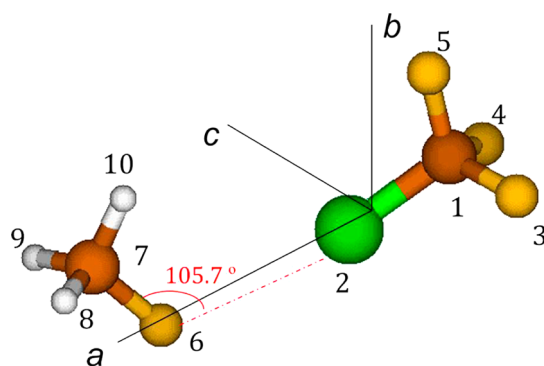

Figure 2. Shape, atomic numbering, and principal axes of the observed configuration of CF₃Cl−CH₃F. The value of the ∠Cl2F6C7 angle, quite smaller than the ab initio datum, is also given.

of 173.8 and 118.7°, respectively. The full ab initio geometry is available in the Supporting Information. By adjusting the value of ∠Cl2F6C7 to 105.7° (see Figure 2), we could satisfactorily reproduce the experimental rotational constants B and C of all isotopologues. The r_0 HaB distance nearly coincides with the ab initio value, $R_{Cl\cdots F} = 2.995$ Å. We also derived the distance $R_{F5H10} = 4.554$ Å, which is larger than that expected for a WHB.

Back to the aforementioned disagreement of the rotational constant A between the fitted values and the calculated values, the enormously large discrepancies can be, as in CF₃Cl−dimethyl ether,[16] accounted for by the effects of free (or almost free) internal rotations of the CF₃ and CH₃ groups about their symmetry axes. We could explain it qualitatively if we take into account the effective rotational constants of the ground state, $\nu = 0$ and $\sigma = 0$ ($\sigma = 0, \pm1$ for A and E species, respectively) and assuming no coupling between the two free internal motions, according to[25]

$$A_{00} = A_r + [W_{00}^{(2)}F\rho_a^2]_{CF3} + [W_{00}^{(2)}F\rho_a^2]_{CH3}$$

$$B_{00} = B_r + [W_{00}^{(2)}F\rho_b^2]_{CF3} + [W_{00}^{(2)}F\rho_b^2]_{CH3}$$

$$C_{00} = C_r + [W_{00}^{(2)}F\rho_c^2]_{CF3} + [W_{00}^{(2)}F\rho_c^2]_{CH3} \quad (2)$$

where A_r, B_r, and C_r are the "rigid" rotational constants in the limit of both infinite barriers. The $W_{00}^{(2)}$ are the Herschbach's barrier-dependent perturbation sums relative to the sublevels of the A symmetry ($\sigma = 0$) species of the torsional ground state ($\nu = 0$) with $\rho_g = \lambda_g I_\alpha/I_g$ depending on the moments of inertia along the symmetry axis α of the internal rotor and the

principal axis g and their directional cosine λ_g. $F = \hbar/[2\cdot(1 - \sum_g \lambda_g I_\alpha/I_g)I_\alpha]$ is the reduced rotational constant of the CH₃ or of the CF₃ top. Tables of the $W_{00}^{(n)}$ as a function of the reduced barrier s are available.[25] The parameter s is, in turn, related to the V_3 barrier according to $V_3 = 0.215sF$.

In Table 3, we report the values of the $F\rho_g^2$ parameters (g = a, b) of the two tops for the four isotopologues. By inspection

Table 3. Values of the $F\rho_g^2$ Parameters for the CF₃ and CH₃ (or CD₃) Tops of the Four Isotopologues of CF₃Cl−CH₃F

		CF₃³⁵Cl−CH₃F	CF₃³⁷Cl−CH₃F	CF₃³⁵Cl−CD₃F	CF₃³⁷Cl−CD₃F
CF₃	$F\rho_a^2$/MHz	17074.0	16932.5	13082.5	12973.4
	$F\rho_b^2$/MHz	16.7	16.6	14.7	14.6
CH₃	$F\rho_a^2$/MHz	17.6	17.6	35.7	35.5
	$F\rho_b^2$/MHz	3.0	3.0	5.2	5.2

of Figure 2, the c-axis of the complex is perpendicular to the internal rotation axis of both the CH₃ and CF₃ tops. Then λ_c, ρ_c, and $F\rho_c^2$ are zero, and the rotational constant C is not affected by the internal rotations of the two tops. On the other hand, one can see that the $F\rho_a^2$ values for the CF₃ groups, which alter the rotational constants A with respect to their rigid values, are 3 orders of magnitude larger than any other term. In addition, their magnitudes, decreasing from CF₃³⁵Cl−CH₃F to CF₃³⁷Cl−CD₃F follow the magnitudes of the A rotational constants.

Because CF₃ has a much larger reduced mass than CH₃, with much larger value of the term $F\rho_g^2$, the contribution to the rotational constants from the internal rotation of CH₃ becomes negligible. The rotational constant B is only slightly affected by the internal rotation of CF₃, because the angle between the internal rotation axis of CF₃ and the principal axis b are almost 90° according to the ab initio geometry. The rotational constants A are much more strongly affected by the free internal rotation of CF₃ because the CF₃ internal rotation axis is nearly parallel to the a-axis.

By applying the differences between the model calculated (after the above-mentioned structural adjustment, $A_r = 4647$, 4639, 4444, and 4436 MHz, for the four isotopologues, respectively) and the experimental values of A (see Table 2) to eq 2, one could calculate the barrier to the internal rotation of CF₃. All four isotopologues give $W_{00}^{(2)} \approx 1.0$, which

corresponds to a very small internal rotational barrier, $V_3 \approx 7$ cal mol^{-1}.

This value of $W_{00}^{(2)}$ can also interpret the near-zero values of the inertial defects, which should be, in the rigid approximation, $\Delta_c = -91.7$ or -95.0 au Å^2 for the CH$_3$ and CD$_3$ forms, respectively. The values of the inertial defects obtained from the experimental rotational constants are 1.7, 1.7, 0.7, and 0.6 au Å^2 for the four isotopologues, respectively. Their uncertainties are relatively large due to large errors on the values of the rotational constants A, but the positive values suggest considerable contributions from the in-plane motions.

This Fourier transform microwave spectroscopy investigation of the rotational spectra of CF$_3$Cl−CH$_3$F and of its isotopologues points out irrefutably that its most stable configuration is established by a Cl···F HaB. This is, to our knowledge, the first time that this interaction is observed and described through a rotational study in an adduct made of two freon molecules. CF$_3$Cl is a prototype halogen donor that we used to structurally, conformationally, and energetically analyze the Cl···O,[15] Cl···N,[17] and Cl···F (this work) HaBs that it forms with H$_2$O, NH$_3$, and CH$_3$F.

In addition, we could discover and interpret the effects of the two free or near-free internal rotations of the two constituent subunits and show how dramatically they change the values of the A rotational constant.

This study provides further interesting experimental evidence on the nature of weak interactions obtained 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 microwave[26] spectrometer (COBRA-type[27]), which covers the range of 6.5−18 GHz, have been described previously.[28]

A gas mixture of ∼1% of CF$_3$Cl and CH$_3$F or CD$_3$F in helium 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 a doublet 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.

■ ASSOCIATED CONTENT

⑤ Supporting Information

(1) Completion of ref 21; (2) Table of transition frequencies; and (3) MP2/6-311++G(d,p) geometry of the observed conformer. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: walther.caminati@unibo.it.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ ABBREVIATIONS

CFC: chlorofluorocarbon
WHB: weak hydrogen bond
HaB: halogen bond
BSSE: basis set superposition error

■ REFERENCES

(1) Vaida, V.; Kjaergaard, H. G.; Feierabend, K. J. Hydrated Complexes: Relevance to Atmospheric Chemistry and Climate. *Int. Rev. Phys. Chem.* **2003**, *22*, 203−219.

(2) See, for example: Hauchecorne, D.; Szostak, R.; Herrebout, W. A.; van der Veken, B. J. C−X···O Halogen Bonding: Interactions of Trifluoromethyl Halides with Dimethyl Ether. *ChemPhysChem* **2009**, *10*, 2105−2115 , and refs therein..

(3) Legon, A. C. Prereactive Complexes of Dihalogens XY with Lewis Bases B in the Gas Phase: A Systematic Case for the Halogen Analogue B···XY of the Hydrogen Bond B···HX. *Angew. Chem., Int. Ed.* **1999**, *38*, 2686−2714.

(4) Legon, A. C. The Halogen Bond: An Interim Perspective. *Phys. Chem. Chem. Phys.* **2010**, *12*, 7736−7747.

(5) Caminati, W.; Melandri, S.; Rossi, I.; Favero, P. G. The C−F···H-O Hydrogen Bond in the Gas Phase. Rotational Spectrum and Ab Initio Calculations of Difluoromethane−Water. *J. Am. Chem. Soc.* **1999**, *121*, 10098−10101.

(6) Caminati, W.; Melandri, S.; Maris, A.; Ottaviani, P. Relative Strengths of the O−H···Cl and O−H···F Hydrogen Bonds. *Angew. Chem., Int. Ed.* **2006**, *45*, 2438−2442.

(7) Caminati, W.; Melandri, S.; Moreschini, P.; Favero, P. G. The C−F···H−C "Anti-Hydrogen Bond" in the Gas Phase: Microwave Structure of the Difluoromethane Dimer. *Angew. Chem., Int. Ed.* **1999**, *38*, 2924−2925.

(8) Blanco, S.; Melandri, S.; Ottaviani, P.; Caminati, W. Shapes and Noncovalent Interactions of Oligomers: The Rotational Spectrum of the Difluoromethane Trimer. *J. Am. Chem. Soc.* **2007**, *129*, 2700−2703.

(9) Feng, G.; Cacelli, I.; Carbonaro, L.; Prampolini, G.; Caminati, W. Oligomers Based on Weak Hydrogen Bond Networks: A Rotational Study of the Tetramer of Difluoromethane. *Chem. Commun.* **2014**, *50*, 171−173.

(10) Gou, Q.; Spada, L.; Vallejo-López, M.; Kisiel, Z.; Caminati, W. Interactions between Freons: a Rotational Study of CH$_2$F$_2$−CH$_2$Cl$_2$. *Chem. Asian J.* **2014**, *9*, 1032−1038.

(11) Politzer, P.; Lane, P.; Concha, M. C.; Ma, Y.; Murray, J. S. An Overview of Halogen Bonding. *J. Mol. Model.* **2007**, *13*, 305−311.

(12) Desiraju, G. R.; Ho, P. S.; Kloo, L.; Legon, A. C.; Marquardt, R.; Metrangolo, P.; Politzer, P.; Resnati, G.; Rissanen, K. Definition of the Halogen Bond (IUPAC Recommendations 2013). *Pure Appl. Chem.* **2013**, *85*, 1711−1713.

(13) Gou, Q.; Feng, G.; Evangelisti, L.; Caminati, W. Lone-Pair···π Interaction: A Rotational Study of the Chlorotrifluoroethylene−Water Adduct. *Angew. Chem., Int. Ed.* **2013**, *52*, 11888−11891.

(14) Caminati, W.; Maris, A.; Dell'Erba, A.; Favero, P. G. Dynamical Behavior and Dipole−Dipole Interactions of Tetrafluoromethane−Water. *Angew. Chem., Int. Ed.* **2006**, *45*, 6711−6714.

(15) Maris, A.; Favero, L. B.; Velino, B.; Caminati, W. Pyridine−CF$_4$: A Molecule with a Rotating Cap. *J. Phys. Chem. A* **2013**, *117*, 11289−11292.

(16) Evangelisti, L.; Feng, G.; Écija, P.; Cocinero, E. J.; Castaño, F.; Caminati, W. The Halogen Bond and Internal Dynamics in the Molecular Complex of CF$_3$Cl and H$_2$O. *Angew. Chem., Int. Ed.* **2011**, *50*, 7807−7810.

(17) Evangelisti, L.; Feng, G.; Gou, Q.; Grabow, J.-U.; Caminati, W. Halogen Bond and Free Internal Rotation: The Microwave Spectrum of CF$_3$Cl−Dimethylether. *J. Phys. Chem. A* **2014**, *118*, 579−582.

(18) Feng, G.; Evangelisti, L.; Gasparini, N.; Caminati, W. On the Cl···N Halogen Bond: A Rotational Study of CF$_3$Cl···NH$_3$. *Chem.—Eur. J.* **2012**, *18*, 1364−1368.

(19) Hauchecorne, D.; Herrebout, W. A. Experimental Characterization of C−X···Y−C (X= Br, I; Y= F, Cl) Halogen−Halogen Bonds. *J. Phys. Chem. A* **2013**, *117*, 11548−11557.

(20) *MASTRO*, version 9.2; Schrödinger, LLC: New York, 2012.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *GAUSSIAN09*; Gaussian, Inc.: Wallingford, CT, 2009.

(22) Boys, S. F.; Bernardi, F. The Calculations of Small Molecular Interactions by the Differences of Separate Total Energies. Some Procedures with Reduced Errors. *Mol. Phys.* **1970**, *19*, 553−566.

(23) Pickett, H. M. Vibration−Rotation Interactions and the Choice of Rotating Axes for Polyatomic Molecules. *J. Chem. Phys.* **1972**, *56*, 1715−1723.

(24) Watson, J. K. G. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: New York/Amsterdam, The Netherlands, 1977; Vol. *6*, pp 1−89.

(25) Herschbach, D. R. Calculation of Energy Levels for Internal Torsion and Over-All Rotation. III. *J. Chem. Phys.* **1959**, *31*, 91−108.

(26) Balle, T. J.; Flygare, W. H. Fabry−Perot Cavity Pulsed Fourier Transform Microwave Spectrometer with a Pulsed Nozzle Particle Source. *Rev. Sci. Instrum.* **1981**, *52*, 33−45.

(27) Grabow, J.-U.; Stahl, W.; Dreizler, H. A Multioctave Coaxially Oriented Beam-Resonator Arrangment Fourier-Transform Microwave Spectrometer. *Rev. Sci. Instrum.* **1996**, *67*, 4072−4084.

(28) Caminati, W.; Millemaggi, A.; Alonso, J. L.; Lesarri, A.; López, J. C.; Mata, S. Molecular Beam Fourier Transform Microwave Spectrum of the Dimethylether−Xenon Complex: Tunnelling Splitting and [131]Xe Quadrupole Coupling Constants. *Chem. Phys. Lett.* **2004**, *392*, 1−6.