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Competition between weak hydrogen bonds: C-H···Cl is preferred to C-H···F in CH2ClF-H2CO, as revealed by rotational spectroscopy

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We measured the pulsed jet Fourier transform microwave spectrum of the 1:1 adduct of CH_2ClF with formaldehyde. Formaldehyde is linked to CH_2ClF through a C-H···Cl rather than a C-H···F weak hydrogen bond, with a H···Cl "bond length" of 2.918 Å. Two additional equivalent C-H···O contacts, with a H···O distance of 2.821 Å, characterize the complex. Tunnelling splittings due to the internal rotation of the formaldehyde moiety have been observed, which allowed estimating the barrier to the internal rotation of formaldehyde to be 125(10) cm^{-1}. The ^{35}Cl quadrupole coupling constants have been determined to be $\chi_{aa} = 31.131(7)$ MHz and $\chi_{bb}-\chi_{cc} = -105.82(1)$ MHz.

Introduction

Rotational spectroscopy investigations of the adducts of water with a variety of organic molecules (ethers, esters, amines, diazines, carboxylic acids, etc.) provided information on "classical" hydrogen bonds (HBs), such as O–H···O, O–H···N, O–H···S, and N-H···O.[1] The corresponding interaction energies are in the range 15-25 kJmol^{-1}. Weaker HBs of the type O–H···F and O–H···Cl (8-10 kJmol^{-1}) link water to halogenated alkanes. It has been found that O–H···Cl is preferred to O–H···F in the complex CH_2ClF-H_2O,[2] but the contrary was found for the molecular system 1,1-Cl,F-ethane-H_2O.[3]

Conversely, rotational studies of molecular complexes formed by freons and other various types of organic molecules, or their oligomers, have shown that the constituent units are primarily held together through weak hydrogen bonds (WHB) like C–H···O,[4] C–H···N,[5] C–H···π[6] and C–H···X (X=F, Cl),[7,8] whose interaction energies have been estimated to be a few kJmol^{-1}. In these cases, small molecular changes can affect the structure dramatically, reflecting the delicate balance of intermolecular forces and the role of HB cooperativity.

We have additionally observed that in complexes of freons with water, like CH_2F_2-H_2O[9], water can be substituted by formaldehyde (H_2CO), which forms C–H···F and C–H···O=C WHBs with CH_2F_2.[10] Moreover, H_2CO has the same symmetry of water, and displays, in the complex with CH_2F_2 the same internal dynamics effects of water, the internal rotation around its C_2 axis.

It thus appears interesting to investigate the complex of H_2CO with CH_2ClF, in order to see which of the two halogen atoms, F or Cl, is the best proton acceptor for the C-H formaldehyde group. Herein, we report the results of the investigation of the rotational spectra of several isotopologues of the complex of CH_2ClF-H_2CO.

Experimental Section

Commercial samples of CH_2ClF and paraformaldehyde were obtained from Aldrich and used without further purification. The rotational spectra in the 6-18.5 GHz frequency region were measured on a COBRA-type[11] pulsed supersonic-jet Fourier-transform microwave (FTMW) spectrometer,[12] described elsewhere.[13]

A gas mixture of 2% CH_2ClF in Helium at a total pressure of 0.3 MPa was streamed over paraformaldehyde which has been earlier heated to 350 K, and expanded through the solenoid valve (General Valve, Series 9, nozzle diameter 0.5 mm) into the Fabry-Pérot-type cavity. Due to the coaxial arrangement of the molecular beam expansion and the resonator axes, each rotational transition displays an enhanced Doppler splitting. 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

In order to estimate the shapes and relative energies of the plausible conformations of CH_2ClF-H_2CO, we performed geometry optimizations at the MP2/6-311++G(d,p) level of theory with Gaussian 03 program.[14] Several stationary points were found, but frequency calculations proved only three of them to be real minima.

Table 1: MP2/6-311++G(d,p) spectroscopic parameters of the plausible conformers of CH_2ClF-H_2CO.

	I	II	III
$\Delta E, \Delta E_0, \Delta E_{CC}$/cm^{-1}	0, 0, 0^a	68, 37, 71	130, 81, 102
ΔE_{BSSE}/cm^{-1}	10	0^b	7
$E_{B0}, E_{B0,BSSE}$/kJmol^{-1}	13.3, 6.4^a	12.8, 6.9	12.3, 7.0
A/MHz	4975.9	6013.6	13387.9
B/MHz	1995.2	1625.1	1196.1
C/MHz	1634.7	1290.1	1105.9
χ_{aa}/MHz	28.21	30.11	-67.35
$(\chi_{bb}-\chi_{cc})$/MHz	-59.08	-102.32	-6.48
Δ_c/uÅ^2	-45.71	-3.29	-3.26
$|\mu_a|, |\mu_b|, |\mu_c|$/D	0.3,0.0,0.4	3.2,0.8,0.0	2.3,0.4,0.0
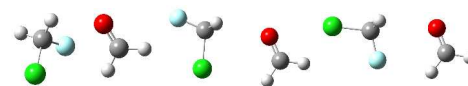
^{a}Relative energies without and with zero point vibrational corrections. Absolute energies are -712.752216 and -712.692134 E_h, respectively.
^{b}Absolute energy = -712.749651 E_h.

Their shapes, relative energies, rotational and quadrupole coupling constants, and dipole moment components are reported in Table 1. In conformer I, one C-H hydrogen of H_2CO is in contact with both the fluorine and chlorine atoms of CH_2ClF, while the oxygen atom interacts with the C-H hydrogen atoms of CH_2ClF. Conformer II displays a C–H$\cdots$Cl interaction and two C–H$\cdots$O=C interactions, whereas conformer III displays a C–H$\cdots$F interaction and two C–H$\cdots$O=C interactions.

In order to remove the well known basis set superposition error (BSSE), we calculated counterpoise corrections[15] to the MP2/6-311++G(d,p) energies. After including these corrections, the three conformers appear almost iso-energetic, with a maximum energy difference of ~10 cm^{-1}. However, the global minimum switched to conformer II. The theoretical structures of conformer I and III are given as ESI†, while the structure of conformer II will be discussed in one of the next sections. We also calculated the zero point dissociation energies without and with BSSE corrections (E_{B0} and $E_{B0,BSSE}$ in Table 1). Finally, we calculated the relative energies of the three conformers at the CCSD//MP2/6-311++G(d,p) level (ΔE_{CC}), also given in Table 1.

Rotational spectra

Following the *ab initio* indications, the first search for rotational transitions was focused on the μ_a-R-type bands of conformer II. We easily identified the $K_a = 0$, 1 transitions of the $J = 3 \leftarrow 2$ band. Each transition appeared as a multiplet, due to the nuclear quadrupole coupling of ^{35}Cl nucleus and to the splitting into two tunnelling states (labelled as $v = 0$ and 1) caused by the internal rotation of H_2CO. Figure 1 shows the tunnelling splitting and the quadrupole hyperfine structure of the $3_{1,3} \leftarrow 2_{1,2}$ transition (in addition, component lines appear as a doublet due to the above mentioned instrumental Doppler effect). One should note that the intensities of the $v = 0$ component lines are about one third of those of the $v = 1$ state, which is in accord with the fact that the exchange of the two protons (which are $I = 1/2$ fermions) requires a total anti-symmetric wave-function and a 3:1 ratio between symmetric and antisymmetric spin functions.
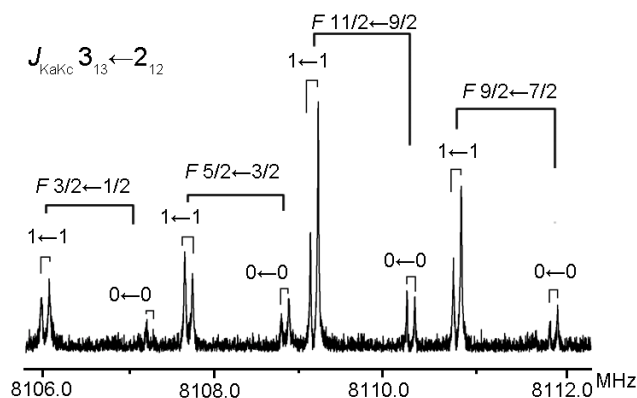
Fig. 1. Recorded $3_{13} \leftarrow 2_{12}$ transition of the observed conformer of CH_2ClF-H_2CO showing the ^{35}Cl hyperfine structure and the tunnelling splitting due to the internal rotation of formaldehyde. In addition, each component line displays the instrumental Doppler doubling.

Then, many more μ_a-type transitions and several μ_b-type transitions were measured. The lines were used to determine the spectroscopic constants collected in the left columns of Table 2. The fits were performed with Pickett's SPFIT program[16] according to the following Hamiltonian:

$$H = H_R(0) + H_R(1) + H_{CD} + H_Q \quad (1)$$

$H_R(0)$ and $H_R(1)$ represent the rigid rotational parts of the Hamiltonian for the $v = 0$ and the $v = 1$ states. The centrifugal distortion part H_{CD} was analyzed using S reduction and I^r representation.[17] H_Q takes into account the interaction of the overall rotation with the ^{35}Cl nuclear spin.[18]

Table 2: Experimental spectroscopic parameters of CH_2ClF-H_2CO.

	^{35}Cl		^{37}Cl	
	0	1	0	1
A/MHz	5984.591(2)^a	5982.678(2)	5818.926(4)	5817.196(4)
B/MHz	1598.0839(4)	1597.4318(4)	1593.4878(3)	1592.8376(3)
C/MHz	1272.0274(4)	1271.9895(4)	1261.4602(2)	1261.4242(2)
Δ_c/uÅ^2	-3.38	-3.53	-3.37	-3.52
χ_{aa}/MHz	31.131(7)		24.56(3)	
$(\chi_{bb}-\chi_{cc})$/MHz	-105.82(1)		-83.55(4)	
D_J/kHz	1.595(2)		[1.595]^b	
D_{JK}/kHz	17.78(4)		[17.78]	
d_1/kHz	-0.329(3)		[-0.329]	
d_2/kHz	-0.086(2)		[-0.086]	
σ^c/kHz	3.0		4.2	
N^d	150		70	

^{a} Error in parentheses in units of the last digit. ^{b} Values in brackets fixed to those of parent species. ^{c} RMS error of the fit. ^{d} Number of lines in the fit.

The spectrum of the ^{37}Cl isotopologue was also measured and fitted similarly. The results are reported in the right columns of Table 2. The search for rotational transitions of other conformers was unsuccessful. All measured transition lines are given in the ESI

Conformation and structure

By comparing the observed rotational and quadrupole coupling constants to the theoretical values of Table 1, it appears straightforward to assign the observed spectrum to conformer II.

As additional argument the substitution coordinates of the Cl atom,[19] $a = \pm0.684(2)$ and $b = \pm1.110(1)$ Å, respectively, are in a good agreement with the *ab initio* values of conformer II ($a = -0.668$ and $b = +1.117$ Å, respectively), confirming the conformational assignment.

Finally, the value of the inertia defect Δ_c (-3.38 for the ground state, see Table 2), is in agreement with the two out of plane methylenic hydrogens of CH_2ClF in conformer II.

**Table 3**: r_0 and r_e (MP2/6-311++G(d,p)) geometries of CH_2ClF-H_2CO.

Bond length/Å		Valence angle/°		Dihedral angel/°	
Cl2C1	1.770				
F3C1	1.370	F3C1Cl2	109.7		
H4C1	1.086	H4C1F3	109.0	H4C1F3Cl2	118.7
H5C1	1.086	H5C1F3	109.0	H5C1F3H4	122.6
O6Cl2	**3.554(8)**^{a}	O6Cl2C1	**61.9(2)**	O6Cl2C1F3	180.0
C7O6	1.215	C7O6Cl2	**83(1)**	C7O6Cl2C1	180.0
H8C7	1.104	H8C7O6	121.6	H8C7O6C1	0.0
H9C7	1.104	H9C7O6	121.6	H9C7O6H8	180.0

Derived structural parameters			
r_1/Å	2.918	α/°	120.8
r_2/Å	2.821	β/°	96.6
R/Å	3.700	γ/°	96.7

^{a}The parameters in bold have been adjusted to reproduce the experimental values of the rotational constants, uncertainties (in parentheses) are given

in units of the last digit. Their ab initio values are: 3.021 Å, 88.4 ° and 120.4°, respectively.

From the six available experimental rotational constants, we calculated a partial r_0 structure, varying the intermolecular distances and angles while keeping the geometry of the CH_2ClF and H_2CO monomers fixed to the *ab initio* values in the complex. The distance between the oxygen atom of H_2CO and the chlorine atom of CH_2ClF, the angles $\angle O\cdots ClC$ and $\angle CO\cdots Cl$ are required to be corrected in order to reduce the discrepancies between experimental and calculated rotational constants. The corrected structure parameters are reported in Table 3 together with the r_e values. The atom numbering and principal axis system are given in Figure 2.

The structural hydrogen bond parameters derived from partial r_0 structure are reported at the bottom of Table 3 (R is the distance between the centres of mass of the two constituent molecules).
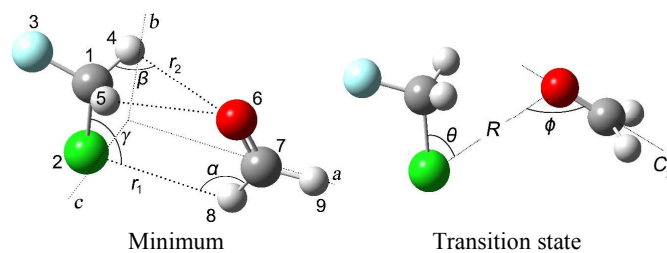
Fig. 2. LEFT: Shape, principal axis system, atom numbering and hydrogen bond structural parameters of the observed complex. RIGHT: shape of the transition state for the internal rotation of H_2CO and parameters relevant to the flexible model calculations.

Internal dynamics

The observed doubling of the rotational transitions allowed estimating the barrier to internal rotation of H_2CO by using Meyer's one dimensional flexible model.[20] The following potential energy function has been chosen:

$$V(\tau) = V_2[1\text{-}\cos(2\tau)] \tag{2}$$

where V_2 is the barrier to the internal motion and τ is the internal rotation coordinate. $\tau = 0°$ represents the equilibrium value with formaldehyde lying in the Cl-C-F plane and $\tau = 90°$ corresponds to the transition state of the internal motion. The structure relaxations of the parameters R, θ and ϕ have been taken into account according to:

$$R(\tau) = R_0 + 1/2 \, \Delta R \, [1 - \cos (2\tau)]$$

$$\theta(\tau) = \theta_0 + 1/2 \, \Delta\theta \, [1 - \cos (2\tau)] \tag{3}$$

$$\phi(\tau) = \phi_0 + 1/2 \, \Delta\phi \, [1 - \cos (2\tau)]$$

where R_0, θ_0 and ϕ_0 are the values of $O\cdots Cl$ distance, the angle C-$Cl\cdots O$ and the angle $Cl\cdots O=C$ at the minimum ($\tau = 0°$). ΔR, $\Delta\theta$, and $\Delta\phi$ are their changes upon a 90° rotation of H_2CO around its C_2 axis (see Figure 2). Since the experimental data are not sufficient to fit all of these parameters, the values of ΔR, and $\Delta\theta$ have been fixed to the values obtained by the *ab initio* calculations ($\Delta R = -0.098$ Å and $\Delta\theta = -2.3°$, respectively).

We used the differences between the planar moments of inertia (ΔM_{gg}) of the $v = 0$ and $v = 1$ tunnelling states to determine the V_2 barrier and $\Delta\phi$. The planar moments of inertia, defined as

$M_{gg} = \Sigma_i m_i g_i^2$ ($g = a$, b or c) are easily obtained from the rotational constants through $M_{aa} = h/(16\pi^2)\cdot(-1/A+1/B+1/C)$, etc. The flexible model results are reported in Table 4. The obtained barrier to internal rotation of H_2CO is quite closed to that *ab initio* value ($V_2 = 120$ cm^{-1}).

Table 4: Flexible model results and potential energy parameters for the internal rotation of H_2CO in CH_2ClF-H_2CO.

	Exptl.	Calc.
$\Delta M_{aa}/u\text{Å}^2$	+0.057	+0.055
$\Delta M_{bb}/u\text{Å}^2$	-0.045	-0.041
$\Delta M_{cc}/u\text{Å}^2$	+0.072	+0.076
$\Delta E_{0+0}/\text{GHz}$	-	5.4

Determined parameter: $\Delta\phi = 12.2(5)°$, $V_2 = 125(10)$ cm^{-1} [a]

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

Dissociation Energy

Assuming the stretching between the two centres of mass of the two subunits (the motion which leads to dissociation) to be isolated from the remaining vibrations, it is possible to roughly evaluate the dissociation energy with pseudo-diatomic approximation.

The stretching force constant (k_s) can be estimated by using the following equation:[21]

$$k_s = 16\pi^4(\mu \, R)^2[4B^4 + 4C^4 - (B - C)^2(B + C)^2]/(h \, D_J) \tag{4}$$

where μ is the pseudo-diatomic reduced mass, D_J is the centrifugal distortion constant. The value of k_s was calculated to be 8.57 Nm^{-1}, which corresponds to a harmonic stretching frequency of 84 cm^{-1}.

The dissociation energy has been estimated by assuming a Lennard-Jones-type potential with the approximate formula:[22]

$$E_B = 1/72 \, k_s \, R^2 \tag{5}$$

The value $E_B = 9.8$ kJ mol^{-1} has been obtained, intermediate with respect to the theoretical E_{B0} and $E_{B0,BSSE}$ values of Table 1 (13.3 and 6.4 kJmol^{-1}, respectively).

The estimated dissociation energy is also quite similar to those of other weakly bonded complexes, as shown in Table 5.

Table 5: Dissociation energies of several molecular complexes in which water or formaldehyde are linked to freons through weak hydrogen bonds.

Complex	Interaction	k_s/Nm^{-1}	E_B/kJmol^{-1}	Ref.
CH_2F_2-H_2O	HO-H$\cdots$F	7.7	7.5	[9]
CH_2FCl-H_2O	HO-H$\cdots$Cl	8.6	8.5	[2]
CHF_2Cl-H_2O	HO-H$\cdots$Cl	5.3	5.5	[23]
CH_3CHClF-H_2O	HO-H$\cdots$F	4.6	5.4	[3]
CH_2F_2-H_2CO	H(O)C-H$\cdots$F	9.3	10.4	[10]
CH_2FCl-H_2CO	H(O)C-H$\cdots$Cl	8.6	9.8	This work

Conclusions

The rotational spectrum of the CH_2ClF-H_2CO complex allowed us to decode the absolute minimum conformation and structure of the 1:1 adduct between CH_2ClF and H_2CO. Only the complex with a C-H$\cdots$Cl linkage has been detected, similarly to the case of CH_2ClF-H_2O, in which the conformer formed via the O-H$\cdots$Cl interaction has been observed. In both the complexes of CH_2ClF (with water or formaldehyde), the chlorine atom of CH_2ClF

behaves as a better proton acceptor than fluorine, either from the O-H or the C-H donors.[2] In addition, again, as water in CH_2ClF-H_2O, H_2CO in CH_2ClF-H_2CO undergoes a feasible internal rotation around its C_2 axis. The observed tunnelling splitting in CH_2ClF-H_2CO complex is a bit larger than that in CH_2ClF-H_2O, indicating a lower barrier (125(10) cm^{-1}) to the internal rotation than that of water (340(10) cm^{-1}).

The H···Cl and C=O···H distances (r_1 = 2.918 Å and r_2 = 2.821 Å, respectively), are longer than those in CH_2ClF-H_2O (r(Cl···H-O) = 2.655 Å and r(O···H-C) = 2.777 Å, respectively). All these data revealed that H_2CO is more flexible to rotate than H_2O molecule in the complex with CH_2ClF despite the fact that H_2CO is heavier than H_2O.

Since only one conformer has been observed in the pulsed jet expansion, most probably the other conformations relax collisionally to the global minimum.[24] It is also likely that the two molecular subunits experience repeated formation and dissociation, which leads to a strong preference for the most stable conformer in the jet expansion.[25]

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Notes and references

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† Electronic Supplementary Information (ESI) available: Table of MP2/6-311++G (d, p) principal axes coordinates (Å) of CH_2FCl-H_2CO. Table of transitions of all the observed isotopomers. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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