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Molecular Beam Rotational Spectrum of Cyclobutanone–Trifluoromethane: Nature of Weak CH···O=C and CH···F Hydrogen Bonds

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Abstract: The molecular beam Fourier transform microwave spectrum of cyclobutanone–trifluoromethane has been assigned and measured. The carbon atom of trifluoromethane lies in the plane of the heavy atoms of cyclobutanone. The complex is stabilized by one C-H···O=C and two C-H···F-C weak hydrogen bonds. The C-H···O=C interaction, involving one carbonylic oxygen, is studied for the first time in detail with rotationally resolved spectroscopy. The two C-H···F-C weak hydrogen bonds involve two fluorine atoms of trifluoromethane and two hydrogens of the same methylenic group in the α position.

Keywords: free jets · hydrogen bonds · molecular complexes · molecular dynamics · rotational spectroscopy

Introduction

Weak hydrogen bonds (WHB) such as C-H···O and C-H···F-C play an important role in biological, atmospheric and supramolecular chemistry.[1] Studies on such WHB have been mainly performed by X-ray diffraction[2] and IR spectroscopy in rare gas solutions.[3] This kind of experimental information on WHB, from solid state or solution investigations, are obscured by other intermolecular interactions which take place in condensed phases. The gas-phase investigations are free from such effects and can give more details on specific or local interactions. Rotational spectroscopy combined with supersonic expansions has been recently applied in order to study structural and energetic features of these weak interactions. C-H···F and C-H···O linkages were revealed to be the main factors in the formation of isolated cages such as difluoromethane[4] and dimethyl ether[5] dimers. The relative strength of these two interactions has been recently estimated through the study of the rotational spectrum of the oxirane–trifluoromethane,[6] oxirane–difluoromethane,[7] 1,1-difluoroethene–dimethyl ether[8] and trifluoroethene–dimethyl ether[8] adducts.

The C-H···O contacts most frequently observed in protein structures,[9] correspond to C-H···O=C interactions in which carbonyl peptide groups are involved. This interaction, which has recently been proposed to stabilize the most stable conformer of neutral *N,N*-dimethylglycine,[10] has been suggested to have a significant contribution in the determination of protein conformation.[11] However, little experimental information on the intrinsic properties of this weak hydrogen bond is known from studies of isolated molecular complexes.

In this work we present a study of the rotational spectrum of jet cooled cyclobutanone–trifluoromethane complex where the C-H···O=C interaction is expected to play a central role. Trifluoromethane (CHF_3, TFM) can be considered as a prototype of weak hydrogen-bond donor due to the polarized character of its aliphatic C−H bond, which is adjacent to three electron withdrawing fluorine atoms. Cyclobutanone (CB) is a four-membered ring which previous far-infrared[12] and microwave[13] studies have found to be consistent with an effectively planar ring skeleton. Its ring-puckering motion is governed by a symmetric double-minimum potential function with a barrier to ring inversion of 6 cm^{-1}, the ground vibrational state lying above the barrier. The higher electron density regions of CB can be associated to

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the C=O group. Two of them are related to the oxygen sp^2 *n* pairs of the oxygen atom, lying on the heavy atom plane of CB.[14] However, additional nucleophilic sites associated with the π cloud of the C=O double bond are available. The formation of the complex TFM–CB could be predicted to occur through the interaction between the electrophilic C-H group of TFM and one of those nucleophilic regions. Additional weak C-H···F-C interactions between the C-H methylene hydrogen atoms and the fluorine atoms of TFM contribute to the WHB stabilization, so that we can distinguish three conformers, depicted as I, II and III in Figure 1. We decided to study this complex in order to explore its conformational behavior, and therefore to obtain a comparative evaluation of the σ (C-H···O_n) and π (C-H···O_π) weak hydrogen bonds which can take place within the C-H···O=C interaction.

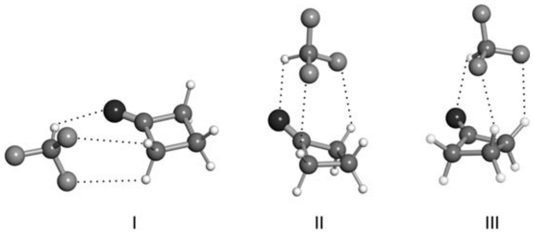

Figure 1. The three most plausible conformations of CB-TFM, I, II and III, display one σ or one π C-H···O=C linkage.

Results

Rotational spectral analysis: According to chemical intuition, we assumed the σ-type C-H···O_n interaction to be stronger than the π-type C-H···O_π WHB, so that we started searching the spectrum of conformation I. We assumed a geometry based upon the structures of CB[13] and TFM[15] monomers and reasonable hydrogen-bond lengths and angles. We found seven μ_a-type R bands, typical of a near-prolate top, evenly spaced by the $B+C$ value and with rotational quantum number J in the range from 5 to 12. We measured several transitions with K_a ranging from 0 to 4. We could also measure some weak μ_b-type lines. The rotational frequencies have been fitted with Watson's Hamiltonian (I^r representation, S reduction),[16] determining all the quartic and two sextic centrifugal distortion constants. There was not any detectable inversion or internal rotation splitting. All measured transitions are listed in Table 1, while the fitted spectroscopic parameters are shown in Table 2.

Abstract in Spanish: *El espectro de rotación del complejo ciclobutanona–triflurometano se ha asignado y medido por espectroscopía de microondas de haz molecular pulsado con transformadas de Fourier. El átomo de carbono del trifluorometano está situado en el plano del esqueleto de la ciclobutanona. El complejo está estabilizado por tres enlaces de hidrógeno débiles, uno C-H···O=C y dos C-H···F-C. La interacción C-H···O=C, que implica un oxígeno carbonílico, se estudia por primera vez en detalle por espectroscopía con resolución de rotación. Los dos enlaces C-H···F-C implican a dos átomos de fluor del trifluorometano y a los dos átomos de hidrógeno del mismo grupo metilénico en posición α.*

Several lines remained unassigned in the spectrum, which, however, do not match the pattern predicted for reasonable structures of other conformers.

Conformation and structure: The conformation of the observed complex can be easily deduced from the values of the planar moments of inertia, defined as $M_{gg} = \Sigma_i m_i g_i^2$ ($g = a, b, c$). These give a measure of the extension of the atomic masses out of the inertial planes of the complex and are related to the rotational constants through equations such as:

$$M_{aa} = h/(16\pi^2)(-1/A + 1/B + 1/C) \tag{1}$$

and cyclic permutations. The M_{cc} value of CB···TFM (see Table 3) is almost exactly the sum of M_{cc} of CB[13] and of M_{bb} of TFM[15] (5.0 and 44.5 uA^2, respectively). This is exactly what it can be expected for species I where the *ab* inertial plane of the complex coincides with the *ab* inertial plane of CB and the *ac* inertial plane of TFM. Instead, for species II we would need M_{bb} of CB···TFM to be approximately the sum of M_{bb} of CB and of M_{bb} of TFM (41.9 and 44.5 uA^2). The experimental values are thus only consistent with the observation of a C_s symmetry conformer I of Figure 1.

A partial r_0 structure was calculated from the three available experimental rotational constants. Two possible arrangements of the subunits may fit this reduced set of experimental rotational constants. We have considered that corresponding to configuration I, since the other with CH_3F close to the C_α and C_β methylene groups has less chemical significance. We kept the geometries of CB and TFM fixed to their r_0 values,[13,15] and fitted the three parameters, r (the H···O distance), α and β of Figure 2. The results obtained are shown in Table 4. The r(C_α-H···F) distances and the $\sphericalangle C_\alpha$-H···F angles, which characterize the existence of C-H···F-C WHB interactions between the methylene C-H groups and the fluorine atoms, have been derived from the partial r_0 structure, and are also reported in Table 4.

The O···H and F···H distances are in line with those observed for the complexes oxirane–TFM,[6] oxirane–difluoromethane[7] and dimethyl ether dimers,[5] once the different nature of C=O···H and C-O···H hydrogen bonds is taken into account. Actually, the F···H distance is slightly longer than that of other complexes (about 0.1 Å).[4,6–8] The deviation from linearity of the C-H···O and C-H···F angles is considerable (51 and 66°, respectively), as seen in previous cases.[5–7] This reveals the weak hydrogen bond nature of both types of competing interactions. The C-H···O bond is bent by presence of the C-H···F interactions and vice versa.

Ab initio calculations: The lack of species II and/or III prompted us to explore the internal dynamics of the com-

Table 1. Measured transitions for CB–trifluoromethane.

J'	K'_a	K'_c	J''	K''_a	K''_c	ν/MHz	$\Delta\nu$/kHz	J'	K'_a	K'_c	J''	K''_a	K''_c	ν/MHz	$\Delta\nu$/kHz
							a-type transitions								
6	0	6	5	0	5	7431.8907	0.3	9	2	8	8	2	7	11155.7655	1.4
6	1	5	5	1	4	7534.1821	-0.5	9	3	6	8	3	5	11164.6299	−0.9
6	1	6	5	1	5	7343.3531	-0.6	9	3	7	8	3	6	11164.0254	−1.0
6	2	4	5	2	3	7448.5096	-0.2	9	4	5	8	4	4	11161.9543	−1.7
6	2	5	5	2	4	7439.5052	-0.4	9	4	6	8	4	5	11161.9543	2.7
6	3	3	5	3	2	7441.8639	0.0	10	0	10	9	0	9	12358.7445	−0.3
6	3	4	5	3	3	7441.7930	2.4	10	1	9	9	1	8	12548.6942	−0.3
6	4	2	5	4	1	7440.9217	-0.4	10	1	10	9	1	9	12231.6106	−0.8
6	4	3	5	4	2	7440.9217	-0.2	10	2	8	9	2	7	12435.5159	0.2
7	0	7	6	0	6	8666.5401	2.2	10	2	9	9	2	8	12393.6544	−1.0
7	1	6	6	1	5	8788.7307	2.0	10	3	7	9	3	6	12406.0735	−0.3
7	1	7	6	1	6	8566.1818	0.1	10	3	8	9	3	7	12405.0378	−0.9
7	2	5	6	2	4	8693.0182	-0.3	11	0	11	10	0	10	13584.9310	1.1
7	2	6	6	2	5	8678.6371	-0.7	11	1	10	10	1	9	13800.4646	−2.5
7	3	4	6	3	3	8682.5701	-0.6	11	1	11	10	1	10	13452.2354	−0.8
7	3	5	6	3	4	8682.4048	-0.9	11	2	9	10	2	8	13686.4440	2.6
7	4	3	6	4	2	8681.2045	0.3	11	2	10	10	2	9	13631.0315	0.8
7	4	4	6	4	3	8681.2045	0.9	11	3	8	10	3	7	13647.8639	2.1
8	0	8	7	0	7	9899.3745	2.1	11	3	9	10	3	8	13646.1799	−1.7
8	1	7	7	1	6	10042.7245	−0.4	11	4	7	10	4	6	13643.0155	−2.6
8	1	8	7	1	7	9788.5367	0.1	11	4	8	10	4	7	13643.0020	2.9
8	2	6	7	2	5	9938.9193	−0.5	12	0	12	11	0	11	14808.6158	0.9
8	2	7	7	2	6	9917.4087	0.9	12	1	11	11	1	10	15051.2856	−1.3
8	3	5	7	3	4	9923.4788	-0.1	12	1	12	11	1	11	14672.1964	−1.6
8	3	6	7	3	5	9923.1484	−0.7	12	2	10	11	2	9	14939.2040	0.8
8	4	4	7	4	3	9921.5447	−1.2	12	2	11	11	2	10	14867.8415	1.9
8	4	5	7	4	4	9921.5447	0.6	12	3	9	11	3	8	14890.0534	−1.7
9	0	9	8	0	8	11130.1730	0.2	12	3	10	11	3	9	14887.4460	0.6
9	1	8	8	1	7	11296.0813	2.0	12	4	8	11	4	7	14883.6900	0.3
9	1	9	8	1	8	11010.3643	1.1	12	4	9	11	4	8	14883.6535	−0.5
9	2	7	8	2	6	11186.3739	−0.4								
							b-type transitions								
2	2	1	1	1	0	11315.9469	0.0	6	1	6	5	0	5	10062.3669	−2.3
4	1	4	3	0	3	7752.7033	0.4	7	1	7	6	0	6	11196.6605	0.0
5	1	5	4	0	4	8914.6846	−0.9	8	0	8	7	1	7	7369.2471	−2.8

Table 2. Spectroscopic parameters for CB–trifluoromethane.

A/MHz	3570.6784(20)[a]
B/MHz	636.00926(10)
C/MHz	604.18927(10)
D_J/kHz	0.36124(20)
D_{JK}/kHz	4.315(8)
D_K/kHz	11.4(4)
d_1/kHz	−0.01020(24)
d_2/kHz	0.00938(10)
H_{JK}/Hz	−0.08(2)
H_{KJ}/Hz	−0.9(4)
N[b]	67
J_{max}	12
σ[c]/kHz	1.4

[a] Errors expressed in units of the last digit. [b] Number of transitions in the fit. [c] Standard deviation of the fit.

Table 3. Results of the MP2/6-311++G** calculations for the minima of CB-TFM.

	Observed	ab initio	
		I	III
A/MHz	3570.679	3619.3	2899.6
B/MHz	636.0095	675.2	810.6
C/MHz	604.1894	643.4	807.0
M_{aa}/uÅ^2	744.8	697.2	537.7
M_{bb}/uÅ^2	91.7	88.3	88.5
M_{cc}/uÅ^2	49.8	51.3	85.8
μ/D		3.5	2.4
ΔE/cm^{-1}		74/0[a]	0/37[a]

[a] BSSE-corrected energies.

plex from ab initio calculations at MP2/6-31G** level with the Gaussian 03 suite of programs.[17] The different stable conformations were obtained by modelling the rotation of the TFM subunit around the C=O bond. The energy profile corresponding to this motion, shown in Figure 3, has been obtained from full geometry optimizations at different values of the dihedral angle τ (see Figure 3). The two equivalent minima corresponding to the predicted more stable forms appear at $\tau \cong \pm 20°$. In these two distorted type III configurations (see Figure 1), the CB ring is puckered and the complex adopts an *endo* shape. The two C-H···F-C contacts take place between the fluorine atoms of TFM and one C_α and one C_β methylene hydrogen atoms. A type II configuration with a C_s symmetry similar to that depicted in Figure 1, which corresponds to a saddle point at $\tau = 0°$. The

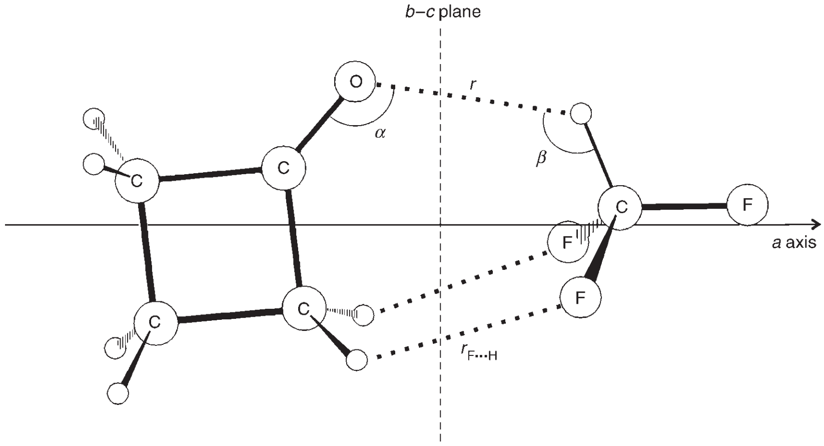

Figure 2. Principal axes system and definition of structural parameters of observed CB-TFM.

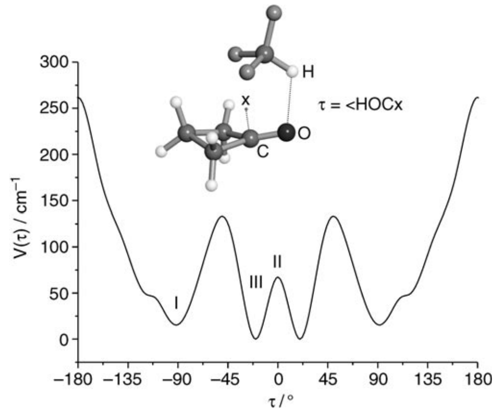

Figure 3. Ab initio potential energy surface of the motion generating conformers I, II and III, the rotation of TFM around the C=O bond. Dummy X lies in the symmetry plane of CB containing the methylenic group in position β. Conformer II results to be a saddle point.

energy of the *exo* configuration II at $\tau = \pm\ 180°$ is much higher than that of the *endo* one. The equivalent minima corresponding to $\tau\ =\ \pm 90°$, predicted to lie 16 cm^{-1} above the most stable conformer, correspond to the observed conformation I of Figure 1, but with the ring of CB slightly puckered.

In a further step, the MP2 method in combination with a more extended basis set 6-311++G** was used to investigate the minima. The results are shown in Table 3 where it can be seen that conformer III is predicted to be more stable than conformer I. However, when using basis set superposition error CP corrections,[18] the results are in better agreement with the experimental evidence in the sense that the relative energy between conformers turns out to be inverted.

The calculated energy differences between conformers I and III are not high enough to prevent the experimental observation of conformer III. The absence of rotational lines of this form in the jet cooled spectrum could be attributed to collisional relaxation from conformer III to the most stable conformer I in the supersonic jet. It is accepted that this process takes place by collisions with the noble carrier gas if the barrier to interconversion between the conformers is low enough. This phenomenon, which is enhanced for heavy carrier gases, has been observed in systems involving only one degree of freedom when barriers are less than about 400 cm^{-1}.[19] In our case a full relaxation is expected, because the interconversion barrier between conformers I and III, which takes place through the internal rotation of TFM around the C=O axis, is expected to be considerably smaller than the limiting value of about 400 cm^{-1} (see Figure 3).

Table 4. Relevant structural parameters in CB-TFM (distances in Å and angles in degrees), see Figure 2 for definition of r, α and β.

	r_0[a]	ab initio[b]
1) r_0 fitted parameters		
r	2.40(1)[c]	2.39
α	122.4(2)	128.3
β	128.9(4)	119.5
2) derived WHB parameter		
$r(F\cdots H)$	2.86(1)	2.87
$\measuredangle(CH\cdots F)$	114(1)	110.9

[a] r, α and β are the fitted parameters. The remaining parameter has been derived from the obtained partial r_0 geometry. [b] MP2/6-311++G** values for the C_s symmetry configuration I. [c] Errors expressed in units of the last digit.

As we mentioned above, the ab initio configuration I does have a slightly puckered ring. When imposing the co-planarity between the heavy atoms of the ring and the TFM frame, configuration I reaches a C_s symmetry, but its MP2/6-31G** energy increases by 41 cm^{-1}. This indicates that the observed species (I) of the complex preserves the double minimum potential function for ring-puckering with a small barrier to planarity lying below the ground vibrational state of isolated CB.[12,13] However, as in bare CB,[13] the ring appears to be effectively planar in its ground vibrational state. The experimental observations—absence of a tunnelling doubling and value of M_{cc}—indicate, indeed, that if this double minimum pathway exists for the complex the barrier should be below the ground state. It seems that the formation of the complex little alters the structural and dynamic properties of the two isolated molecules.

We also calculated the internal rotation of TFM around its CH axis for C_s conformer I (τ of Figure 3 fixed at 90°) and a threefold periodic potential function with a barrier of about $V_3 = 360\ cm^{-1}$ was obtained at the MP2/6-311++G-(d,p) level, stating that the configuration with only one fluorine atom lying in the symmetry plane close to the C_α methylene group corresponds to a saddle point. In this configura-

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tion this “in plane” F atom establishes a bifurcated interaction with the C-H groups.

Dissociation energy: Looking at the geometry and symmetry of the complex, it is likely that the stretching motion leading to the dissociation of the complex should be almost parallel to the principal inertial *a* axis. This allows us to estimate the stretching force constant (k_s) by using the approximated Equation (2):[20]

$$k_s = 16\pi^4 (\mu R_{CM})^2 [4B^4+4C^4-(B-C)^2(B+C)^2]/(hD_J) \qquad (1)$$

where B and C are the rotational constants, and μ, 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 $k_s = 4.8\,\mathrm{N\,m^{-1}}$, corresponding to a harmonic stretching frequency of $48\,\mathrm{cm^{-1}}$, has been obtained. The dissociation energy (E_D) has been evaluated to be $7.5\,\mathrm{kJ\,mol^{-1}}$ by assuming a Lennard–Jones potential function, using the approximated equation[21] $E_D = 1/72\, k_s R_{CM}{}^2$. Such a dissociation energy gives a binding energy of about $2.5\,\mathrm{kJ\,mol^{-1}}$ for each C-H···F or C-H···O linkages. This value is similar to the corresponding values for the WHB adducts such as (difluoromethane)$_2$, (dimethyl ether)$_2$, oxirane–TFM and difluoromethane–dimethyl ether (ref. [4–8], $E_D = 4.7$–$6.7\,\mathrm{kJ\,mol^{-1}}$).

Conclusion

The jet-cooled rotational spectrum of CB–TFM shows only the presence of conformer I. This experimental result allow us to establish that the σ-type C-H···O_n interaction is stronger than the π-type C-H···O_π one, both of which take place between the acidic C-H group of TFM and the keto oxygen atom of CB. This result is consistent with the observations of the complex of CB with a more acid proton donor HCl.[14]

The failure to observe conformer III, which has been predicted to have an energy not very different from conformer I, could be attributed to collisional relaxation processes of this conformer to the most stable conformer, which take place in the supersonic jet expansion.

The observed conformer shows in its ground vibrational state an effective structure in which the CB skeleton is coplanar with the FCH symmetry plane of TFM. The C−H bond is forming a WHB with the oxygen atom at the lone pairs regions and the symmetrical out-of-plane fluorine atoms define two C-H···F-C WHB interactions with the methylene C_α-H groups.

The intermolecular interaction energies in complexes such as CB···TFM are of the order of magnitude of van der Waals interactions, so that one could ascribe them to dispersion forces. However, the directionality of the σ C-H···O_n and C-H···F-C linkages observed at both the proton-donor and proton-acceptor sites, indicates that these should be classified as WHBs.

The results reported herein show the importance of rotational resolved spectroscopies in order to obtain detailed chemical information, hardly achievable by other techniques.

Experimental Section

Commercial samples of CB and TFM (Aldrich) have been used without further purification.

The MB-FTMW spectrum in the 6–18.5 GHz frequency region was measured by using a Balle–Flygare based,[22] COBRA type,[23] molecular beam Fourier-transform microwave (MB-FTMW) spectrometer described elsewhere.[24] A gas mixture of 2% of TFM in He at a total pressure of 2.5 bar was flown over liquid CB at room temperature, and expanded through the solenoid valve (General Valve, Series 9, nozzle diameter 0.5 mm) into the Fabry–Pérot cavity. The frequencies were determined after Fourier transformation of the 8k data points time domain signal, recorded with 100 ns sample intervals. Each rotational transition is split by a Doppler effect due to the coaxial arrangement of the supersonic jet and resonator axes. The rest frequency is calculated as the arithmetic mean of the frequencies of the Doppler components. The estimated accuracy of frequency measurements is better than 2 kHz. Lines separated by more than 7 kHz are resolvable.

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