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Blue-shifted hydrogen-bonded complexes. II. $\text{CH}_3\text{F} \cdots (\text{HF})_{1 \leq n \leq 3}$ and $\text{CH}_2\text{F}_2 \cdots (\text{HF})_{1 \leq n \leq 3}$

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Abstract

The equilibrium structures, binding energies, and vibrational spectra of the clusters $\text{CH}_3\text{F} \cdots (\text{HF})_{1 \leq n \leq 3}$ and $\text{CH}_2\text{F}_2 \cdots (\text{HF})_{1 \leq n \leq 3}$ have been investigated with the aid of large-scale ab initio calculations performed at the Møller–Plesset second-order level. In all complexes, a strong C–F \cdots H–F halogen–hydrogen bond is formed. For the cases $n = 2$ and $n = 3$, blue-shifting C–H \cdots F–H hydrogen bonds are formed additionally. Blue shifts are, however, encountered for all C–H stretching vibrations of the fluoromethanes in all complexes, whether they take part in a hydrogen bond or not, in particular also for $n = 1$. For the case $n = 3$, blue shifts of the $\nu(\text{C–H})$ stretching vibrational modes larger than 50 cm^{-1} are predicted. As with the previously treated case of $\text{CHF}_3 \cdots (\text{HF})_{1 \leq n \leq 3}$ complexes (A. Karpfen, E. S. Kryachko, J. Phys. Chem. A 107 (2003) 9724), the typical blue-shifting properties are to a large degree determined by the presence of a strong C–F \cdots H–F halogen–hydrogen bond. Therefore, the term blue-shifted appears more appropriate for this class of complexes. Stretching the C–F bond of a fluoromethane by forming a halogen–hydrogen bond causes a shortening of all C–H bonds. The shortening of the C–H bonds is proportional to the stretching of the C–F bond.

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1. Introduction

The last 5 years have been marked by an enormous growth of studies on blue-shifting hydrogen bonds of the C–H \cdots X-type, mainly initiated by the two pioneering papers by Hobza and Havlas [1,2]. A contraction of the C–H bond, a blue shift of its stretching vibrational mode, the accompanied decrease of its infrared intensity, and the absence of a direct relationship between the hydrogen bond interaction energy and the magnitude of the blue shift are the key features of blue-shifting hydrogen bonds C–H \cdots X [3–21], unequivocally placing

them in a sharp contrast to the conventional hydrogen bonds [22–25]. A major motivation of many of these studies on blue-shifting hydrogen bonds has been purely theoretical. Actually, the goal has been to shed light on the following basic issues: (i) whether the class of blue-shifting H-bonds is exceptional and includes only few representatives, or whether it can be extended to a larger variety of complexes; (ii) whether these blue-shifting hydrogen bonds should be treated as some natural extension of the conventional ones; (iii) what the upper limit of the blue shifts is [1,2,7]; and at last, (iv) what their very nature is [1–4,10–14], and what a theoretical model underlying the blue-shifting mechanism will be.

Regarding the issue (i), let us notice that most of the theoretical work in this area has so far been focused on C–H \cdots O and C–H \cdots N interactions [1–21]. Investigations on more general blue-shifting complexes of the

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A–H...X type have been rather limited in number and have covered only few particular cases [12,14–18]. Several theoretical approaches have recently been invoked to resolve the issues (ii) and (iv): (a) the charge-transfer natural bond orbital analysis; (b) modelling the formation of the C–H...X via embedding into a homogeneous electric field [10,11,13], (c) the energy decomposition scheme [6], (d) repulsive (Pauli) steric interactions [12] and (e) an interplay of hyperconjugation and rehybridization [14].

We have recently suggested [26] (paper I) that blue-shifting hydrogen bonds C–H...F with large blue shifts may be obtained when embedding CHF₃ in cyclic complexes of hydrogen fluoride molecules. In this way, we have, first, theoretically predicted the existence of new, experimentally still unobserved, hydrogen-bonded complexes, CHF₃–(HF)_{1 ≤ n ≤ 3} (referred therein as *blue-shifted* rather than the common *blue-shifting* ones), thus partially answered on (i), and secondly, demonstrated that one of them, CHF₃... (HF)₃, features the largest calculated C–H...X blue shift of 60 cm^{−1}, ever reported in the literature for neutral complexes and, therefore, extended the known upper limit for a blue shift. The present work pursues the motif started in paper I [26] by offering several more complexes of the type CH_{4−m}F_m... (HF)_n (1 ≤ m ≤ 2, 1 ≤ n ≤ 3) which all show blue-shifted hydrogen bonds. Several of them display blue shifts of a similar magnitude as CHF₃–(HF)₃. The analysis of the structure of these novel blue-shifted hydrogen-bonded complexes unequivocally implies that the contraction of their C–H bond(s) is largely explained by the *intrinsic behavior* of fluoromethanes and is caused by the strong elongation of the C–F bond participating in the formation of the (C)F...HF hydrogen bond.

2. Computational methodology and reference molecules

All calculations of the complexes CH₃F... (HF)_{1 ≤ n ≤ 3} and CH₂F₂... (HF)_{1 ≤ n ≤ 3}, framing the present work, were performed using the *GAUSSIAN 98*

Table 1

Selected MP2/aug-cc-pVTZ-calculated properties of the CH₃F and CH₂F₂ molecules

Property	CH ₃ F ^a	CH ₂ F ₂
r(C–H) (Å)	1.0870	1.0869
r(C–F) (Å)	1.3884	1.3590
ν(C–H) (cm ^{−1})	3088, 3190 ^b	3120, 3204
A(C–H) (km/mol) ^c	32, 44	37, 23
Total energy (hartree)	−139.541533	−238.688661
ZPVE (kcal/mol)	25.05	20.91

^a For a comparison see the recent QCISD(T)/cc-pVQZ data [35]. (r(C–H) = 1.0864 Å, r(C–F) = 1.3799 Å and ZPVE = 24.44 kcal/mol.

^b Doubly degenerate.

^c Infrared intensity.

Table 2

Selected MP2/aug-cc-pVTZ-calculated properties of the complexes CH₃F–HF and CH₂F₂–HF^a

Property	CH ₃ F–HF	CH ₂ F ₂ –HF
Δr(C–F') ^b	+16.8	+19.0
Δr(C–F)		−8.5
Δr(C–H)	−1.3, −2.0	−0.7, −1.4
Δr(F–H)	+9.8	+6.3
Δν(C–H)	+16, +26, +29	+13, +20
ΔA(C–H)	−9, −14, −11	−13, −12
Δν(C–F') ^c	−44	−47
Δν(F–H)	−215	−134
ΔE	−6.1	−4.3
ΔE(CP)	−5.5	−3.7

^a Bond lengths changes with respect to monomers in mÅ, frequency shifts relative to monomers in cm^{−1}, infrared intensity reductions relative to monomers in km/mol, stabilization energies in kcal/mol.

^b C–F bond involved in the (C)F...HF hydrogen bond.

^c Shift of the C–F stretching mode involved in the (C)F...HF bond of the dimer.

suite of programs [27] applying the second-order perturbation Møller–Plesset method (MP2). The extended Dunning-type basis set aug-cc-pVTZ [28,29] was used.

Due to the floppy nature of the studied complexes, all geometry optimizations were conducted using the option “tight”. Their harmonic vibrational frequencies were calculated in order to properly characterize stationary points. The effect of the counterpoise (CP) correction [30] to the basis-set superposition error (BSSE) has also been calculated.

Selected calculated structural and spectroscopic features of the monomers CH₃F and CH₂F₂ relevant for the following discussion are collected in Table 1. Corresponding data for the (HF)_{1 ≤ n ≤ 3} clusters may be found in Table 2 of paper I. The latter clusters have already been amply discussed in the literature [31–34] and their structures and vibrational spectroscopic properties are well known.

3. The complexes CH₃F... (HF)_{1 ≤ n ≤ 3} and CH₂F₂(HF)_{1 ≤ n ≤ 3}

In this Section, the most stable hydrogen-bonded complexes CH₃F... (HF)_{1 ≤ n ≤ 3} and CH₂F₂... (HF)_{1 ≤ n ≤ 3} are compared with the case of CHF₃... (HF)_{1 ≤ n ≤ 3}, previously discussed [26]. We provide a complete and consistent descriptive picture of the effect of the fluorine substitution (1 ≤ m ≤ 3) of methane on the key properties of the H-bonded complexes CH_{4−m}F_m... (HF)_m, primarily focussing on the change of the C–H bond length(s) and on the accompanying blue shift of the stretching mode(s) ν(C–H). In addition, we also monitor the changes in C–F bond distances and the corresponding shifts of the ν(C–F) stretching modes. The optimized structures, the bond distances, and a few selected bond angles of the most stable structures of the CH₃F...

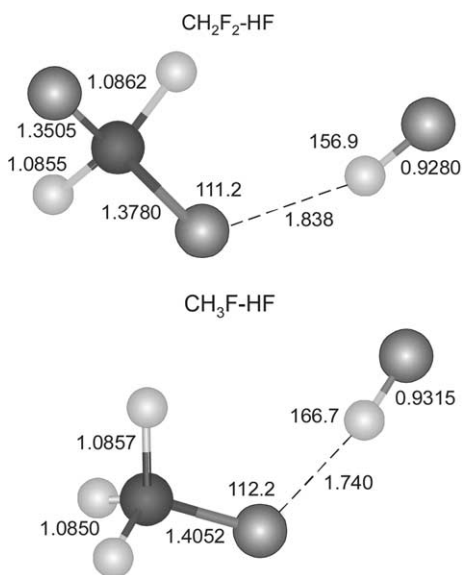


Fig. 1. MP2/aug-cc-pVTZ optimized structures of the complexes $\text{CH}_2\text{F}_2 \cdots \text{HF}$ and $\text{CH}_3\text{F} \cdots \text{HF}$. Bond lengths in Å and bond angles in degrees.

$(\text{HF})_{1 \leq n \leq 3}$ and $\text{CH}_2\text{F}_2 \cdots (\text{HF})_{1 \leq n \leq 3}$ complexes are shown in Figs. 1–3.

3.1. The complexes $\text{CH}_3\text{F} \cdots \text{HF}$ and $\text{CH}_2\text{F}_2 \cdots \text{HF}$

More detailed discussions and characterizations of the various stationary points on the energy surfaces of

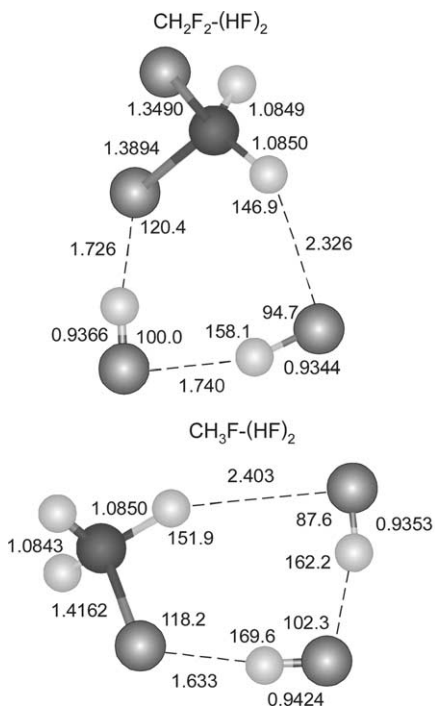


Fig. 2. MP2/aug-cc-pVTZ optimized structures of the complexes $\text{CH}_2\text{F}_2 \cdots (\text{HF})_2$ and $\text{CH}_3\text{F} \cdots (\text{HF})_2$. Bond lengths in Å and bond angles in degrees.

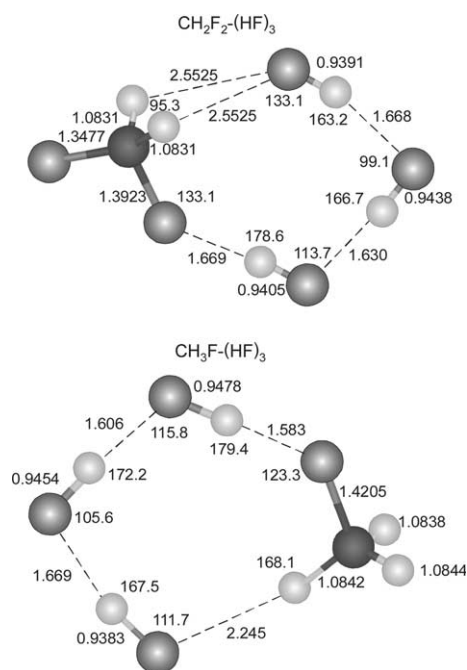


Fig. 3. MP2/aug-cc-pVTZ optimized structures of the complexes $\text{CH}_2\text{F}_2 \cdots (\text{HF})_3$ and $\text{CH}_3\text{F} \cdots (\text{HF})_3$. Bond lengths in Å and bond angles in degrees.

the two dimers will be reported separately. Here, we concentrate solely on the global minima shown in Fig. 1. The $\text{CH}_3\text{F} \cdots \text{HF}$ dimer has C_s symmetry, $\text{CH}_2\text{F}_2 \cdots \text{HF}$ is C_1 -symmetric only. Bond length relaxations, frequency shifts relative to the monomers and stabilization energies are compiled in Table 2. No $\text{C-H} \cdots \text{F}$ hydrogen bonds are formed. In both complexes, structures with $\text{C-F} \cdots \text{H-F}$ hydrogen bonds are the most stable. These two structures are closely related to the second most stable minimum (structure 1c in [26]) of $\text{CHF}_3 \cdots \text{HF}$. In all three cases, the relative orientation of the HF monomer is approximately in the direction of the lone pair at the fluoromethane F atom involved in the $\text{C-F} \cdots \text{H-F}$ hydrogen bond.

The intermolecular $\text{C-F} \cdots \text{H}$ distance in $\text{CH}_3\text{F} \cdots \text{HF}$ is shorter than in $\text{CH}_2\text{F}_2 \cdots \text{HF}$ by about 0.1 Å. This is in line with the larger stabilization energy of the $\text{CH}_3\text{F} \cdots \text{HF}$ complex. The trends in the stabilization energies of the three complexes $\text{CHF}_3 \cdots \text{HF}$, $\text{CH}_2\text{F}_2 \cdots \text{HF}$, and $\text{CH}_3\text{F} \cdots \text{HF}$ (−2.9, −4.3, −6.1 kcal/mol) correlate very well with the optimized C–F bond lengths encountered in the fluoromethane monomers (1.336, 1.359, 1.388 Å).

The formation of the $\text{C-F} \cdots \text{H-F}$ hydrogen bond leads to a significant elongation of this C–F bond in both complexes. Simultaneously, all other (C–F or C–H) fluoromethane bond lengths are contracted. $\nu(\text{C-F})$ as well as $\nu(\text{F-H})$ of the $\text{C-F} \cdots \text{H-F}$ hydrogen bond are both red-shifted. This particular feature, *the shrinking of all available fluoromethane C–F and C–H bonds*

caused by the stretching of the C–F bond involved in the C–F···H–F hydrogen bond can evidently be traced back to an *intrinsic property of the fluoromethanes*. Therefore, despite the absence of C–H···F hydrogen bonds in the global minima of CH₂F₂···HF and CH₃F···HF, quite substantial blue shifts of $\nu(\text{C–H})$ are predicted for both complexes (+20 cm^{−1} for CH₂F₂···HF and +29 cm^{−1} for CH₃F···HF), a consequence of the C–H bond length shortenings.

Instead of using the notion *hydrogen-bonded*, one could also consider the term *halogen-bonded* as being appropriate to characterize the structures of the dimers. The term *halogen bonding* has frequently been used to describe the interaction of molecules carrying X–Hal bonds with a variety of partner molecules, mainly amines [36–39]. The halogen bond has much in common with the *conventional* hydrogen bond, in particular the widening of the X–Hal distances, the typical red shift of $\nu(\text{X–Hal})$, and the increased infrared intensity of $\nu(\text{X–Hal})$. Indeed, both concepts apply. Adjacent hydrogen and halogen bonds are encountered in the C–F···H–F bond of these fluoromethane–HF dimers, and, hence, we suggest to use the term *halogen–hydrogen bond*.

3.2. The complexes CH₃F···(HF)₂ and CH₂F₂···(HF)₂

Calculated bond length relaxations, frequency shifts relative to the monomers and stabilization energies relative to infinitely separated fluoromethanes and (HF)₂, ΔE_{a} , and with respect to isolated monomers, ΔE_{b} , are compiled in Table 3. As with the previously treated case of CHF₃···(HF)₂ [26], both trimeric complexes are cyc-

Table 3
Selected MP2/aug-cc-pVTZ-calculated properties of the complexes CH₃F–(HF)₂ and CH₂F₂–(HF)₂^a

Property	CH ₃ F–(HF) ₂	CH ₂ F ₂ –(HF) ₂
$\Delta r(\text{C–F}')^{\text{b}}$	+27.8	+30.4
$\Delta r(\text{C–F})$		−10.0
$\Delta r(\text{C–H}')^{\text{c}}$	−2.0	−1.9
$\Delta r(\text{C–H})$	−2.7	−2.0
$\Delta r(\text{F–H})$	+20.7, +13.6	+14.9, +12.7
$\Delta \nu(\text{C–H})$	+22, +39, +40	+24, +38
$\Delta A(\text{C–H})$	−6, −13, −22	−13, −21
$\Delta \nu(\text{C–F}')^{\text{d}}$	−72	−80
$\Delta \nu(\text{F–H})$	−373, −173	−277, −204
$\Delta E_{\text{a}}^{\text{e}}$	−9.8 (−8.8) ^f	−7.7 (−6.7)
$\Delta E_{\text{b}}^{\text{g}}$	−14.5 (−13.0) ^f	−12.4 (−10.9)

^a Bond length changes with respect to monomers in mÅ, frequency shifts in cm^{−1}, infrared intensity reductions in km/mol, stabilization energies in kcal/mol.

^b C–F bond involved in the (C)F···HF hydrogen bond.

^c C–H bond involved in the (C)H···FH hydrogen bond.

^d Shift of the C–F stretching mode involved in the (C)F···HF bond.

^e Stabilization energy with respect to fluoromethane and (HF)₂.

^f CP-corrected values in parentheses.

^g Stabilization energy with respect to infinitely separated monomers.

Table 4

Selected MP2/aug-cc-pVTZ-calculated properties of the complexes CH₃F–(HF)₃ and CH₂F₂–(HF)₃^a

Property	CH ₃ F–(HF) ₃	CH ₂ F ₂ –(HF) ₃
$\Delta r(\text{C–F}')^{\text{b}}$	+32.1	+33.3
$\Delta r(\text{C–F})$		−11.3
$\Delta r(\text{C–H}')^{\text{c}}$	−2.8	−3.8 ^d
$\Delta r(\text{C–H})$	−2.6, −3.2	
$\Delta r(\text{F–H})$	+26.1, +23.7, +16.6	+22.1, +18.8, +17.4
$\Delta \nu(\text{C–H})$	+26, +42, +52	+43, +58
$\Delta A(\text{C–H})$	0, −14, −20	−23, −16
$\Delta \nu(\text{C–F}')^{\text{e}}$	−84	−94
$\Delta \nu(\text{F–H})$	−577, −445, −329	−490, −361, −330
$\Delta E_{\text{a}}^{\text{f}}$	−8.1 (−7.0) ^g	−6.3 (−5.2)
$\Delta E_{\text{b}}^{\text{h}}$	−23.6 (−21.2) ^g	−21.7 (−19.4)

^a Bond length changes with respect to monomers in mÅ, frequency shifts in cm^{−1}, infrared intensity reductions in km/mol, stabilization energies in kcal/mol.

^b C–F bond involved in the (C)F···HF hydrogen bond.

^c C–H bond involved in the (C)H···FH hydrogen bond.

^d Bifurcated hydrogen bond.

^e Shift of the C–F stretching mode involved in the (C)F···HF bond.

^f Stabilization energy with respect to fluoromethane and (HF)₃.

^g CP-corrected values in parentheses.

^h Stabilization energy with respect to infinitely separated monomers.

lic. In addition to C–F···H–F halogen–hydrogen bonds, C–H···F–H hydrogen bonds between the fluoromethane and the (HF)₂ moiety are now formed as well.

Compared to the isolated monomers, the by far largest structural modification of the fluoromethanes occurs for the C–F bond length in the C–F···H–F hydrogen bond. The combined halogen–hydrogen bond results in increases of $\Delta R(\text{C–F})$ of about 28 and 30 mÅ for CH₃F···(HF)₂ and CH₂F₂···(HF)₂, respectively, short F···H contacts of 1.63 and 1.74 Å, and $\Delta R(\text{F–H})$ elongations close to 17 and 12 mÅ. This fits to the conventional pictures of halogen and hydrogen bonding. A quite different behavior is observed for the C–H···F–H hydrogen bond. Firstly, the intermolecular H···F distances are with 2.33 and 2.40 Å much larger than the F···H distances in the C–F···H–F halogen–hydrogen bond, indicating that the C–H···F bond is the weakest intermolecular contact in this three-membered ring (counting molecules). Secondly, the C–H bond is slightly shortened by about 2 mÅ for both trimers, showing the typical feature of blue-shifting hydrogen bonds. However, all the other fluoromethane C–H and C–F bonds, not involved in intermolecular hydrogen bonding, are contracted too.

All the observations just discussed for the structures are mirrored in the stabilization energies and, particularly, in the vibrational frequency shifts. $\Delta E_{\text{a}}(\text{CP})$ amounts to −8.8 and −6.7 kcal mol^{−1} for CH₃F···(HF)₂ and CH₂F₂···(HF)₂. All C–H stretching frequencies are blue-shifted (+22 to +40 cm^{−1}), the C–F stretching frequency of the halogen bond is significantly red-shifted by −70 to −80 cm^{−1}.

Summarizing our data on $\text{CH}_3\text{F}\cdots(\text{HF})_2$ and $\text{CH}_2\text{F}_2\cdots(\text{HF})_2$, we can characterize these cyclic complexes as being governed to a large degree by the formation of a $\text{C-F}\cdots\text{H-F}$ halogen–hydrogen bond which results in a distinct lengthening of the C–F bond. This in turn leads to a shortening of *all other* C–H and C–F fluoromethane bonds, whether being involved in intermolecular contacts or not, and to blue-shifts of all their stretching vibrations. The very same picture has already been observed for the complexes $\text{CHF}_3\cdots(\text{HF})_{1\leq n\leq 3}$ [26]. Therefore, we suggested to use the term *blue-shifted* rather than *blue-shifting*. An important, if not the *primary cause* of the $\nu(\text{C-H})$ blue-shifts in these complexes is the elongation of the equilibrium $R(\text{C-F})$ distance in the complexes relative to that in the isolated fluoromethane as a consequence of forming a halogen–hydrogen bond.

3.3. The complexes $\text{CH}_3\text{F}\cdots(\text{HF})_3$ and $\text{CH}_2\text{F}_2\cdots(\text{HF})_3$

The calculated properties are collected in Table 4. As with the previously treated case of $\text{CHF}_3\cdots(\text{HF})_3$ [26], both tetrameric complexes are cyclic with $\text{C-F}\cdots\text{H-F}$ halogen–hydrogen bonds and with

$\text{C-H}\cdots\text{F-H}$ and $\text{F-H}\cdots\text{F-H}$ hydrogen bonds. The $\text{CH}_3\text{F}\cdots(\text{HF})_3$ complex has C_1 symmetry, the equally conceivable C_s -symmetric structure is a first-order saddle point. The optimized structure of the $\text{CH}_2\text{F}_2\cdots(\text{HF})_3$ complex has C_s symmetry and a bifurcated $\text{CH}_2\cdots\text{FH}$ bond (see Fig. 3). In these tetramers, the C–F bond length elongations are even slightly larger than in the trimers. The same applies to the C–H bond length shrinkings. The calculated $\nu(\text{C-H})$ blue shifts are in the region from +26 to +52 cm^{-1} for $\text{CH}_3\text{F}\cdots(\text{HF})_3$ and +43 to +58 cm^{-1} for $\text{CH}_2\text{F}_2\cdots(\text{HF})_3$. The calculated red shifts of the C–F stretching mode are large in absolute value and amount to –84 and –94 cm^{-1} for $\text{CH}_3\text{F}\cdots(\text{HF})_3$ and $\text{CH}_2\text{F}_2\cdots(\text{HF})_3$, respectively. The stabilization energies $\Delta E_a(\text{CP})$ of both tetramers are by about 2 kcal/mol smaller in absolute value than those of the trimers.

3.4. Systematic trends in the series

In this section, we compare the most important trends of our data gained on $\text{CH}_3\text{F}\cdots(\text{HF})_n$ and $\text{CH}_2\text{F}_2\cdots(\text{HF})_n$ with those calculated for $\text{CHF}_3\cdots(\text{HF})_n$ [26]. We restrict this discussion to the C–F bond of the

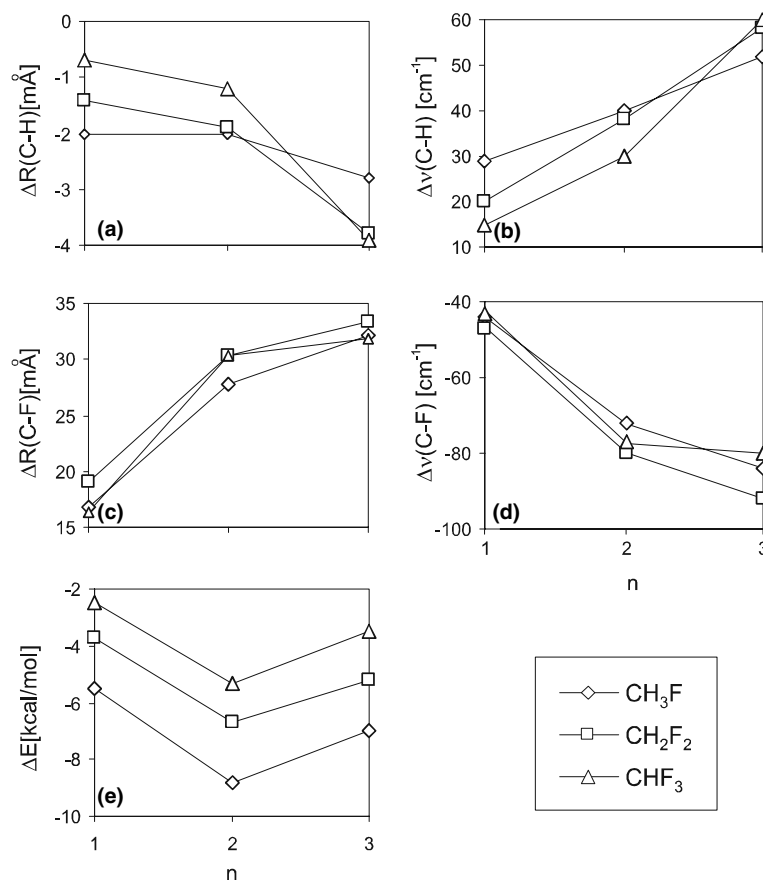


Fig. 4. Trends in structural changes, vibrational frequency shifts and stabilization energies in the series of $\text{CH}_{4-m}\text{F}_m(\text{HF})_n$ ($1 \leq m \leq 3$; $1 \leq n \leq 3$) complexes. (a) $\Delta R(\text{C-H})$, (b) $\Delta \nu(\text{C-H})$, (c) $\Delta R(\text{C-F})$, (d) $\Delta \nu(\text{C-F})$, (e) ΔE_a .

C–F···H–F halogen–hydrogen bond and the C–H bond of the blue-shifted C–H···F–H hydrogen bond. We define $R_m^n(\text{X–Y})$ and ΔE_m^n as a distance between the atoms X and Y and the binding energy of the complex $\text{CH}_4-m\text{F}_m\cdots(\text{HF})_n$ relative to the infinitely separated CH_4-mF_m and $(\text{HF})_n$ moieties. Here the subscript m determines the degree of the F substitution in methane and the superscript n indicates the number of participating HF molecules. Fig. 4 contains plots of the calculated trends in $\Delta R_m^n(\text{C–H})$, $\Delta v_m^n(\text{C–H})$, $\Delta R_m^n(\text{C–F})$, $\Delta v_m^n(\text{C–F})$, and ΔE_m^n .

For all m , i.e., independent of the fluoromethane chosen, $\Delta R_m^n(\text{C–H})$ becomes more negative with increasing n . $R_m^n(\text{C–H})$ is thus progressively shortened. Again independent of m , $\Delta R_m^n(\text{C–F})$ increases with increasing n . The trends in $\Delta v_m^n(\text{C–H})$ and $\Delta v_m^n(\text{C–F})$ follow the same pattern, again rather independent of the nature of the fluoromethane. With increasing n , the blue shift of the C–H stretching vibration, $\Delta v_m^n(\text{C–H})$, increases, reaching values between +50 and +60 cm^{-1} , respectively, for $n = 3$. The red shift of the C–F stretching vibration, on the other hand, is largest in absolute value for $n = 3$, with values between –80 and –90 cm^{-1} . Even more regular is the stabilization energy ΔE_m^n . The difference in the binding energies already obtained for the three fluoromethane–HF dimers remains nearly constant upon increasing n . The trends in the different H–F bond lengths and the corresponding H–F stretching vibrational frequencies (see Tables 2–4) follow the usual behavior well-known from conventional hydrogen

bonding in HF-clusters [31–34] and are, therefore, not discussed in detail.

4. Some features of the energy surfaces of isolated fluoromethanes $\text{CH}_m\text{F}_{4-m}$ ($1 \leq m \leq 3$)

In this section, we investigate the coupling between the different bond stretching degrees of freedom in the three fluoromethanes. To this end, potential surface scans have been performed by systematically fixing $R(\text{C–H})$ or $R(\text{C–F})$ in a regular mesh and optimizing all other degrees of freedom. Selected results as obtained at the MP2/aug-cc-pVTZ level for all three fluoromethanes are shown in Fig. 5. Only the stretch–stretch couplings are discussed explicitly. In the interesting region, i.e., ± 50 mÅ around the equilibrium distances, bond angle changes are consistently smaller than 2° and hence negligible.

Fig. 5(a) and (c) demonstrate that $R(\text{C–F})$ and $R(\text{C–H}')$ shrink, when $R(\text{C–H})$ is stretched, independent of the fluoromethane. Even more important, Fig. 5(b) and (d) show that $R(\text{C–H})$ and $R(\text{C–F}')$ shrink, when $R(\text{C–F})$ is stretched, again independent of the nature of the fluoromethane. Thus, the intramolecular response to pulling on any bond of a fluoromethane, is a shortening of all the other bonds. Of particular significance for the case in hand: *stretching the C–F bond of a fluoromethane by forming a halogen–hydrogen bond causes a shortening of all C–H bonds. The shortening of the C–H*

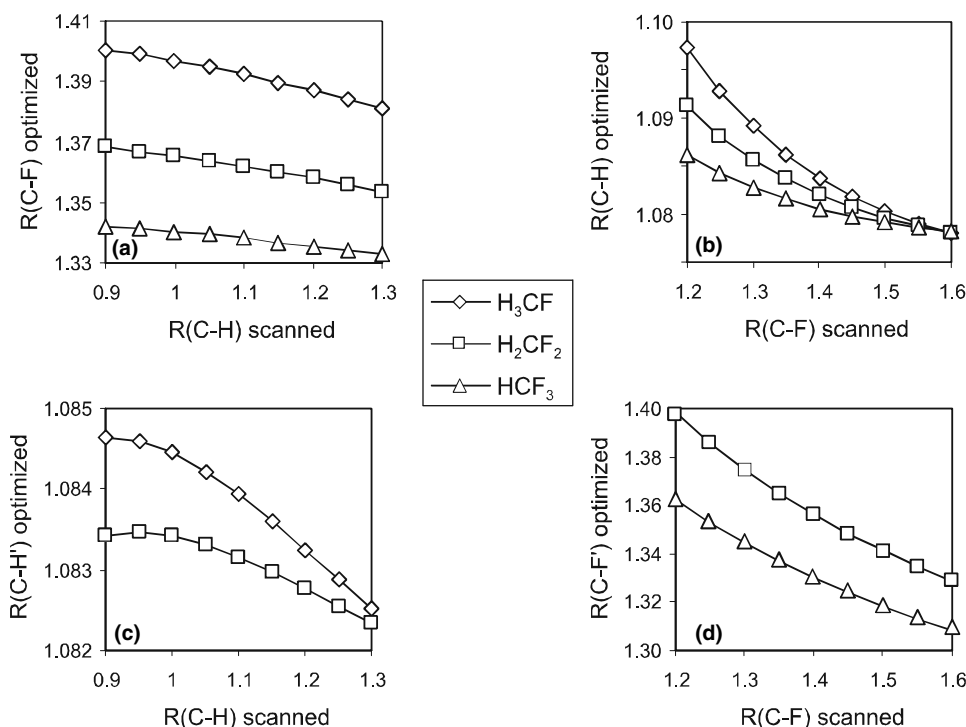


Fig. 5. Intramolecular response to selected scans of fluoromethane energy surfaces.

bonds is proportional to the stretching of the C–F bond. Evidently, these features must be a consequence of the structure of the intramolecular force fields of the fluoromethanes.

5. Summary and conclusions

In this work, the results of high-level ab initio calculations on clusters formed between the two fluoromethanes CH_3F and CH_2F_2 and $(\text{HF})_n$ species were presented. So far, no experimental data are available for these complexes. The dimers $\text{CH}_3\text{F} \cdots \text{HF}$ and $\text{CH}_2\text{F}_2 \cdots \text{HF}$ have *open* structures with C–F \cdots H–F halogen–hydrogen bonds. All other clusters $\text{CH}_3\text{F} \cdots (\text{HF})_n$ and $\text{CH}_2\text{F}_2 \cdots (\text{HF})_n$ with $n = 2, 3$ are cyclic, with stronger, red-shifting C–F \cdots H–F halogen–hydrogen bonds and weaker, C–H \cdots F–H blue-shifted hydrogen bonds. The trends observed for the two series are in full analogy with the features reported previously for $\text{CHF}_3 \cdots (\text{HF})_{1 \leq n \leq 3}$ clusters [26]. The strongest blue shifts of the C–H stretching frequencies and the strongest red shifts of the C–F stretching frequencies are predicted for $n = 3$. There, the calculated blue shifts of the C–H stretching modes are of the order of 50–60 cm^{-1} and are thus among the largest for neutral C–H \cdots X systems. Even more marked, particularly in view of the mass difference, are the calculated red shifts of the C–F stretching modes in the range of –80 to –90 cm^{-1} .

One aspect that emerged from the current study is that the features of the intramolecular force fields of the fluoromethanes need to be considered in greater detail, when discussing blue-shifting complexes of fluoromethanes with hydrogen bond acceptors. We have shown that the stretching of one C–X ($X = \text{F}, \text{H}$) bond of an isolated fluoromethane results in a shrinking of all other C–X ($X = \text{F}, \text{H}$) bonds. Thus, the relaxation consists of a negative response. This intramolecular coupling is of importance for an understanding of these complexes.

For the stability of all of the above complexes the formation of a C–F \cdots H–F halogen–hydrogen bond is energetically more important than the formation of the C–H \cdots F–H hydrogen bond. The formation of the C–F \cdots H–F halogen–hydrogen bond in the fluoromethane– $(\text{HF})_n$ complexes leads to a very significant stretching of the fluoromethane C–F bond which in turn causes a shortening of all other bonds in the fluoromethane, being involved in a hydrogen bond or not.

Evidently, this basic feature of the intramolecular $\text{CH}_4 - m\text{F}_m$ ($1 \leq m \leq 3$) coupling in fluoromethanes does not suffice to fully explain the phenomenon of blue-shifting hydrogen-bonded complexes. All other conventional mechanisms of the theory of intermolecular interaction are operative, too. However, for the cases of the cyclic complexes treated in this work, this intrinsic

behavior of the fluoromethanes appears to be the basic mechanism for their stability and for the presence of strongly *blue-shifted* C–H \cdots F hydrogen bonds.

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