The C−F···H−O Hydrogen Bond in the Gas Phase. Rotational Spectrum and ab Initio Calculations of Difluoromethane-Water

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Abstract: The free jet millimeter wave spectra of four isotopomers of the 1:1 complex between difluoromethane and water have been observed and assigned. The water molecule lies in the FCF plane of difluoromethane, linked through an O−H···F hydrogen bond to one fluorine atom, and *entgegen* to the second one. The H bond parameters are $r(F···H) = 2.20$ Å, $\angle(F···H−O) \cong 135°$, and $\angle(C−F···H) \cong 93°$, respectively. The oxygen is *zusammen* to the C atom, and the "free" water hydrogen is *entgegen* to the difluoromethane moiety. The value of 90° of the C−F···H angle is indicative of the preservation of the p character of the lone pairs of fluorine in the adduct.

Introduction

A large amount of experimental information on the structure and dynamics of weakly bound molecular complexes has been obtained in the last 20 years.[1] Nevertheless, only a few data are available on the structure, dynamics, and energetics of adducts of water with molecules containing fluorine atoms. Detailed experimental results, based on rotationally resolved spectroscopy, have been reported only for water−hydrogen fluoride[2−4] and water−molecular fluorine (F_2).[5] In the first case the hydrogen-bonded species $H_2O···HF$, where HF acts as proton donor, has been identified. HF tunnels between two equivalent configurations through a barrier of 126 cm^{-1} .[2] In the second case the experimental observation was more difficult because water reacts vigorously with fluorine. A fast mixing nozzle was necessary to prevent the reaction,[5] which allowed for the identification of $H_2O···F_2$ as a pre-reactive complex in which water acts as the Lewis base.[5]

No data are available in the literature on the linkages of H_2O with Freons, a family of very stable halogenated compounds, which are thought to be responsible for the depletion of ozone in the upper atmosphere. To obtain information on this kind of interaction, we focused our attention on the complex between Freon 331 and water (difluoromethane−water, DFM−W). This is a molecular system small enough to allow high-level ab initio calculations, and with a promisingly strong microwave spectrum. The F−C bond being very different from the F−F bond, chemical intuition suggests that a hydrogen bond of the type O−H···F−C should represent the main intermolecular linkage.

This kind of hydrogen bond has already been observed at the intramolecular level in 2-fluoroethanol[6] and 3-fluoropropan-1-ol,[7] and it was suggested by ab initio calculations on the fluorobenzene−water and difluorobenzene−water systems.[8]

Figure 1 shows the four plausible conformations of this adduct. Species **III** and **IV** display a double hydrogen bond, but species **I**, with the dipole moments of the two moieties nearly anti-aligned, should be, according to our experience, the most stable one.[9]

To measure the rotational spectra we used free jet millimeter wave absorption spectroscopy, a technique that we recently introduced for the study of molecular complexes,[10] obtaining the first data from high-resolution spectroscopy on the solvation of ethers,[11] cyclic amines,[12] and diazines[9] through the study of the 1/1 complexes with water. Information on the O−H···O, O−H···N, O−H···S, O−H···π, N−H···N, N−H···O, X−H···N, and X−H···O (X = F, Cl, CN) hydrogen bonds has generally been obtained from molecular beam Fourier transform microwave spectroscopy, as reported by Novick.[1] This bibliography does not report, however, on the O−H···F−C linkage.

Experimental Section

The 60−78 GHz Stark and pulse modulated free jet absorption millimeter-wave spectrometer used in this study has been described

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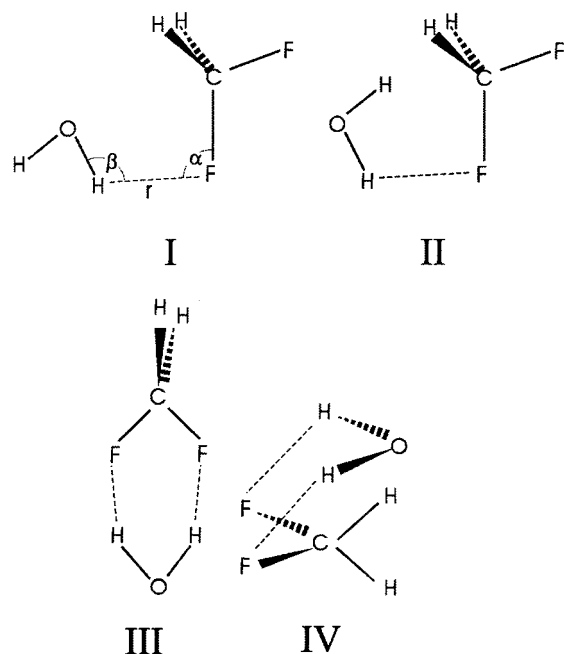
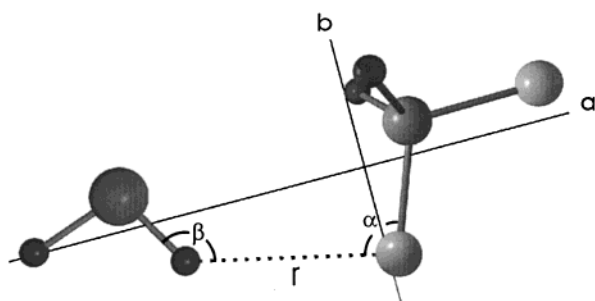**Figure 1.** Plausible conformations for the DFM−W complex.

Figure 2. Observed conformer of DFM−W.

Table 1. Spectroscopic Constants for the DFM−W Complex

	DFM-- H$_2$O	DFM- -DOH	DFM- -D$_2$O	DFM- -H$_2^{18}$O
A/MHz	18667(6)^a	18622(6)	18542(6)	18533(5)
B/MHz	2667.48(4)	2604.92(4)	2470.47(4)	2508.84(3)
C/MHz	2371.52(4)	2322.48(4)	2213.86(4)	2243.04(3)
D_J/kHz	5.812(8)	5.448(9)	4.711(7)	5.305(6)
D_{JK}/kHz	5.56(10)	−2.89(11)	−2.19(10)	5.56(11)
d_1/kHz	−0.95(3)	−0.82(3)	−0.95(3)	−0.95(3)
H_{KJ}/Hz	−107(2)	−89(2)	−82(2)	−98(3)
N^b	38	26	33	32
J_{max}	15	15	16	16
σ/MHz	0.07	0.05	0.07	0.05
M_{cc}/uÅ^{2c}	1.715	1.773	1.772	1.700

^{a} Errors in parentheses are expressed in units of the last digit. ^{b} Number of transitions in the fit. ^{c} The M_{cc}, the planar moment of inertia, for isolated DFM is 1.652 uÅ^2.

probably due to its accidentally low value. To locate exactly the position of the water atoms in the complex, the microwave spectra of three isotopomers (DFM with H$_2^{18}$O, D′OH, and D$_2$O) were assigned. We were not able to observe the spectrum of the DFM···H′OD species (the primed hydrogen participates in the hydrogen bond). This latter effect has been observed in several of the mentioned investigations of complexes and it is related to the relaxation of DFM···H′OD, during the supersonic expansion, to the DFM···D′OH species, which has a lower zero-point energy. The measured transition frequencies of all isotopic species are available as Supporting Information. None of the observed transitions was split for large amplitude motion effects of the water moiety, suggesting that water should be quite "rigid" within the DFM···H$_2$O complex.

The rotational frequencies have been fit to Watson's Hamiltonian[16] (I^r, representation; S, reduction) and the results of this fit are shown in Table 1. Besides the rotational constants, three quartic and one sextic centrifugal distortion parameters have been determined. The high values of the centrifugal distortion parameters are related to the motions of water with respect to the rest of the molecule, as we will discuss later. It appears difficult to understand the inversion of the sign of D_{JK} when the hydrogen involved in the hydrogen bond is replaced with a deuterium.

Structure and Conformation

The planar moment of inertia M_{cc} (=$\sum_i m_i c_i^2$), obtained from the rotational constants through the relation $M_{cc} = h/(16\pi^2)(-1/C + 1/A + 1/B)$, represents the mass extension along the principal axis c, which is perpendicular to the heavy atom plane (see Figure 2). The M_{cc} values of the four isotopic species, reported at the bottom of Table 1, are very similar to that of DFM (corresponding to the two out-of-plane methylenic hydrogens) so that the water moiety must lie in the CFF plane. From the experimental rotational constants we obtained a local r_0 structure at the H-bond, fixing the geometries of DFM and H$_2$O as in the isolated molecules, and the r_s substitution coordinates[17] of the water atoms. These data are reported in Table 2. Although the large-amplitude motions of the water moiety and the Ubbelhode effect,[18] that is the shrinking of the O−H bond upon deuteration, make the r_s substitution coordinates quite unreliable, they are precise enough for conformational discrimination. It is easy to see that the experimental data nicely match the calculated values for configuration **I** of Figure

elsewhere.[10,13] The adducts were formed flowing a mixture of ca. 5 mol % of DFM in argon (or neon) at room temperature and at a pressure of ca. 0.8 bar over a sample of water and expanding the whole to about 5×10^{-3} mbar through a pulsed nozzle (repetition rate 5 Hz) with a diameter of 0.35 mm. An estimated "rotational" temperature of about 10 K has been reached. All samples were commercial and have been used without further purification. The accuracy of the frequency measurements was estimated to be 0.05 MHz.

The signal-to-noise ratio was about 10/1 for the most intense absorption lines.

Rotational Spectrum

Trial rotational constants for the conformations reported in Figure 1 were calculated based on the geometries of isolated DFM[14] and water[15] and assuming hydrogen bond parameters similar to those of the O···H−O hydrogen bond in water−ethers.[11]

The rotational lines (μ_a-R type lines) of the normal isotopic species, which was investigated first, could match only configurations **I** and **II** of Figure 1. Configuration **I** (we will see later that it is the observed one) is drawn to scale in Figure 2, where also the principal axes of inertia and the hydrogen bond parameters are indicated. Although a μ_b dipole moment component is expected, no μ_b-type transitions have been observed,

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Table 2. Substitution Coordinates of the Water Atoms and Hydrogen Bond Geometry of DFM−Water (Å and deg)

(1) r_s Coordinates

atom	$|a|$ exptl	$|a|$ calcd[a]	$|b|$ exptl	$|b|$ calcd	$|c|$ exptl	$|c|$ calcd
O	2.480(1)[b]	2.502	0.341(6)	−0.355	0.09(3)	0.0
H_{H-bond}	2.128(2)	1.997	0.09(4)	0.46	0.24(2)	0. 0
H_{free}[c]	3.290(2)	3.416	0.32(2)	0.070	0.02(20)	0.0

(2) Hydrogen Bond Parameters (see Figure 2)

	r	α	β
exptl (r_0)	2.20(1)	93(1)	135(3)
ab initio	2.52	96	99

[a] Calculated with the r_0 structure (see last line of this table and text). [b] Fit error (in parentheses) is expressed in units of the last digit. [c] Extrapolated from the coordinates in the principal axes system of CF_2H_2−DOH.

1. The small non-zero $|c|$-values are likely due to the large-amplitude motions which are usually present in this kind of molecular complex, and therefore are compatible with a configuration with $|c| = 0$ equilibrium values. The discrepancies between experimental and model calculated values were much higher, at least for one of the nine substitution coordinates, for configurations **II**−**IV** of Figure 1.

Dissociation Energy

Upon formation of the molecular complex, the three translational and the three rotational degrees of freedom of the isolated water molecule are replaced by six low-energy vibrational modes. One of these motions can be considered as the stretching of the centers of mass of the two constituent molecules, while the remaining ones can be thought of as two bends and three internal rotations of the water moiety. In the case of phenol−water[19] and pyrazine−water[9] these internal rotations connect equivalent minima, and generate Coriolis doubling of rotational lines. This is not the case with DFM−H_2O for which only one set of rotational lines has been observed. As to the stretching and bending motions of water with respect to DFM, their effects are reflected in the anomalously high values of the D_J and D_{JK} centrifugal distortion parameters, as it was suggested also for several of the complexes of aromatic molecules with rare gases. For asymmetric top complexes in which the stretching coordinate is near-parallel to the inertial a-axis (condition satisfied for DFM−W, see Figure 2), the stretching force constant (k_s) can be estimated by approximating the complex to a molecule made of two rigid parts, by using equations of the type:[20]

$$k_s = 16\pi^4(\mu_D R_{CM})^2[4B_D{}^4 + 4C_D{}^4 -$$
$$(B_D - C_D)^2(B_D + C_D)^2]/(hD_J) \quad (1)$$

where μ_D, R_{CM}, and D_J are the reduced mass, the distance between the centers of mass, and the first-order centrifugal distortion constant, respectively. The value $k_s = 7.7$ N/m, corresponding to a harmonic stretching frequency of 98 cm^{-1}, has been obtained. Our O−H···F internal hydrogen bond appears to be rather strong, almost as strong, for instance, as the O−H·

··O internal hydrogen bond of the water dimer[21] ($k_s = 10.8$ N/m). The dissociation energy (E_D) has been evaluated to be 7.5 kJ/mol by assuming a Lennard-Jones potential function, using the approximated equation:[22]

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

Ab Initio Calculations

We also performed a computational study of the potential energy surface associated with the DFM−W cluster at the MP2 level[23] using the 6-311+G(d) basis set.[24] Three stationary points have been found and characterized by means of analytic Hessian matrix calculations. The zero-point vibrational energy (ZPVE) corrections have also been determined by scaling the MP2 harmonic vibrational frequencies using the 0.9748 factor suggested by Scott and Radom.[25]

The highest energy point is the C_{2v} structure labeled **III** in Figure 1, where the water molecule forms two weak hydrogen bonds with both fluorine atoms. This structure cannot be associated with a stable cluster since the Hessian calculation shows that it is a transition state (TS). An Intrinsic-Reaction Coordinate (IRC)[26−28] calculation shows that this transition state is connected to two equivalent C_1 minima (corresponding to a slightly distorted form of **I** in Figure 1, with H_{free} 13° out of the plane), almost 6 kJ/mol more stable than **III**. These two minima are also interconverted by passing through a TS of C_s symmetry (**I** of Figure 1). However, inclusion of ZPVE corrections changes the topology of the PES: the two C_1 structures are raised higher than the C_s structure, which becomes the most stable structure on the potential energy surface. This result is consistent with the experimental evidence.

The binding energy for the **I** cluster structure has also been evaluated by performing single-point CCSD(T)[29]/6-311+G(d) calculations at the cluster and fragment MP2/6-311+G(d) optimized geometries. The basis set superposition error (BSSE) has been evaluated by means of the counterpoise[30] procedure. The binding energy is calculated to be 9.9 kJ/mol, in good agreement with the value obtained using eq 2. Table 3 summarizes the ab initio results for the energy calculations, while the theoretical H-bond structure is compared in Table 2 to the experimental data.

Calculations at the same level have been performed also for the F_2−water complex: the conformation found experimentally by Cooke et al.[5] (H_2O···F_2) was confirmed as the theoretical global minimum. Calculations starting from a conformation of DFM−W with a similar linkage (H_2O···F−CH_2F) did not correspond to a stable minimum, and converged to species **I**.

All the calculations were performed using the Gaussian-94[31] program.

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Table 3. Ab Initio and Experimental Potential Energies (E) and Zero-Point Energies ($E_{0,0}$) of the Various Conformers of DFM—W Relative to the Isolated DFM and H_2O (kJ/mol) for the Calculated Stationary Points [BSSE correction (relative to structure **I**) is included]

conformer	MP2		CCSD(T)		exptl $E_{0,0}{}^a$
	E	$E_{0,0}$	E	$E_{0,0}$	
III[b]	−9.19	−4.89			
I-C_1	−15.94	−10.47			
I-C_s	−15.90	−14.01	−11.23	−9.91	−7.5

[a] The experimental value is an $E_{0,0}$ value, except that does not include the correction to the zero-point energy for the stretching describing the dissociation. [b] Transition state.

Conclusions

The absolute minimum conformation and structure of the 1:1 adduct of DFM and water has been established by investigating the rotational spectra of several isotopic species and it is shown in Figure 2. All atoms, except the two methylenic hydrogens, are coplanar, and the "free" water hydrogen is *entgegen* with respect to the methylenic group. Also ab initio calculations suggest this one to be the only stable form. The present study, the first high-resolution spectral investigation of a 1:1 adduct of water with an aliphatic fluoride, indicates that the geometry of the C—F···H—O hydrogen bond is considerably different from those of the O—H···O and O—H···N hydrogen bonds. The α angle (see Figure 2) decreases from 110−120° to about 90°, suggesting that the character of the lone pairs at fluorine is p rather than sp³. Other effects such as dipole−dipole interaction energy and secondary interaction of the type O···H_2C can contribute to the stabilization of the observed conformation. The ab initio calculated value of *r* is much higher and that of *β* much smaller than the experimental data (see Table 2 and Figure 2). This suggests that ab initio calculations underestimate the strength of the C—F···H—O bond and overestimate the strength of the attraction between the methylenic hydrogens and the lone pairs of the oxygen.

Finally we would like to emphasize that the three complexes of water with fluorinated compounds investigated so far with rotationally resolved spectroscopy revealed completely different linkages: H_2O···HF, H_2O···F_2, and C—F···H—O for hydrogen fluoride−water, fluorine−water, and DFM—W, respectively.

Supporting Information Available: Table of experimental transition frequencies of four isotopic species of difluoromethane−water (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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