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Theoretical Study of the Effect of Hydrogen-Bonding on the Stability and Vibrational Spectrum of Isolated 2,2,2-Trifluoroethanol and Its Molecular Complexes

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The structural and spectroscopic effects of hydrogen bonding on isolated 2,2,2-trifluoroethanol (TFE) and its molecular complexes are theoretically investigated at the MP2/aug-cc-pVDZ level. As a result, previous interpretations of the relative stability of the trans and gauche conformers of the isolated molecule are revised. We show that the prevalence of the gauche form is due to a decrease of repulsion forces, rather than to the formation of an intramolecular hydrogen bond. We find that the instability of the trans geometry is caused by repulsion forces between the oxygen electronic pair and the fluorine atom clouds, which are significantly stronger in *trans*-TFE. Molecular agents capable of weakening the repulsion produce stabilization. These results lead to a reinterpretation of the stabilizing factors of halogenated compounds. To analyze complexation, two small molecules (water and ammonia) have been chosen. Water can form four different molecular aggregates with TFE. The most stable corresponds to a species where H_2O acts as hydrogen donor and TFE presents the cis−gauche conformation, forming two intramolecular hydrogen bonds. For NH_3, the cis−gauche conformation loses stability, because of steric hindrance. In this case, TFE varies the relative stability of its conformers, with *trans*-TFE becoming the preferred structure. Hydrogen bond formation between NH_3 and *trans*-TFE produces vibrational shifts of −354, −17, and +518 cm^{-1} for the OH stretching, the OH bending, and the OH torsion, in agreement with the experimental findings. We found complexation to produce an important variation of the position of the infrared bands corresponding to the hydroxyl group.

Introduction

The effect of intermolecular hydrogen bond formation on the relative stabilities of nonrigid molecules conformers is attracting interest in spectroscopy.[1−7] Molecules that easily form aggregates cannot be preserved as isolated species in the laboratory. Under experimental pressure and temperature conditions, such systems could contain mixtures of isolated molecules, polymers, and molecular aggregates with the impurities. All these species can change the structure, position, and intensity of the vibrational bands.

Although *trans*- and *gauche*-ethanol are almost isoenergetic,[8] the favorite geometry of haloethanols is always a gauche conformer.[9−11] It is generally accepted that stabilization can be explained by the formation of an intramolecular hydrogen bond between the hydroxyl hydrogen and one halogen atom.[9−17] Polymerization requires the breaking of an internal bond, producing a variation on the relative stability of conformations. For the most well-known compound of the series, 2,2,2-trifluoroethanol (TFE, CF_3CH_2OH),[10−17] the assumption of the internal hydrogen bond has never been questioned. However, its existence has not been proved and some questions concerning the TFE spectrum interpretation have yet to be solved.

TFE is a polar organic solvent, usually employed in protein folding investigations, that produces hydrogen bonding. Recently, we have published an ab initio study of the TFE far-IR (far-infrared) spectra,[9] where we compared our results with the measurement of Durig and Larsen.[18] The molecule shows two torsional modes, CF_3 and OH, which are responsible for its nonrigidity. The trifluoromethyl group (CF_3) intertransforms between three equivalent minima, whereas the hydroxyl group (OH) generates a trans and a cis−gauche minima (see Figure 1). Calculations at the MP4/cc-pVTZ level[9] show the trans

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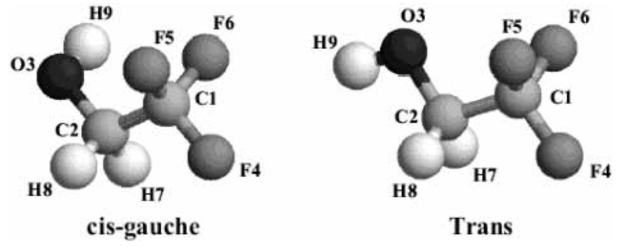

Figure 1. Numbering convention and structures of the trans and cis−gauche conformers of TFE.

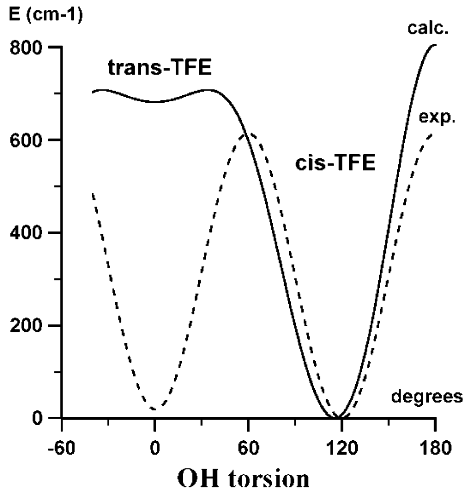

Figure 2. Potential energy surface for the OH torsion of TFE. The continuous line corresponds to the MP4/cc-pVTZ results of ref 9. The dashed line corresponds to the potential fitted from the bands assigned in ref 18.

conformer lies 681.5 cm^{-1} above the absolute cis−gauche minimum. Our results for the cis−gauche geometry are in good agreement with those of Li−H Xu et al.[17] and Durig and Larsen.[18] However, the discrepancies in the trans conformer zone are unsatisfactory. Durig and Larsen[18] have observed patterns that they assign to the isolated *trans*-TFE. They fitted a restricted potential for the OH torsion to the experimental data and obtained an energy difference between the cis−gauche and trans conformers of 19 cm^{-1} (see Figure 2). This value is approximately 600 cm^{-1} lower than the MP4(SDQ)/cc-pVTZ result (681.5 cm^{-1}).[9] The computational errors and the inadequacy of the theoretical models do not justify a difference of this order. Our experience shows that such differences are always smaller than 50 cm^{-1}, if extended basis set and correlated methods are employed.

The vibrational spectrum of TFE has been recorded in the gas phase,[5,13−14,16,18] in condensed phases,[14−16] and in argon and nitrogen matrixes.[15] The spectrum has been assigned using different conformational criteria. The rotational spectrum has been also recorded for the cis−gauche geometry.[17] As a result of previous works, the feasibility of nonequivalent minima in TFE is under controversy. Whereas a cis−gauche conformer of greater stability is generally accepted,[5−7,9,12−19] some authors favor[12,18] and some authors disapprove[5,13−15] the existence of a second stable conformer in the gas phase. In addition, there is no consensus with respect to the energy difference value between minima. Different workers show very different values such as, 1161,[12] 19,[18] or 681.5 cm^{-1}.[9]

The aim of the present paper is the evaluation and revision of the assumptions commonly employed for the interpretation of the spectra of halogen derivatives, using TFE as a prototype system. For these reasons, we analyze the origin of the relative stability of the two isolated TFE conformers, and the effect of intermolecular hydrogen bond formation. On the base of the Orza et al. studies[5,6] on hydrogen-bonded systems, we assume that the different behavior observed for TFE with different techniques is due to the existence of polymeric forms and molecular aggregates in the experimental mixtures with the isolated molecules. Orza et al.[6] have recorded the gas-phase Fourier transform infrared spectra of the TFE complexes with bases such as dimethyl ether, acetone, tetrahydrofuran, ammonia and trimethyl- and triethylamine. The spectra of the complexes show well-defined features, clearly different from those seen in the spectra of the pure alcohol. These features can be understood in terms of conformational interconversion.

Computational Details

Calculations on isolated TFE and on the different molecular aggregates have been performed at the MP2 level, with the correlation consistent plus diffuse and polarization functions, aug-cc-pVDZ basis set.[20] Diffuse and polarization functions are used to describe the hydrogen bonding. All the molecular structures are determined after full geometry optimization. Calculations are carried out using the Gaussian 98 package.[21]

The starting cis−gauche and trans geometries for TFE are taken from the previous MP2/cc-pVTZ fully optimized results.[9] The numbering convention is shown in Figure 1.

All hydrogen bonds are fully characterized by determining the corresponding bond critical points (BCP) using atoms in molecules (AIM) theory.[22,23] AIM theory is applied from the MP2 one-electron density using the Morphy98 package.[24] Critical points are identified after assessing that the needed Poincaré-Hopf relationship[22,23] is satisfied.

Molecular electrostatic potential maps are obtained from the 3D electrostatic potential distribution computed with Gaussian 98. From this information, we generate two-dimensional cuts on the plane of the molecule (C1C2O3) using software developed at our laboratory, which performs a quadratic interpolation to generate the data grids. Maps are drawn using the Surfer 8 Contouring and 3D Surface Mapping System.[25]

Results and Discussion

H_2O and NH_3 have been chosen for the theoretical evaluation of the effect of hydrogen bond formation on the spectrum, and on the relative stability, of the TFE conformers. Both species are small molecules, bearing electronic pairs on the heavy atoms, suitable for hydrogen bonding. Moreover, water is the most common impurity in the spectroscopic mixtures. In turn, ammonia represents the smallest species for which the vibrational switch effect on TFE has been measured.[6]

The stable forms of the isolated TFE molecule, and of the molecular aggregates, have been obtained after full geometry optimization. For TFE the only two stable conformers (cis−gauche and trans) are considered. The search for equilibrium structures of the molecular aggregates was started by approaching an H_2O or NH_3 molecule to the two TFE conformers. The initial orientation was selected by taking into account the fact that ammonia can act as a hydrogen acceptor, whereas water acts also as a hydrogen donor. Table 1 collects the absolute and relative energies (in au) of the isolated TFE, H_2O−TFE, and NH_3−TFE stable forms. To account for the effect of the vibrational residual energy, the zero point vibrational energy (ZPE) has been determined and incorporated into the computation of relative energies; see Table 1. It can be observed that the effect of the ZPE is a reduction of the energy difference between conformers. Table 1 also shows that after including

TABLE 1: Absolute, E_a, and Relative, ΔE, Energies of the TFE Conformers and the Stable Forms of the NH_3−TFE and H_2O−TFE Complexes at the MP2/cc-pVDZ Level[a]

	E_a (au)	ΔE (cm^{-1})	ZPE (kcal/mol)	ΔE_{ZPE} (cm^{-1})	μ (D)
cis−*gauche*-TFE	−451.81720	0	36.13	0	2.0323
trans-TFE	−451.81419	661	35.87	572	3.7989
H_2O←*cis*−*gauche*-TFE	−528.09104	0	51.36	0	3.0617
H_2O←*trans*-TFE	−528.08683	922	50.96	781	5.9084
H_2O→*cis*−*gauche*-TFE	−528.08691	905	51.14	828	2.3537
H_2O→*trans*-TFE	−528.08423	1492	50.93	1343	2.4400
NH_3←*trans*-TFE	−508.23478	0	59.28	0	6.4469
NH_3←*cis*−*gauche*-TFE	−508.22581	1967	58.72	1772	2.1268

[a] Zero point vibrational energies, ZPE, are included. ΔE_{ZPE} corresponds to energy differences including the effect of the ZPE. Symbols 6 and 7 to the right of H_2O or NH_3 mean that the molecule acts as a hydrogen donor or acceptor with respect to the TFE hydroxyl group. Dipole moments in Debyes.

TABLE 2: Electronic Density Values, ρ_a, and Laplacian of the Electron Density, $\nabla^2\rho_a$, at the BCP Found for Nonncovalent Interactions in the Different Complexes between Water and Ammonia with TFE (All Data in Atomic Units)

	atoms[a]	CP type[b]	ρ_a	$L^2\rho_a$
H_2O←*cis*−*gauche*-TFE	H9···O10	BCP	0.02683	0.11416
	F5···H12	BCP	0.00937	0.04413
	H12, O10, H9, O3, C2, C1, F5	RCP	0.00493	0.03122
H_2O←*trans*-TFE	H9···O10	BCP	0.02681	0.11735
H_2O→*cis*−*gauche*-TFE	O3···H12	BCP	0.02014	0.08205
H_2O→*trans*-TFE	O3···H12	BCP	0.02120	0.08345
NH_3←*trans*-TFE	N10···H9	BCP	0.03311	0.11531
NH_3←*cis*−*gauche*-TFE	N10···H9	BCP	0.01152	0.00637
	H11···F5	BCP	0.03173	0.02713
	H11, F5, C1, C2, O3, H9 N10	RCP	0.00406	0.02210

[a] This column collects the atoms involved in the critical point. [b] BCP and RCP stand for bond critical point and ring critical point, respectively.

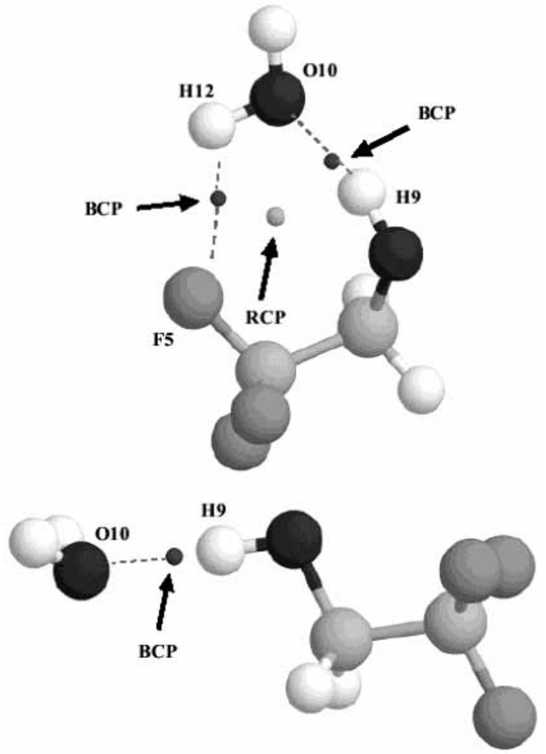

Figure 3. H_2O−TFE molecular complexes. Water acting as hydrogen acceptor. Numbering referred to that of Figure 1.

the ZPE the order of energetic stability is preserved, except between the water (as a hydrogen donor)−*cis*−*gauche*-TFE, and the water (as a hydrogen acceptor)−*trans*-TFE complexes, where it is reversed. In contrast to ethanol,[8] the preferred geometry of TFE is the cis−gauche form. The energy difference between the isolated conformers is 661 cm^{-1} (572 cm^{-1} including ZPE), which is in good agreement with the previous 681.5 cm^{-1} found at the MP2/cc-pVTZ level.[9]

To characterize hydrogen bond formation, atoms in molecules (AIM) theory is applied.[22,23] AIM characterizes a bond by an atomic interaction line (AIL), that is, a line through the electron density, ρ, along which ρ is a maximum with respect to any neighboring line. On the AIL lies the bond critical point (BCP), a second-order saddle point where ρ reaches a minimum on the AIL. The value of the electronic density at the BCP for a given bond, ρ_a, can be correlated to the concept of bond order,[22,23] with higher values of ρ_a corresponding to stronger bonds. The sign of the Laplacian of the charge density at the BCP, $\nabla^2\rho_a$, defines the kind of interaction responsible for the bonding.[22,23] A negative sign implies a shared interaction, where the electronic charge is shared by the two nuclei, as in a covalent bond. On the other hand, a positive sign corresponds to a closed-shell interaction, where the electronic charge is concentrated around each nucleus. This is the typical case for ionic or hydrogen bonds.

For our molecular systems, the existence of a hydrogen bond between two atoms is determined after locating an AIL with a corresponding BCP and a positive sign of $\nabla^2\rho$. The results for the different isolated molecules and molecular complexes are collected in Table 2 and Figures 3−5. The first interesting result in Table 2 is that no AIL is found in the cis−gauche conformation, linking the hydroxyl hydrogen and a fluorine atom. This is true, despite the fact that the needed topological Poincaré-Hopf relationship[22,23] between critical points is satisfied. However, as shown in Figure 1, an intramolecular hydrogen bond in the cis−gauche conformation would lead to a closed structure, and a ring critical point (RCP) should appear in the AIM analysis.[22,23] In other words, the missing BCP and the RCP are linked. Because the BCP and the RCP enters the Poincaré-Hopf relationship with opposite sign, an agreement of the relationship by itself does not ensure we have located all the BCP. Because the Morphy98 package uses a number of threshold parameters to simplify the numerical computation of

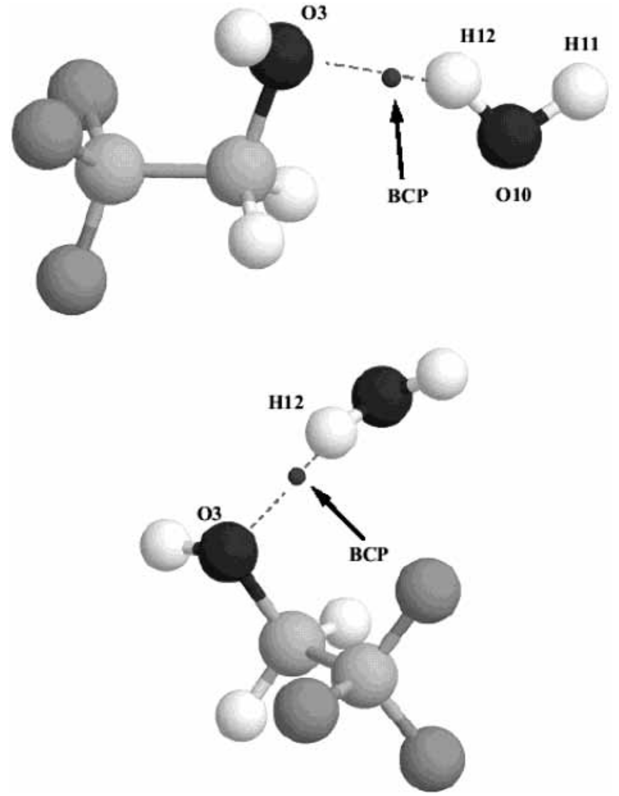

Figure 4. H_2O−TFE molecular aggregates. Water acting as hydrogen donor. Numbering referred to that of Figure 1.

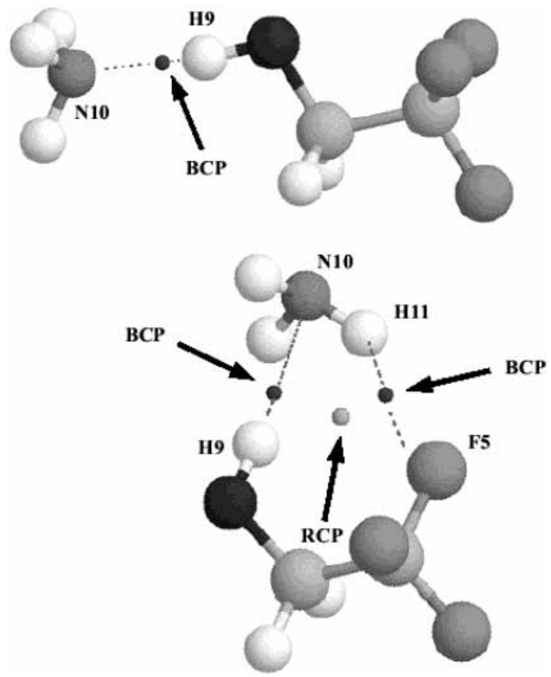

Figure 5. NH_3−TFE molecular aggregates. Numbering referred to that of Figure 1.

BCP, we changed the defaults to remove approximations in the computations. No additional BCP appear for any value of the threshold parameters.

TABLE 3: Components of the Total Energy for the Cis−Gauche and Trans Conformers of TFE[a]

	cis−gauche-TFE	*trans*-TFE	increment
T	450.452764	450.454054	1.29×10^{-3}
V_{en}	−1613.799967	−1614.539183	−0.739216
V_{nn}	271.555838	271.819361	0.263523
V_{ee}	439.974165	440.451581	1.477416

[a] T, V_{en}, V_{nn}, and V_{ee} stand for the kinetic, attractive electron−nucleus, repulsive nucleus−nucleus, and repulsive electron−electron energy, respectively. The increments are obtained as trans value minus cis−gauche value. All data in atomic units.

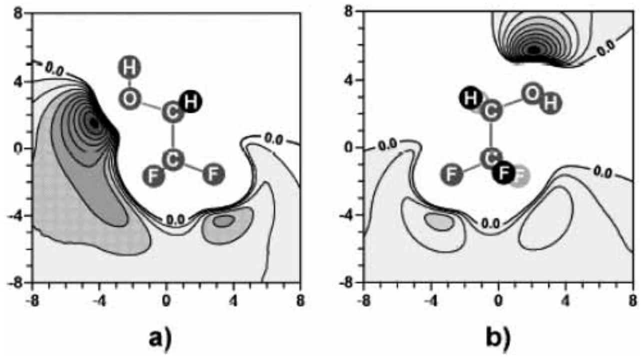

Figure 6. Electrostatic potential maps of TFE on the C1C2O3 plane. Only the electronegative zone is drawn: (a) trans conformation; (b) cis−gauche conformation. Interval between isocontour lines 0.005 au (3.1 kcal/mol), distances in bohrs. Darker zones correspond to more electronegative zones.

Without exception, the different structural behavior between ethanol and haloethanols has been explained in terms of intramolecular bonds. However, our AIM calculations show that a hydrogen bond does not exist between the OH and the CF_3 groups. In addition, the F−HO distance is too large (2.5263 Å) for a hydrogen bond. To determine the origin of the higher stability of the cis−gauche conformation, the total energy of the cis−gauche and trans structures is decomposed in its components. This technique has proven useful in the analysis of the origin of the torsion barrier in acetaldehyde.[26] Thus, Table 3 collects the kinetic, T, attractive electron−nucleus, V_{en}, repulsive nucleus−nucleus, V_{nn}, and repulsive electron−electron, V_{ee}, components of the total energy for the two TFE stable conformers. Table 3 also collects the increment of the components obtained as the difference between the higher energy conformer (trans) and the most stable one (cis−gauche). The results show that the higher increment corresponds to the reduction of the interelectronic repulsion, V_{ee}, term. In addition, Table 3 shows also that $\Delta V_{ee} > \Delta T + \Delta V_{en} + \Delta V_{nn}$. (1.477 416 au versus −0.474 403 au). Thus, the change in electron−electron repulsion is the determining factor for the cis−gauche form to be the most stable.

Why this reduction of interelectronic repulsion occurs can be visualized using the molecular electrostatic potential distribution. Figure 6, shows the molecular electrostatic potential maps for the two TFE conformers in the C1C2O3 plane. The molecular electrostatic map of *trans*-TFE, Figure 6a), shows that the electronegative zones corresponding to the oxygen electron pair and the negative clouds of fluorine atoms interact directly. On the other hand, Figure 6b) shows that in the cis−gauche form this interaction is reduced, because the two electronegative zones are placed at different sides of the molecule. Therefore, the prevalence of the gauche form is due to a reduction of repulsive forces between the electronic clouds of the fluorine atoms and the electron pairs of oxygen. Thus, it has nothing to do with the existence of a hydrogen bond between one of the halogen atoms and the OH hydrogen, as is generally accepted.

For the complexes, Table 2 shows that the strongest hydrogen bond corresponds to the NH_3 (acceptor)−*trans*-TFE system, with a ρ_a value of 0.033 11 au. In contrast, the weakest hydrogen bond appears for the H_2O (acceptor)−*cis−gauche*-TFE complex, with a ρ_a value of 0.009 37 au. As shown in Table 2, the H_2O (acceptor)−*cis*−*gauche*-TFE and the NH_3 (acceptor)−*cis*−*gauche*-TFE system exhibit two intermolecular hydrogen bonds, giving rise to a closed structure and a corresponding RCP.

Three factors determine the stability of the molecular aggregates. Following the order of strength, these are the number of intermolecular hydrogen bonds, the steric interaction, and the effect of external bond formation on the internal repulsion forces of the trans conformer. In the case of water, the steric interactions do not play an important role. Water forms four molecular aggregates behaving as hydrogen donor or acceptor (see Figures 3 and 4). Table 1 shows that with respect to the isolated molecule, when water acts as an acceptor, the energy difference between the cis−gauche and trans conformers augments from 572 to 781 cm^{-1} (including ZPE). However, if it acts as donor, the difference decreases to 515 cm^{-1} (1343−828 cm^{-1}).

The data in Table 1 show that the increase in energy for the water acceptor case is due to the stabilization of the cis−gauche complex. As Table 2 and Figure 3 indicate, this fact is due to the existence of two hydrogen bonds. The values of ρ_a, Table 2, show that the H9···O10 hydrogen bond, with H9···O10 distance 1.8688 Å, is the stronger of the two. In addition, just this bond is comparable in strength to the hydrogen bond for the trans complex; see Table 2. The other hydrogen bond is much weaker than the previous one (see Table 2), with an F5···H12 distance of 2.3224 D. As a result, the H9···F5 distance enlarges from 2.5263 to 2.7112 D. In addition, the O3−H9 and C1−F5 bond distances increase from 0.9682 to 0.9760 D and from 1.3655 to 1.3717 D, respectively. For the water acceptor trans complex, the hydrogen bond presents a distance of 1.8612 D between the H9···O10 atoms.

On the other hand, for the water donor complexes, the ρ_a data in Table 2 show that in this case the hydrogen bond for the trans complex is stronger than for the cis−gauche form. This can also be observed in the value of the O3···H12 distances, 1.9975 and 2.0068 Å for the trans and cis−gauche conformers, respectively. This fact, and the interelectronic repulsion forces still acting, explains the decrease of the difference of the conformers as a consequence of the stabilization of the trans form. The proximity of the water oxygen augments the hydroxyl group negative charge, whereas the approach of the water hydrogen breaks the repulsion forces of *trans*-TFE. The water hydrogen stabilizes the molecule and plays the role of the OH hydrogen in the *cis*−*gauche*-TFE.

From these results, and with respect to water, we can conclude that the apparent stabilization of the trans form observed experimentally (see Figure 2) is not explained by the attack of a single molecule. However, it could be explained by the proximity of more than one. This effect has to be considered because water is the most common impurity in the spectroscopic mixtures, and more than one molecule could attack TFE. Because $H_2O \leftarrow$*cis*−*gauche*-TFE shows more than one hydrogen bond, the attack of a second water molecule is less probable than in the case of the remaining species. In addition, possible solvation effects have to be considered. In Table 1, the dipole moment of all the species, are collected. Complexation produces a shift of electric properties. If water acts as acceptor, the dipole moments of the gauche and trans conformers differ greatly. However, if water acts as donor the value of the two dipole moments converges. The largest dipole moment corresponds to $H_2O \leftarrow$*trans*-TFE (5.9084 D). Thus, a large solvation effect may be expected for this system.

In the case of ammonia, steric effects prevent the formation of some complexes. For this reason, only two stable molecular aggregates have been established. In both cases, the nitrogen atom acts by accepting the TFE hydroxyl hydrogen. The NH_3- - -TFE hydrogen bond formation inverts the stability of the conformers. Thus, the trans form appears as the favorable geometry for TFE, with the cis−gauche conformer lying 1967 cm^{-1} (1772 cm^{-1} with ZPE) above; see Table 1. The change of the order of stabilities is explained by the steric effects arising from the NH_3 size and form. Whereas NH_3 can approach the *trans*-TFE without impediment, closeness is limited in the *cis*−*gauche*-TFE. This observation is shown in Table 2, where we find the ρ_a value for the NH_3−*cis*−*gauche*-TFE hydrogen bond to be much smaller (about 3 times) than that for the trans complex. Therefore, the hydrogen bond in *trans*-TFE is much stronger. This can be attributed to the steric (repulsive) effects from the electron pair of nitrogen. For this reason, the N10···H9 bond length equals 1.8669 D in *trans*-TFE, and 2.3799 D in *cis*−*gauche*-TFE.

For the water complex with *cis*−*gauche*-TFE a second hydrogen bond is exhibited (see Table 2 and Figure 5), giving rise to a cyclic structure. Here, the NH_3 acts as a hydrogen donor to one of the fluorines. As shown in Table 2, the bond is stronger than the other existing in the cis−gauche form. To form the cycle, the O3−H9 distance enlarges from 0.9682 Å, in the isolated *cis*−*gauche*-TFE, to 0.9714 Å. In addition, the distances H9- - -NH_3 and F5- - -HNH_2 are found to be 2.3799 and 2.4843 Å, respectively.

It can be generalized that large molecules with electronegative groups prefer to form complexes with *trans*-TFE rather than with *cis*−*gauche*-TFE, as a consequence of steric effects. The stabilization of *trans*-TFE observed by Durig and Larsen[18] could be explained by TFE dimerization, which would favor the trans geometry. In this context it is interesting to note the high value of the dipole moment for the trans form (see Table 1) could translate into an important solvent effect.

The effect of complexation on the vibrational frequencies of TFE is determined by computing the harmonic frequencies for the isolated conformers and their complexes at the equilibrium geometry. The results are collected in Tables 4 and 5, where we also include the fundamental frequencies of water and ammonia. In the complexes, six new low-frequency vibrations appear, corresponding to the three translational and three rotational degrees of freedom lost on formation of the molecular aggregates. These frequencies lie close to the torsional modes, behaving as large amplitude vibrations and are difficult to assign.

Table 6 collects the observed frequencies of low-pressure gaseous samples of TFE and the TFE−NH_3 complex, taken from refs 5 and 6. Details of the far-infrared TFE spectrum, as reported by Durig and Larsen,[18] have been already discussed in our previous work on the torsional spectra of TFE[9] and will not be reproduced here. In agreement with our structural calculations, the comparison of the calculated frequencies of the two isolated TFE conformers, Table 5, with the observed frequencies, Table 6, clearly points to the cis−gauche conformer as the favorite form in gaseous TFE.

Hydrogen-bonding complexation of TFE with organic bases, as described in refs 5 and 6, favors the trans configuration for the TFE moiety of the complex. Thus, it is interesting to compare the calculated vibrational spectra of both conformers. According to our calculations (see Table 4) the main differences are found for the OH vibrational modes. We observe frequency increments ($\Delta\nu = \nu_{\mathrm{trans}} - \nu_{\mathrm{cis}}$) of +33 cm^{-1} for the OH stretching (ν(OH)), and −139 and −140 cm^{-1} for the OH bending and torsion modes (δ(OH) and t(OH)), respectively. Positive $\Delta\nu$ values of 16, 49, 36, and 35 cm^{-1} are calculated

TABLE 4: Harmonic Frequencies (cm^{-1}) for the Isolated TFE Conformers, Water Monomer, and the Water−TFE Hydrogen-Bonded Complexes

			H_2O−*cis*−*gauche*-TFE		H_2O−*trans*-TFE		
cis−*gauche*-TFE	*trans*-TFE	H_2O	$H_2O\leftarrow$	$H_2O\rightarrow$	$H_2O\leftarrow$	$H_2O\rightarrow$	assign
			32	11	7	39	
			98^b	59	44	41	
			167	136	86	79	
			203^b	146^b	146^b	166	
			264	333	193	189^b	
			302	506	277	561	
121	109		114	111	127	118	CF_3 torsion
220	231		227	242	234	229	CF_3 def.
309	169		687	372	701	361	OH torsion
376	352		350	311	351	350	CF_3 def
411	413		412	412	419	411	CCO bend
517	520		515	518	519	518	CF_3 def
534	539		533	537	539	537	CF_3 def
651	639		653	652	645	642	CF_3 def
822	821		818	825	824	821	C−C−str
942	977		943	938	975	971	CH_2 def
1095	1104		1117	1083	1120	1086	C═O str
1139	1175		1140	1136	1173	1172	CH_2 def
1163	1138		1157	1168	1142	1141	CF_3 str
1262	1300		1281	1257	1298	1295	CF_3 str
1303	1301		1306	1303	1299	1310	CF_3 str
1385	1246		1430	1384	1323	1256	OH bend
1443	1492		1470	1449	1496	1483	CH_2 wag
1484	1500		1477	1484	1514	1496	CH_2 bend
		1622	1619	1635	1626	1639	H_2O bend
3091	3076		3084	3106	3063	3095	CH_2 sym str
3183	3142		3168	3203	3124	3162	CH_2 asym str
		3804	3790	3735	3794	3727	H_2O.sym str
3812	3845		3649	3809	3667	3835	OH str
		3938	3922	3910	3921	3900	H_2O asym str

[a] $H_2O\rightarrow$ and $H_2O\leftarrow$ mean water acting as hydrogen donor or acceptor, respectively. Band assignment is included. [b] Harmonic frequencies for hydrogen bond stretchings.

for the four angular CH_2 modes, as well as a frequency increment of 38 cm^{-1} (1300−1200 cm^{-1}) for the intermediate CF_3 stretching. Negative $\Delta\nu$ values of 25 and 24 cm^{-1} are found for the lower CF_3 stretching mode, and for the second CF_3 deformation mode in the cis−gauche conformer.

We have already objected in ref 9 to the Durig and Larsen assignments of the TFE far-IR spectrum,[18] as well as their interpretation of the coexistence of the two conformers. In this context, the present calculations do not support the presence of both conformers in the gas phase. However, as also noted in ref 5, the vibrational spectra of liquid TFE closely follows the main characteristics of the *trans*-TFE hydrogen-bonded complexes, probably meaning that the liquid is mainly constituted by hydrogen-bonded dimers or polymers. Gaseous samples at (relatively) high pressures could show traces of the dimers.

At the MP2/AUG-cc-pVDZ level, the three fundamentals of water lie at 3938 cm^{-1} (ν_3), 3804 cm^{-1} (ν_1), and 1622 cm^{-1} (ν_2); see Table 4. Table 4 also shows that in the molecular aggregates the ν_1 and ν_3 fundamentals are displaced to lower frequencies, whereas ν_2 displaces to higher frequencies (except for the *cis*−*gauche*-TFE complex with H_2O as hydrogen acceptor). All these shifts are larger when water acts as hydrogen donor. The effect of complexation on the TFE fundamental frequencies is greater for the modes directly involved in hydrogen bonding, i.e., the OH stretching, the OH bending, the OH torsion, as well as the CO stretching mode. The frequency shifts for all these modes are collected in Table 7. With respect to the OH stretching mode, $\Delta\nu$(OH), Table 7 shows that a red shift is observed on complexation. The magnitude of the shift clearly shows that TFE is a much stronger acid (hydrogen donor) than H_2O. We observe, also, that as a hydrogen donor the *trans*-TFE conformer is stronger than the cis−gauche isomer.

Good agreement is also found between the frequencies measured in the infrared spectrum of the NH_3−TFE complex, Table 6, and the frequencies calculated for the NH_3−*trans*-TFE, Table 5. On the other hand, we observe experimentally an upward shift of about +114 cm^{-1} (see Table 6) for the hydrogen-bonded NH_3 inversion mode in the gas phase. The corresponding calculated shifts (see Table 5) are +81 cm^{-1} for the trans and −180 cm^{-1} for the cis−gauche configurations. These data suggest clearly that the NH_3−*trans*-TFE conformer is present in the gas sample.

In Table 7 we collect the main frequency shifts for the TFE vibrational modes affected by hydrogen bonding, calculated from the theoretical data of Tables 4 and 5. However, the experimentally observed shifts correspond to the reaction of gaseous TFE (i.e., the cis−gauche conformer) with organic bases, including ammonia, to give *trans*-TFE hydrogen-bonded complexes.[6] In this case, the effects of hydrogen bonding and conformational changes are superposed on each other. The observed shifts for the OH vibrational modes of the NH_3 complex and the calculated shifts for the NH_3 *trans*-TFE are collected in Table 8. The results fully agree with the trans complex being the experimentally observed form.

Some other observed shifts are related to the conformational changes. Thus, the calculated and observed shifts for the CF_3 stretching vibrations support an argument previously presented in ref 5. In the isolated form, the CF_3 group is placed in a very asymmetric environment, as long as we consider the gauche isomer. However, the environment is much more symmetric in the trans NH_3 complex, and the CF_3 group should approach C_{3v} symmetry. Therefore, in the NH_3 trans complex, the CF_3 stretching modes should approximately exhibit two bands of A and +E symmetry. The observed values[6] for the three CF_3

TABLE 5: Harmonic Frequencies (cm^{-1}) for the Isolated TFE Conformers, NH_3 Monomer, and the NH_3−TFE Hydrogen-Bonded Complexes[a]

cis−*gauche*-TFE	*trans*-TFE	NH_3	NH_3←*cis*−*gauche*-TFE	NH_3←*trans*-TFE	assign
			19	8	
			57	18	
			59^b	53	
			87^b	161^b	
			209	225	
			283	317	
121	109		131	125	CF_3 torsion
220	231		231	251	CF_3 def
309	169		492	827	OH torsion
376	352		350	351	CF_3 def
411	413		411	421	CCO bend
517	520		521	519	CF_3 def
534	539		535	540	CF_3 def
651	639		652	649	CF_3 def
822	821		821	827	C−C str
942	977		944	976	CH_2 def
		1044	864	1125	NH_3 inver
1095	1104		1101	1131	C═O str
1139	1175		1139	1172	CH_2 def
1163	1138		1165	1141	CF_3 str
1262	1300		1267	1298	CF_3 str
1303	1301		1304	1299	CF_3 str
1385	1246		1400	1368	OH bend
1443	1492		1444	1496	CH_2 wag
1484	1500		1482	1536	CH_2 bend
		1649	1636	1646	NH_3 Str
		1649	1638	1648	NH_3 str
3091	3076		3084	3050	CH_2 symm str
3183	3142		3182	3110	CH_2 asym str
		3481	3490	3480	NH_3 sym str
		3636	3666	3625	NH_3 asym str
		3636	3669	3628	NH_3 asym str
3812	3845		3740	3458	OH str

[a] NH_3← means ammonia acting as hydrogen acceptor. Band assignment is included. [b] Harmonic frequencies for hydrogen bond stretchings.

TABLE 6: Observed Vibrational Frequencies (cm^{-1}) of Gaseous 2,2,2-Trifluoroethanol (TFE), Ammonia, and the NH_3−TFE Hydrogen-Bonded Complex[6,18]

TFE	TFE−NH_3	NH_3	TFE	TFE−NH_3	NH_3
	3544		1088	1115	
3657	3347				
	3146			104^6	931.58^a
		3335.9			
		3337.5			
			940	952	
3001	2979		829	827	
2949	2934		665	665	
2896	2884		548	540	
			500		
		1627.5	424		
			364		
1458	∼1453		281	720	
1414	∼1407		230		
1366	1350		∼120		
1292	1288				
1263					
1182	1165				
1141	∼1150				

[a] Nitrogen inversion mode.

stretching modes in the isolated form are found to be 1292, 1263, and 1183 cm^{-1}. The corresponding frequencies observed for the NH_3 complex are 1288, 1288, and 1165 cm^{-1}. These data can be compared to the results collected in Table 5 for the *cis*−*gauche*-TFE (1303, 1262, and 1163 cm^{-1}) and the NH_3−*trans*-TFE (1299, 1298, and 1141 cm^{-1}). Our data are in agreement with the interpretation of a cis−gauche form for the isolated TFE, and a trans conformation for the NH_3−TFE complex.

TABLE 7: Calculated Frequency Shifts (TFE Complex − Isolated TFE), for the Molecular Aggregates of *cis*−*gauche*- and *trans*-TFE with Water and Ammonia (All Data in cm^{-1})

	H_2O−*cis*−*gauche*-TFE		H_2O−*trans*-TFE		NH_3−TFE	
	H_2O←	H_2O→	H_2O←	H_2O→	cis−gauche	trans
$\Delta\nu_1$	−14	−69	−10	−77	+9	−1
$\Delta\nu_2$	−3	+13	+4	+17	−180	+81
$\Delta\nu_3$	−16	−28	−17	−38	$33/30^a$	$-8/-11^a$
$\Delta\nu_4$					$-11/-13^b$	$-1/-3^b$
$\Delta\nu$ (OH)	−163	−3	−178	−10	−72	−387
$\Delta\delta$ (OH)	+45	−1	+77	+10	+15	+122
Δt (OH)	+378	+63	+532	+192	+183	+658
$\Delta\nu$ (CO)	+22	−12	+16	−18	+6	+27

[a] NH_3 asymmetric stretching. [b] NH_3 symmetric stretching.

TABLE 8: Observed Shifts for the OH Vibrational Modes of the NH_3−TFE Complex[a]

$\Delta\nu$ (cm^{-1})	$\Delta\nu$ (OH)	δ (OH)	t(OH)	$\Delta\nu$ (CO)
calculated	−354	−17	518	36
observed	−310	−17	435	27

[a] The data are compared to the calculated shifts for the NH_3−*trans*-TFE complex.

Conclusions

The effect of the formation of hydrogen-bonded complexes on the structure and vibrational spectrum of TFE is theoretically analyzed. TFE shows two minimum energy geometries, cis−gauche and trans, with the cis−gauche form as the most stable one. We found that the higher stability of the cis−gauche form is due to a reduction of interelectronic repulsion between the electron pair of the OH oxygen and the fluorine atoms, relative to the trans conformer. Opposed to the current explanation, our results show that a hydrogen bond is not formed between the hydroxyl hydrogen and any of the fluorine atoms.

We found that TFE forms molecular hydrogen-bonded complexes with molecules that are able to act as a hydrogen donor or acceptor. If the molecules are relatively small, the intermolecular hydrogen bond formation favors the most stable *cis*−*gauche*-TFE geometry, which is able to form more than one hydrogen bond. On the other hand, if the additional molecule is relatively large, the *cis*−*gauche*-TFE presents steric impediments to the aggregate formation. In this case, complexation favors the *trans*-TFE geometry with respect to the cis−gauche conformer. On these grounds, it can be expected that TFE dimerization favors the trans−gauche geometry. In this context, comparison of the experimental and calculated data for the vibrational frequencies fully supports the hypothesis of a trans form for the NH_3−TFE complex.

The effect of formation of hydrogen-bonded complexes on the vibrational spectrum is a variation of the band positions of the isolated *cis*−*gauche*- and *trans*-TFE forms. These variations are specially important for the modes involved in the formation of the hydrogen bonds. The effect is clearly observed in the OH torsion and stretching vibrations. Our results could explain the complexity of the experimental spectrum of TFE, and its sometimes incompatible interpretations, as due to the existence of different molecular hydrogen-bonded aggregates in the experimental mixture.

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