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Blue-Shifted Hydrogen-Bonded Complexes $CF_3H-(HF)_{1\leq n\leq 3}$

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The present work demonstrates the existence of cyclic structures in complexes of the CF_3H molecule with hydrogen fluoride clusters, $(HF)_{1\leq n\leq 3}$, due to the formation of two types of hydrogen bonds, C−F···H−F and C−H···F. For the case of $n = 3$, a significant blue shift of the ν(C−H) stretching vibrational mode of fluoroform of about 60 cm^{-1} is predicted. This is indeed the largest theoretical estimate of a blue shift in a C−H···X system ever reported in the literature. The present analysis of the geometrical, energetical, and spectroscopic features of the cyclic $CF_3H-(HF)_{1\leq n\leq 3}$ structures shows that the C−F···H−F bond is stronger than the C−H···F interaction. Therefore, they may be referred to as *blue-shifted* rather than *blue-shifting* complexes.

1. Introduction

The last four years have been marked by an enormous number of studies of blue-shifting hydrogen bonds of the C−H···X-type, mainly due to the pioneering work by Hobza and Havlas.[1] Blue-shifting hydrogen bonds C−H···X[2,3] are characterized by a contraction of the C−H distance, a blue shift of the C−H stretching vibrational mode, and a reduction of its infrared intensity, features which are in sharp contrast to those rooted to the conventional hydrogen bonds.[4] The major focus in the studies of blue-shifting hydrogen bonds has been purely theoretical, and the key issues have thus been the following: (i) whether these blue-shifting hydrogen bonds should be treated as some natural extension of the conventional ones;[2] (ii) what is the upper limit for a blue shift;[1,2e] and (iii) what is their very nature?[3] Three approaches have recently been used to resolve issues i and iii: (a) the charge-transfer natural bond orbital analysis; (b) modeling the formation of the C−H···X via embedding into a homogeneous electric field;[2k,3a,3c] (c) the energy decomposition scheme.[2y,3c]

Actually, the first experimental evidence of such puzzling behavior of some hydrogen bonds C−H···X might be at least referred to the late fifties to seventies.[5] Nevertheless, till now only a few blue-shifting hydrogen bonds have been experimentally recorded.[6,7] A central practical interest in the nature and functioning of the C−H···X hydrogen bonds came from crystallography, where vast amounts of data on C−H···X (largely X = O and less X = N) contacts have been collected and analyzed.[8] These structural data are regrettably not of much help when trying to categorize these intermolecular contacts as belonging to either weakly red- or blue-shifting hydrogen bonds. Since the classical definition of hydrogen bonding mainly relies on the behavior of specific vibrational modes,[4] experimental vibrational spectra or reliable theoretical calculations are the adequate tools to discern between the two cases.

Most of the theoretical studies on such blue-shifting hydrogen-bonded complexes have so far been focused on C−H···O interactions;[2,3,7] in a few cases more general A−H···X systems were investigated as well.[2f−k,3b,7a,b] The largest calculated blue shifts for neutral C−H···X systems are close to 50 cm^{-1}.

Let us assume that the blue-shifting hydrogen bonds are treated as some extreme case[2a,c,d] of the conventional ones, A−H···X,[4] where A is an electronegative proton donor and X an electronegative proton acceptor. By a straightforward analogy with the conventional hydrogen bond, we may therefore suggest that the strength of the C−H···X bond increases in the order X = N < O < F. This is precisely the impetus of the present work aiming to theoretically predict the existence of several new, still experimentally unobservable, blue-shifting hydrogen-bonded complexes, $CF_3H-(HF)_{1\leq n\leq 3}$ and, furthermore, to show that for one of them, $CF_3H-(HF)_3$, the calculated blue shift is among the largest ever reported in the literature for neutral complexes. Notice that experimental data on $CF_3H-(HF)_n$ clusters are not available yet.

2. Method of Calculation

All calculations reported in the present work were performed using the *GAUSSIAN 98* suite of packages.[9] We have applied the second-order perturbation Møller−Plesset method[10] (MP2) within the frozen-core (fc) approximation using two extended basis sets: 6-311++G(2d,2p)[11−14] and aug-cc-pVTZ.[15,16] Because of the floppy nature of these complexes, all geometry optimizations were carried out with the TIGHT option. MP2 harmonic vibrational frequencies were calculated for the complexes using both basis sets in order to allow for a proper characterization of stationary points. The effect of the counterpoise (CP) correction[17] to the basis-set superposition error (BSSE) has also been taken into account.

3. Results

3.1. The Monomers. *3.1.1. Fluoroform, CF_3H.* The most relevant structural and spectroscopic properties of fluoroform as obtained with MP2 are collected in Table 1.

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TABLE 1. Selected MP2-Calculated Properties of the CF_3H Molecule

	basis set	
property	6-311++G(2d,2p)	aug-cc-pVTZ
total energy (hartree)	−337.710395	−337.846364
r(C−H) (Å)	1.0818	1.0856
ν(C−H) stretch (cm^{-1})	3222	3200
A(C−H)[a] (km mol^{-1})	24	22
r(C−F) (Å)	1.3386	1.3361

[a] Infrared intensity.

TABLE 2. Selected MP2-Calculated Properties of $(HF)_n$ Clusters

		basis set	
$(HF)_n$	property	6-311++G(2d,2p)	aug-cc-pVTZ
HF	total energy (hartree)	−100.303060	−100.340891
	r(H−F) (Å)	0.9179	0.9217
	ν(H−F) stretch (cm^{-1})	4164	4124
	A(H−F)[a] (km mol^{-1})	127	121
$(HF)_2$, C_s	ΔE (kcal mol^{-1})	−4.9 (−3.9)[b]	−4.7 (−4.2)
	r(F···F) (Å)	2.762	2.746
	r(F···H) (Å)	1.846	1.827
	r(H−F) (Å)	0.9234, 0.9210	0.9280, 0.9249
	ν(H−F) (cm^{-1})	4050, 4122	3989, 4082
	A(H−F) (km mol^{-1})	466, 135	474, 137
$(HF)_3$, C_{3h}	ΔE (kcal mol^{-1})	−15.7 (−12.7)	−15.5 (−14.1)
	r(F···F) (Å)	2.631	2.608
	r(F···H) (Å)	1.801	1.769
	r(H−F) (Å)	0.9333	0.9392
	ν(H−F) (cm^{-1})	3907, 3800[c]	3832, 3711[c]
	A(H−F) (km mol^{-1})	1319	1403
$(HF)_4$, C_{4h}	ΔE (kcal mol^{-1})	−32.0 (−24.5)	−29.1 (−28.5)
	r(F···F) (Å)	2.560	2.515
	r(F···H) (Å)	1.640	1.583
	r(H−F) (Å)	0.9420	0.9520
	ν(H−F) (cm^{-1})	3542, 3707,[c] 3774	3348, 3556,[c] 3638
	A(H−F) (km mol^{-1})	3292	3754

[a] Infrared intensity. [b] CP-corrected interaction energy with respect to infinitely separated monomers in parentheses. [c] Doubly degenerate.

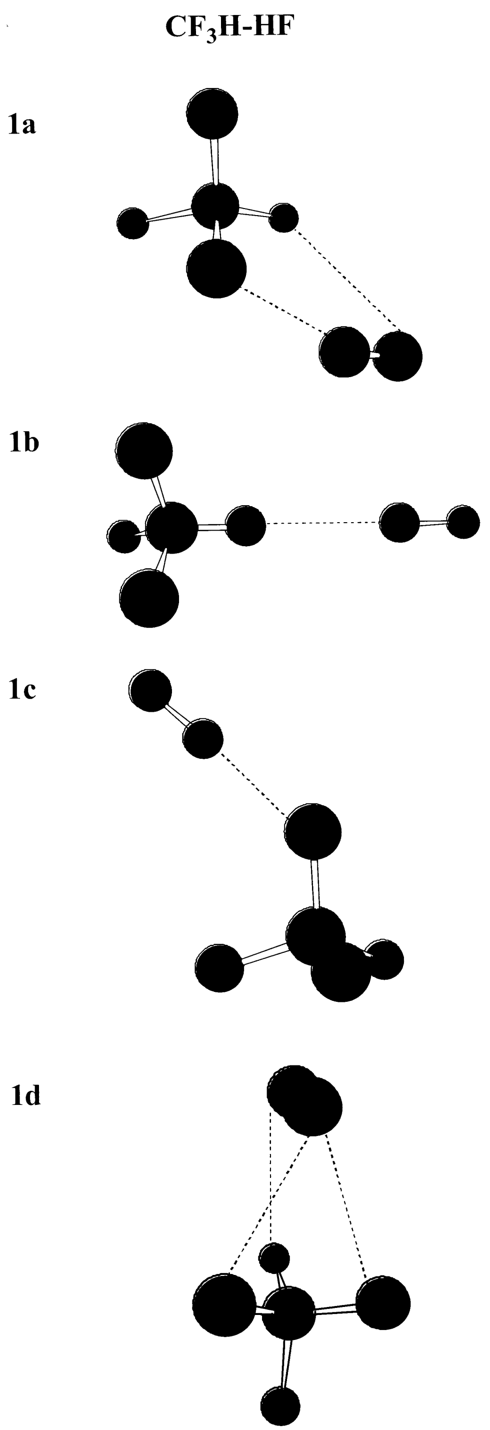

Figure 1. Stationary points on the energy surface of CF_3H−HF.

3.1.2. Hydrogen Fluoride Clusters, $(HF)_{1\leq n\leq 4}$. The structural and spectroscopic properties of hydrogen fluoride clusters have already been amply discussed in the literature,[4c,18] and the basic structural and vibrational spectroscopic features of these complexes are well-known. Whereas $(HF)_2$ adopts an open-chain structure, cyclic structures are preferred in the case of $(HF)_3$ and $(HF)_4$. The most important structural and energetic quantities of $(HF)_n$ clusters as calculated in this work and needed for the following discussion are compiled in Table 2.

3.2. The Complex CF_3H−HF. This complex has served as a typical case for the occurrence and analysis of a blue-shifting hydrogen bond in a recent theoretical investigation.[3b] In that work, a sizable blue shift of 46 cm^{-1} was calculated for a nearly linear C−H···F hydrogen bond.

In the course of our investigations, we have performed a rather extended, although by no means complete, investigation of the intermolecular energy surface of this complex. We have detected four bound stationary points. These are shown in Figure 1. Structure **1a**, the global minimum, has a cyclic configuration of C_s symmetry with two hydrogen bonds, C−H···F and C-F···H−F, the latter being substantially shorter. For symmetry reasons, there are actually three equivalent minima of this type on the intermolecular energy surface of CF_3H−HF. Structure **1b** has C_{3v} symmetry, has a strictly linear C−H···F−H arrangement, and is a second-order saddle point at the MP2/aug-cc-pVTZ level, converting to a shallow minimum with MP2/6-311++G(2d,2p). Structure **1c** is another minimum of C_s symmetry with a nearly linear C-F···H−F hydrogen bond. Again, three minima of this type exist. Structure **1d** has again C_s symmetry and is a first-order saddle point having a C−H···F hydrogen bond and a *bifurcated* F−H···F_2C contact. Structures **1a** and **1d** may be thought of as originating from the second-order saddle point **1b** by bending the HF molecule either in the direction of one C−F bond (such a pathway links to **1a**) or in the opposite direction (**1d**-linker). Alternatively, **1d** is a threefold degenerate saddle point governing the rotation of the HF molecule between the minima of type **1a**. The calculated interaction energies of the four stationary points of CF_3H−HF are reported in Table 3. With both basis sets employed in the present work, structure **1a** is the most stable, with and without CP correction (Table 3). The remaining three stationary points are very close in energy. In view of the shallow and complicated

TABLE 3. MP2-Calculated Interaction Energies of the Complex CF_3H-HF (kcal mol^{-1})

	basis set	
structure	6-311++G(2d,2p)	aug-cc-pVTZ
1a	−3.3 (−2.2)[a]	−3.1 (−2.5)
1b	−2.4 (−1.8)	−2.2 (−1.9)
1c	−2.9 (−1.9)	−2.6 (−2.0)
1d	−2.7 (−1.8)	−2.5 (−2.1)

[a] Counterpoise-corrected interaction energies in parentheses.

TABLE 4. Selected MP2-Calculated Structural Parameters of Different Stationary Points of the Complex CF_3H-HF (Å)

	optimized	basis set	
structure	distances	6-311++G(2d,2p)	aug-cc-pVTZ
1a	C−H	1.0811 (−0.0007)[a]	1.0849 (−0.0007)
	C−F[b]	1.3558 (0.0172)	1.3525 (0.0164)
	C−F	1.3336 (−0.0050)	1.3315 (−0.0046)
	H−F	0.9213 (0.0034)	0.9252 (0.0035)
	(F)H···F	2.0496	2.0610
	(C)H···F	2.6046	2.5757
1b	C−H	1.0797 (−0.0021)	1.0841 (−0.0015)
	C−F	1.3406 (0.0020)	1.3380 (0.0019)
	H−F	0.9189 (0.0010)	0.9229 (0.0012)
	(C)H···F	2.2509	2.2573
1c	C−H	1.0813 (−0.0005)	1.0848 (−0.0008)
	C−F[b]	1.3546 (0.0161)	1.3517 (0.0156)
	(C−F)[c]	1.3327 (−0.0060)	1.3302 (−0.0059)
	H−F	0.9203 (0.0024)	0.9246 (0.0029)
	(F)H···F	1.9806	1.9650
1d	C−H	1.0798 (−0.0020)	1.0836 (−0.0020)
	C−F[b]	1.3412 (0.0026)	1.3393 (0.0032)
	C−F	1.3390 (0.0004)	1.3353 (−0.0008)
	H−F	0.9196 (0.0017)	0.9235 (0.0018)
	(F)H···F	2.8747	2.9536
	(C)H···F	2.5547	2.5188

[a] Bond length changes with respect to free monomers in parentheses. [b] C−F bond(s) involved in hydrogen bond formation. [c] Mean value for C−F bonds not involved in hydrogen bonding.

TABLE 5. Selected MP2-Calculated Harmonic Vibrational Frequencies ν, Frequency Shifts, and Infrared Intensities at Different Stationary Points of the Complex CF_3H-HF[a]

	frequencies	basis set	
structure	and shifts	6-311++G(2d,2p)	aug-cc-pVTZ
1a	ν(C−H)	3238 (16)[b] [9][c]	3215 (15) [8]
	ν(F−H)	4105 (−59) [189]	4060 (−64) [181]
1b	ν(C−H)	3263 (41) [1.7]	3233 (33) [1.5]
	ν(F−H)	4150 (−14) [157]	4107 (−17) [151]
1c	ν(C−H)	3231 (9) [17]	3212 (12) [16]
	ν(F−H)	4120 (−44) [346]	4066 (−58) [357]
1d	ν(C−H)	3251 (29) [12]	3228 (28) [12]
	ν(F−H)	4139 (−35) [126]	4099 (−25) [122]

[a] Frequencies and frequency shifts with respect to the monomers in cm^{-1}; infrared intensities in km mol^{-1}. [b] Frequency shifts in parentheses. [c] Infrared intensities in square brackets.

energy surface and the floppy nature of this complex, calculated harmonic zero point vibrational energy corrections are expected to be unreliable and are therefore not reported.

As a quite general feature and in line with the weak interaction (see Table 4), we observe that, for all four stationary points, changes in the intramolecular bond lengths upon complex formation are small, with the exception of those cases, **1a** and **1c**, where a C−F bond is involved in the formation of a C−F···H−F hydrogen bond. In that case, the C−F bond is lengthened. The calculated C−H bond contractions are considerably smaller for the two minima than for the two saddle points. The shortest intermolecular contact occurs for the F−H···F−C hydrogen bond of structure **1c**. For the global minimum, **1a**, the F−H···F−C hydrogen bond is distinctly shorter than the C−H···F one. The shortest C−H···F contact occurs, as expected, for structure **1b**.

The calculated vibrational frequencies, collected in Table 5, show that, for all four stationary points, blue shifts do occur for C−H streching frequencies and red shifts for F−H stretching frequencies, irrespective of whether hydrogen bonds are formed or not. However, the C−H blue shifts are largest for the saddle point **1b** (41 cm^{-1} with MP2/6-311++G(2d,2p), 33 cm^{-1} with MP2/aug-cc-pVTZ), which corresponds to the structure used in ref 3b, followed by the saddle point **1d** (about 30 cm^{-1} with both basis sets employed), and significantly smaller for the two minima. The typical strong infrared intensity reduction is only encountered for **1b**. The F−H red shifts are largest for the two minima, **1a** and **1c**; the infrared intensity enhancement characteristic for conventional hydrogen bonds is most prominent for structure **1c**.

Summarizing our results for the CF_3H-HF complex, we observe a quite complicated and topologically rich energy surface, indicating an interesting dynamics with a variety of large amplitude motions. The global minimum, at least without explicit inclusion of zero point energy corrections, is the cyclic structure **1a** with C−H···F and C-F···H−F hydrogen bonds, for which a modest C−H blue shift of about 15 cm^{-1} is predicted.

3.3. The Complexes $CF_3H-(HF)_2$ and $CF_3H-(HF)_3$. Guided by the stability of the cyclic CF_3H-HF complex, it appears natural to probe whether cyclic $CF_3H-(HF)_n$ clusters are also conceivable candidates for blue-shifting complexes. These complexes may be viewed as originating either from an insertion of CF_3H in an already preformed $(HF)_n$ ring (in the special case of $CF_3H-(HF)_2$ formation of a three-membered ring) or by substitution of one HF molecule of an $(HF)_{n+1}$ ring by CF_3H. This search for cyclic $CF_3H-(HF)_n$ complexes turned out to be successful for $n = 2$ and for $n = 3$ but unsuccessful for $n > 3$. Both cyclic complexes, $CF_3H-(HF)_2$ and $CF_3H-(HF)_3$ are quite stable clusters. $CF_3H-(HF)_2$, in particular, is strongly bound with respect to $(HF)_2$ and CF_3H. But also, $CF_3H-(HF)_3$ is stable with respect to dissociation into cyclic $(HF)_3$ and CF_3H. At the same time, these two clusters are characterized by a large amplitude motion for an out-of-plane rotation of the CF_3H molecule with respect to the ring plane formed by two or three HF molecules and the HCF group of CF_3H. With both basis sets, $CF_3H-(HF)_2$ has effectively C_s symmetry, although with the aug-cc-pVTZ basis there is a formal C_1 minimum which is, however, exceedingly close in energy to the C_s structure ($\Delta E < 0.01$ kcal mol^{-1}). In the case of $CF_3H-(HF)_3$, there are two equivalent minima of C_1 symmetry. The energy difference compared to the C_s saddle is, however, larger with about 0.37 and 0.21 kcal mol^{-1} at MP2/6-311++G(2d,2p) and MP2/aug-cc-pVTZ, respectively. The optimized structures of the complexes $CF_3H-(HF)_2$ and $CF_3H-(HF)_3$ are sketched in Figure 2. The calculated stabilization energies with respect to infinitely separated molecular monomers, $\Delta E_a = E(CF_3H-(HF)_n) - E(CF_3H) - nE(HF)$, and with respect to $(HF)_n$ and CF_3H monomers, $\Delta E_b = E(CF_3H-(HF)_n) - E(CF_3H) - E((HF)_n)$, are shown in Table 6.

The CP-corrected binding energy of $CF_3H-(HF)_2$ with respect to CF_3H and $(HF)_2$, ΔE_b, is close to −5 kcal mol^{-1}, quite independent of the basis set applied. The total interaction energy, ΔE_a(CP), with respect to infinitely separated monomers amounts to about −9 kcal mol^{-1}. Cyclic $(HF)_3$ (see Table 2), with an MP2/aug-cc-pVTZ ΔE_a(CP) of −14 kcal mol^{-1}, is evidently more strongly bound, implying that the formation of

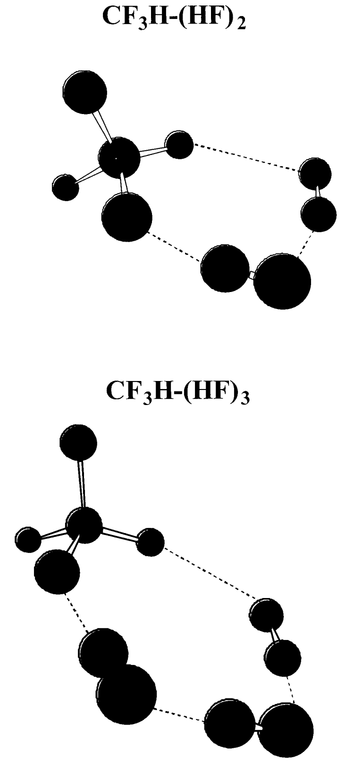

Figure 2. Optimized structures of the complexes $CF_3H-(HF)_2$ and $CF_3H-(HF)_3$.

TABLE 6. MP2-Calculated Interaction Energies of the Complexes $CF_3H-(HF)_2$ and $CF_3H-(HF)_3$ (kcal mol^{-1})

complex	interaction energies[a]	basis set: 6-311++G(2d,2p)	basis set: aug-cc-pVTZ
$CF_3H-(HF)_2$	ΔE_a	−11.2 (−8.5)[b]	−10.9 (−9.4)
	ΔE_b	−6.3 (−4.7)	−6.2 (−5.3)
$CF_3H-(HF)_3$, C_1	ΔE_a	−20.5 (−15.8)	−20.1 (−17.5)
	ΔE_b	−4.8 (−2.6)	−4.6 (−3.5)

[a] For definition see text. [b] Counterpoise-corrected interaction energies in parentheses.

TABLE 7. MP2/aug-cc-pVTZ-Calculated Bond Distances of the Complexes $CF_3H-(HF)_2$ and $CF_3H-(HF)_3$ (Å)

distances	$CF_3H-(HF)_2$	$CF_3H-(HF)_3$ (C_1)	$CF_3H-(HF)_3$ (C_s)
C−H	1.0844 (−0.0012)[a]	1.0817 (−0.0039)	1.0835 (−0.0021)
C−F[b]	1.3664 (0.0303)	1.3679 (0.0318)	1.3718 (0.0356)
C−F[c]	1.3285 (−0.0076)	1.3287 (−0.0074)	1.3274 (−0.0087)
H−F	0.9338 (0.0121)	0.9421 (0.0204)	0.9419 (0.0202)
H−F	0.9321 (0.0104)	0.9386 (0.0169)	0.9393 (0.0176)
H−F		0.9358 (0.0141)	0.9358 (0.0141)
(F)H···F	1.7828	1.6713	1.6639
(F)H···F		1.6498	1.6492
(F)H···F(C)	1.8677	1.7571	1.7440
(C)H···F	2.2393	2.2444	2.1193

[a] Bond length changes with respect to free monomers in parentheses. [b] C−F bond involved in hydrogen bond formation. [c] Mean value for C−F bonds not involved in hydrogen bonding.

TABLE 8. Selected MP2-Calculated Harmonic Vibrational Frequencies, ν, Frequency Shifts, and Infrared Intensities of the Complex $CF_3H-(HF)_2$[a]

frequencies and shifts	basis set: 6-311++G(2d,2p)	basis set: aug-cc-pVTZ
ν(C−H)	3255 (33)[b] [1.6][c]	3230 (30) [1.8]
ν(F−H)	3933 (−231) [361]	3864 (−260) [389]
ν(F−H)	4011 (−154) [522]	3948 (−156) [543]

[a] Frequencies and frequency shifts with respect to the monomers in cm^{-1}; infrared intensities in km mol^{-1}. [b] Frequency shifts in parentheses. [c] Infrared intensities in square brackets.

TABLE 9. Selected MP2-Calculated Harmonic Vibrational Frequencies, ν, Frequency Shifts, and Infrared Intensities of the Complex $CF_3H-(HF)_3$[a]

symmetry	frequencies and shifts	basis set: 6-311++G(2d,2p)	basis set: aug-cc-pVTZ
C_s	ν(C−H)	3276[b] (54)[c] [5]	3245 (45) [7]
	ν(F−H)	3786 (−378) [541]	3678 (−446) [653]
	ν(F−H)	3882 (−282) [934]	3792 (−332) [989]
	ν(F−H)	3955 (−209) [555]	3870 (−254) [596]
C_1	ν(C−H)	3283 (61) [3]	3260 (60) [3]
	ν(F−H)	3786 (−378) [595]	3679 (−445) [659]
	ν(F−H)	3890 (−274) [821]	3800 (−324) [897]
	ν(F−H)	3949 (−215) [524]	3868 (−256) [579]

[a] Frequencies and frequency shifts with respect to the monomers in cm^{-1}; infrared intensities in km mol^{-1}. [b] Frequency shifts in parentheses. [c] Infrared intensities in square brackets.

two hydrogen bonds between HF molecules is energetically preferred compared to the formation of the C−F···H−F and C−H···F hydrogen bonds. The MP2/aug-cc-pVTZ-calculated ΔE_b(CP) of $CF_3H-(HF)_3$ with respect to CF_3H and $(HF)_3$ is about −3.5 kcal mol^{-1} and, therefore, distinctly smaller than that of $CF_3H-(HF)_2$. Again, cyclic $(HF)_4$ (ΔE_a(CP) = −28.5 kcal mol^{-1}) is much more stable than $CF_3H-(HF)_3$ (ΔE_a(CP) = −17.5 kcal mol^{-1}). Nevertheless, under appropriate experimental conditions, $CF_3H-(HF)_2$ and $CF_3H-(HF)_3$ should be observable.

The contraction of the C−H bond in $CF_3H-(HF)_3$ (−3.9 mÅ in the C_1 minimum, −2.1 mÅ in the C_s saddle) is considerably larger than that in $CF_3H-(HF)_2$ (−1.2 mÅ) and in CF_3H-HF (−0.7 mÅ) (see Table 7). However, the by far largest bond length distortions actually occur for the C−F bond of CF_3H involved in hydrogen bonding, with lengthenings by more than 0.03 Å. Quite similar distortions were already observed for the CF_3H-HF complex. The calculated H−F bond stretchings in $CF_3H-(HF)_2$ and $CF_3H-(HF)_3$ are slightly smaller than those in $(HF)_3$ and $(HF)_4$, in line with the trends in interaction energies.

The calculated blue shifts for ν(C−H) of $CF_3H-(HF)_2$ (see Table 8) are in the vicinity of 30 cm^{-1}. The infrared intensity reduction is quite remarkable and at all calculational levels below 2 km mol^{-1}. In the case of $CF_3H-(HF)_3$, we obtain much larger blue shifts (Table 9). For the C_s saddle we arrive at 54 and 45 cm^{-1} with MP2/6-311++G(2d,2p) and MP2/aug-cc-pVTZ, respectively. The corresponding shifts for the C_1 minima are, with 61 and 60 cm^{-1}, even more pronounced. Taking into account that at the MP2/aug-cc-pVTZ level the effect of the CP correction is already quite small, these blue shifts are probably the largest predicted so far for neutral C−H···X systems. The C−H stretching infrared intensity for $CF_3H-(HF)_3$ is similar to that in $CF_3H-(HF)_2$. The predicted red shifts of the H−F stretching modes of $CF_3H-(HF)_3$ are larger than those in $(HF)_3$ but smaller than those in $(HF)_4$.

3.4. The Complexes $CF_3H-(HF)_4$. On the basis of a thorough computational analysis of the potential energy surface of $CF_3H-(HF)_4$, we conclude that, due to the high stability of the $(HF)_4$ ring, a five-membered, cyclic $CF_3H-(HF)_4$ complex, analogous to $CF_3H-(HF)_2$ and $CF_3H-(HF)_3$, does not exist. However, there does exist, at the MP2/6-311++G(2d,2p) level, the complex $CF_3H-(HF)_4$ consisting of a cyclic $(HF)_4$ moiety and a CF_3H molecule attached either above the $(HF)_4$ ring (structure **3a** in Figure 3, the energy minimum) or laterally (structure **3b** with C_s symmetry, the saddle point of the first order). (The structures as obtained at the MP2/6-311++G(2d,2p) level are displayed in Figure 3. The structure with C_s

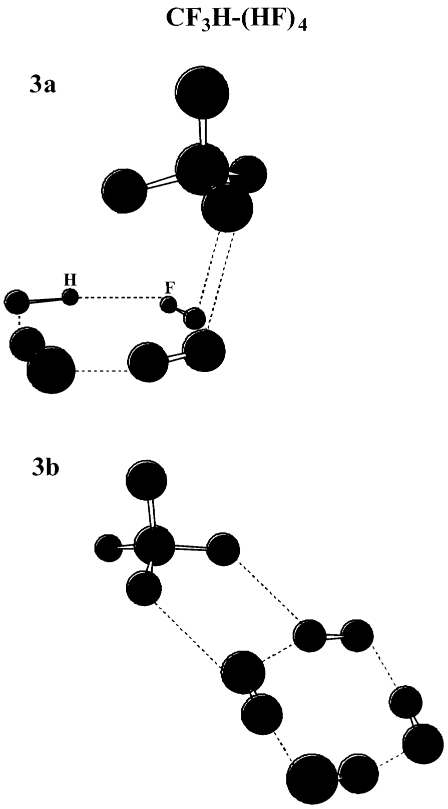

Figure 3. Global-minimum (a) and the C_s transition-state (b) structures of $CF_3H-(HF)_4$.

TABLE 10. Summary of Systematic Structural and Spectroscopic Changes in the Series of $CF_3H-(HF)_{1\leq n\leq 3}$ Complexes As Obtained at the MP2/aug-cc-pVTZ Level

	CF_3H-HF	$CF_3H-(HF)_2$	$CF_3H-(HF)_3$
ΔE_a(CP) (kcal mol^{-1})	−2.5	−9.4	−17.5
ΔE_b(CP) (kcal mol^{-1})	−2.5	−5.3	−3.5
Δr(C−H) (Å)	−0.0007	−0.0012	−0.0039
Δr(C−F) (Å)	0.0164	0.0303	0.0318
$\Delta \nu$(C−H) (cm^{-1})	15	30	60
A(C−H) (km mol^{-1})	8	2	3
r(C)H···F (Å)	2.576	2.239	2.244
r(F)H···F(C) (Å)	2.061	1.868	1.757

symmetry, **3b**, is a first-order saddle point; **3a** is a minimum.) The reason for the failure to obtain a five-membered ring structure is the high stability of the $(HF)_4$ ring. This implies that the insertion of a CF_3H molecule, accompanied by the formation of C−H···F and (C)F···H−F hydrogen bonds, thereby breaking one of the strong F···H−F hydrogen bonds of $(HF)_4$, is energetically unfavorable. For the minimum, **3a**, and saddle point, **3b**, structures of the $CF_3H-(HF)_4$ complex, only small blue shifts of 14 and 23 cm^{-1} are predicted at the same computational (MP2/6-311++G(2d,2p)) level. Therefore, the case $n = 3$ yields the largest blue shifts in $CF_3H-(HF)_n$ complexes. Notice that they are, hence, very fragile entities which cannot be likely observed experimentally.

4. Blue-Shifting and Blue-Shifted Hydrogen Bonds: Conclusions and Thoughts

The most important results on those properties of $CF_3H-(HF)_n$ clusters which are related to blue-shifting hydrogen bonds C−H···F are summarized in Table 10: (i) The clusters are stable for $1 \leq n \leq 3$ due to the formation of two hydrogen bonds, viz., C−H···F−H and C−F···H−F. For $n = 4$, the strongly nonadditive behavior of the F−H···F hydrogen bonds in the $(HF)_4$ ring does not allow formation of a stable, ring-shaped $CF_3H-(HF)_4$ cluster. (ii) The calculated blue shifts increase with cluster size ($1 \leq n \leq 3$). The blue shift of about 60 cm^{-1} calculated for $CF_3H-(HF)_3$ is among the largest ever reported in the literature for neutral C−H···X systems, although, as follows from Table 10, juxtaposing, for example, ΔE_b(CP) and r(C)H···F, the C−H···F bond in $CF_3H-(HF)_3$ is not the strongest one among all studied complexes. (iii) The infrared intensities are quite small for $n = 2$ and $n = 3$, a key characteristic feature of blue-shifting hydrogen bonds. (iv) Throughout the series, the intermolecular (F)H···F(C) distances are always substantially shorter than the (C)H···F contacts. The former are only about 0.1 Å larger than the strong (F)H···F hydrogen bonds between HF molecules in the rings. (v) The overwhelming majority of C−H···X systems discussed in the literature are isolated hydrogen bonds. Compared to those, the nonadditive behavior of the studied hydrogen-bonded rings with strong F−H···F and C−F···H−F bonds predetermines the energetics of the complex.

There are several arguments to support our view that the C−H···F hydrogen bond plays a secondary role, in the energetic sense, in the studied molecular complexations. The first one is that the change of the intramolecular C−F bond length in the C−F···H−F bond is larger than that of the intramolecular C−H bond in C−H···F by a factor of 8−24, despite the well-known fact that fluoroform is a rather specific molecule among haloforms in that its C−F bond is stronger than the C−H one, since the dissociation energy of the former is equal to 4.8−5.4 eV compared to 4.67 eV of the latter.[19] Second. The intermolecular F···H distances in the C−F···H−F bonds are much shorter than those in the C−H···F bonds (see Tables 4 and 7) for all $CF_3H-(HF)_n$ complexes. Overall, this implies that the elongation of the intramolecular C−F bond in the C−F···H−F bond also contributes to the contraction of the intramolecular C−H bond in the C−H···F hydrogen bond in the studied complexes.

Therefore, the *blue-shifting* C−H···F hydrogen bonds in these and related clusters might therefore also be dubbed as *blue-shifted* (this term was first used by Schlegel and co-workers[3b]). We thus suggest the existence of a rather clear-cut borderline between the blue-shifting and blue-shifted hydrogen bonds, the precise definition of which would, however, indeed demand a far more detailed elaboration than that presented in this work. Nevertheless, the present results demonstrate a certain shortcoming in interpreting the nature of blue-shifting hydrogen bonds exclusively within the external homogeneous electric field model.

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