풀루오르화메탄들과 암모니아 및 물과의 수소결합 이량체들에 관한 Ab Initio 연구

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Ab Initio Studies on Hydrogen-Bonded Dimers of Fluoromethanes with Ammonia and Water

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요 약. CH_4, CH_3F, CH_2F_2, CHF_3과 NH_3 및 H_2O와의 수소결합 이량체들에 대하여 9s5p/5s 및 9s5p1d/5s 1p의 basis sets를 사용하여 체계적인 ab initio 계산을 하였다. 이들 이량체들의 바닥상태성질을 구하여 독립된 단위체들의 대응하는 성질과 비교하였으며, 평형기하구조, 안정화에너지, 쌍극자모멘트 및 분자간 결합의 힘상수 등을 보고하였다. 사슬형 소중합체들에서 수소결합의 비가감적 거동의 결과로부터 일어나는 여러가지 효과들을 논의하고, SCF 근사법의 사용에 따른 체계적 및 조직적인 오차들과 계산결과들의 basis sets 의 존성을 지적하였다.

ABSTRACT. Systematic ab initio SCF calculations have been performed on the hydrogen-bonded dimers of fluoromethanes involving CH_4, CH_3F, CH_2F_2 and CHF_3 with ammonia and water applying basis sets of 9s5p/5s and 9s5p1d/5p1d. Various ground state properties of these stable dimeric complexes have been evaluated. We compared these with corresponding properties of isolated monomers. We report equilibrium geometries, stabilization energies, dipole moments and force constants of intermolecular bonds. The effects arising as a consequence of the non-additive behavior of hydrogen bonding in chain-like oligomers are discussed. Systematic, methodical errors due to the use of the SCF approximation and the basis set dependence of the computed results are pointed out.

INTRODUCTION

In the last years a large number of works on hydrogen-bonded systems have been reported. On one hand due to their variety and the advent of large-scale computational facilities, on the other hand because of their importance in biological processes as well as in biochemical and chemical processes hydrogen-bonded aggregates give a continuous challenge to both the theorist and the spectroscopist nowadays. So we can find out a recent review of these works elsewhere and a wealth of results from them are available[1~5]. In small complexes, aggregates or oligomers theoretical results are generally close to the experimental values. For the relatively larger complexes, however, full geometry optimization is avoided and small basis sets are applied. Because full geometry optimization is tedious and time-consuming task, intramolecular geometry of each system is kept constant, and only intermolecular coordinates are optimized generally. In simple complexes, geometry changes of subsystems are negligible substantially. However, if the directions of polarity of subsystems are different from those of the comple-

xes, severe geometry changes of subsystems in complexes may be found. So to get the results which have good agreement with experimental values large scale basis sets and full geometry optimization are required as a prerequisite.

Systematic theoretical or experimental studies on the hydrogen bonding of fluoromethanes with ammonia and water are seldom so far. Only in the case of CF_3H--NH_3 and CF_3H--OH_2 which give relatively larger hydrogen bonding energy a few works have been reported[6~10]. In the theoretical studies they used small basis sets and performed partial geometry optimization. From their systematic survey of crystallographic data[11] R. Taylor and O. Kennard have pointed out that C-H--N or C-H--O bond may be a significant factor in determining the structures of amino acids, nucleosides and other organic molecules and that the energy of the hydrogen bond is very sensitive to the nature of the (C-)H atom. So we intend to furnish theoretical structural information to suppliment spectroscopic and crystallographic studies on the C-H--N and C-H--O hydrogen bonds by performing full geometry optimization with relatively larger basis sets.

METHOD OF CALCULATION

The standard ab initio SCF method has been applied to the monomers and dimers discussed below. The COLUMBUS program system[12,13] has been used which contains SCF and analytic gradient programs written by Pitzer based on HONDO routines[14,15]. 9s5p and 9s5p1d (in the following abbreviated as 9, 5 and 9, 5, 1) basis sets were chosen for C, N, O and F, respectively, and 5s and 5s1p for H. All s and p basis sets were taken from Huzinaga's compilation[16,17]. As exponents for the taken from Huzinaga's compilation[16,17]. As exponents for the polarization functions we chose: C(1.0), N(0.95), O(1.0), F(1.6) and H(0.75). These basis sets were contracted into [5,3] and [5,3,1] for C, N, O and F, respectively, and to [3] and [3,1] for H. For the small sized monomers NH_3 and H_2O, an additional basis set 11s7p2 d/6s1p approaching to near-Hartree-Fock quality
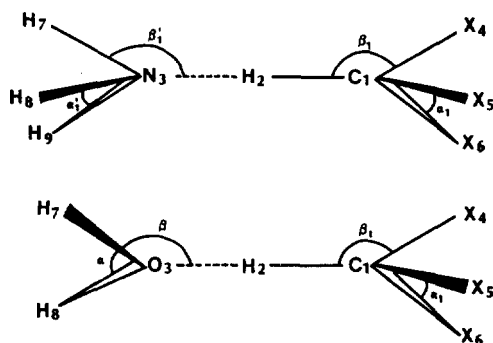

Fig. 1. Structures and internal coordinates of dimers. Here X's represent hydrogen or fluorine atoms. Bond angles are $\alpha_2 = <X_4CX_5$, $\alpha_3 = <X_4CX_6$, $\alpha_2' = <H_7NH_8$, $\alpha_3' = <H_7NH_9$, $\beta_2' = <H_2NH_8$, $\beta_3' = <H_2NH_9$, $\beta = <H_2$ OH_7. In C_s symmetry $\alpha_2 = \alpha_3$, $\alpha_2' = \alpha_3'$, $\beta_2' = \beta_3'$, $\beta = <$ $H_2OH_7 = <H_2OH_8$, $r(C-X_5) = r(C-X_6)$, $r(N-H_8) = r(N-H_9)$ and $r(O-H_7) = r(O-H_8)$.

at least for valence shell properties is applied to demonstrate the basis set dependence of the computed results. This was contracted into [5,3,2] for N and O, and to [3,1] for H. As exponents for the polarization functions 0.95 and 0.3 for N, 1.2 and 0.15 for O and 0.75 for H, respectively.

Equilibrium geometries were obtained with the aid of gradient optimization[18]. Full geometry optimization were carried out far all the monomers and dimers, and Cs symmetry was retained for both of them. Standardized internal coordinates suggested by P. Pulay, *et al.*[19,20] were employed. The assumed structures of dimers were defined as shown in *Fig.* 1.

RESULTS AND DISCUSSION

Monomers. Computed ground state properties of the monomers NH_3 and H_2O which act as proton acceptors are compiled in *Table* 1 and those of the monomers CH_4, CH_3F, CH_2F_2 and CHF_3 which act as proton donors in *Table* 2, and confronted with experimental data in order to assess the systematic, methodical errors of our SCF calculations and the basis set dependence of the computed results. The performance of such calculations is generally well known. We nevertheless

Table 1. Ground state properties of ammonia and water[a]

	NH₃			
	9, 5/5	9, 5, 1/5, 1	11, 7, 2/6, 1	exp.
r(NH)(Å)	0.9927	1.007	1.0010	1.008
<HNH (degree)	115.05	107.98	107.58	107.3
E(hartree)	−56.18286	−56.21104	−56.21986	−
μ(debye)	1.44	1.72	1.64	1.47
A(cm⁻¹)	−	6.4	−	6.3
B(cm⁻¹)	−	10.3	−	9.3
C(cm⁻¹)	−	−	−	−

	H₂O			
	9, 5/5	9, 5, 1/5, 1	11, 7, 2/6, 1	exp.
r(OH)(Å)	0.9482	0.9430	0.9426	0.958
<HOH (degree)	112.52	106.25	106.00	104.45
E(hartree)	−76.01415	−76.04850	−76.06153	−
μ(debye)	2.50	2.14	1.96	1.84
A(cm⁻¹)	−	29.4	−	27.3
B(cm⁻¹)	−	14.7	−	14.7
C(cm⁻¹)	−	9.8	−	9.5

[a]Experimental results from refs. [21~23].

recapitulate shortly the most important deviations from experimental data. At this SCF level of approximation bond distances are consistently too short. Therefore it has been pointed out before that corresponding stretching frequencies are too high and rotational constants are too large[28,29]. We can see these trends of the C-H stretching force constant in Table 2 and of the rotational constants in Table 1 and 2. It may be noted specially that the computed bond angles applying our 9, 5/5 basis set without polarization functions show relatively larger deviation from the experimental values. Similarly dipole moments are overestimated with the exception of 9, 5/5 basis set in ammonia which gives poorer geometry results compared to the larger basis sets. The dipole moments calculated using smaller 9, 5/5 basis set are almost always larger than those calculated using 9, 5, 1/5,1 basis set. The ab initio calculations predict a regular decrease in C-H bond lengths going from CH₄ to CHF₃. Such a decrease is not found experimen-

tally and is certainly not realistic[30]. These trends may be thought to reflect the systematic, methodical errors due to the use of the Hartree-Fock approximation and eventual deficiencies of the basis set applied. Evidently these errors will persist in the SCF results for the dimers built up from these monomers.

Dimers. Only those dimeric structures are considerd in which methane and fluoromethanes act as hydrogen-bond donors and ammonia and water as hydrogen-bond acceptors. In cases of F₃ CH--NH₃ and F₃CH---OH₂, however, the configurations investigated here do correspond to the experimentally confirmed dimer orientations[8,10]. We have performed full geometry optimization applying the same basis sets as in the monomers.

In Table 3 equilibrium geometries, total energies, stabilization energies, dipole moments, rotational constants and force constants of interest of the dimers which are formed between fluoromethanes and ammonia are compiled. The corresponding results for the dimers of fluoromethanes with water are presented in Table 4. Not many of these data can be compared to experiment.

Concerning intramolecular equilibrium distances we expect to observe the same errors as in the monomers. At our SCF level the smaller 9, 5/5 basis set always calculates intra- and intermolecular distances shorter then the larger 9, 5, 1/5, 1 basis set does. Intramolecular geometry relaxations occurring upon dimer formation are almost quantitatively the same in the both two basis sets. r_{C-F}'s of the hydrogen-bond donors in the two series of dimers are longer by about 0.005 Å with our 9, 5, 1/5, 1 basis set and 0.006 Å with 9, 5/5 basis set compared to the corresponding bonds in the monomers. Intermolecular geometry distorsions upon comples formation are very small in the dimer CH₄--NH₃, CFH₃--NH₃, CH₄--OH₂ and CFH₃--OH₂. Because in these dimers the directions of polarities of the subunits remain practically unchanges. However, in the cases of CFH₃-- NH₃, CF₂H₂--NH₃, CFH₃--OH₂ and CF₂H₂--OH₂ the directions of polarities of the subunits are quite different from those of the isolated monomers. Thus, intermolecular geometry distorsions

Table 2. Ground state properties of methane and fluoromethanes[a]

	CH_4			CH_3F		
	9, 5/5	9, 5, 1/5, 1	exp.	9, 5/5	9, 5, 1/5, 1	exp.
$r(CH)(Å)$	1.0813	1.0829	1.085	1.085	1.0811	1.105
$r(CF)(Å)$	–	–	–	1.4155	1.3602	1.385
<HCH(degree)	109.47	109.47	109.5	110.86	109.86	109.9
<HCF(degree)	–	–	–	108.02	109.08	–
E(hartree)	−40.18741	−40.20937	–	−139.03667	−139.08005	–
μ(debye)	0	0	0	2.67	2.13	–
A(cm^{-1})	–	–	–	–	5.3	–
B(cm^{-1})	–	5.3	–	–	0.9	–
$f_{CH, CH}$(mdyn/Å)	–	5.749	–	–	5.806	5.26
	CH_2F_3			CHF_3		
	9, 5/5	9, 5, 1/5, 1	exp.	9, 5/5	9, 5, 1/5, 1	exp.
$r(CH)(Å)$	1.0713	1.0786	1.091	1.0666	1.0750	1.098
$r(CF)(Å)$	1.3803	1.3320	1.358	1.3514	1.3094	1.332
<HCH(degree)	114.33	111.06	112.1	–	–	–
<HCF(degree)	109.89	109.73	–	110.80	110.40	–
<HCF(degree)	107.76	108.41	108.2	108.11	108.52	108.8
E(hartree)	−237.89731	−237.96947	–	−336.76044	−336.86919	–
μ(debye)	2.87	2.24	–	2.42	1.87	1.65
A(cm^{-1})	–	1.70	–	–	0.20	–
B(cm^{-1})	–	0.37	–	–	0.36	–
C(cm^{-1})	–	1.32	–	–	–	–
$f_{CH, CH}$(mdyn/Å)	–	5.942	4.888	–	6.171	5.23

[a]Experimental results from refs. [24~27].

upon dimer formation are relatively larger than the previous dimers. These trends will be seen from the values of <CHN, <CHO and other intramolecular bond angles in *Table* 3 and 4. and affect the dipole moments of the dimers. With our 9, 5, 1/5, 1 basis set the intermolecular distances are overestimated by about 0.1 Å compared to experimental ones. Therefore the computed rotational constants are expected to be too small and also the intermolecular force constants be small. The rotational spectrum of CF_3H--NH_3 has been obtained using a pulsed nozzle Fourier transform microwave spectrometer[10]. The hydrogen bond length was 2.314(5) Å, B_0 was 1996.903(2) MHz and the week bond stretching force constant was 0.066(2) mdyne/Å. These experimental values are respectively compared to our computed ones 2.3975 Å, 1963 MHz and 0.093 mdyn/Å. In spite of the overestimation of the calculated intermolecuar bond distance the calculated stretching force constant is larger than the experimental one by about 0.027 mdyne/Å. These trends reflect well the systematic, methodical errors due to the use of the SCF approximation and to the basis set limitations.

As expected the stabilizatoin energies ΔE's in the two series of dimers CH_4--NH_3, CFH_3--NH_3, CF_2H_2--NH_3, CF_3H--NH_3 and CH_4--OH_2. CFH_3--OH_2, CF_2H_2--OH_2, CF_3H--OH_2 are uniformly increasing with going from CH_4 to CF_3H in accordance with the acidity of the proton-donor molecule. and ranging from −0.498 to −6.874 kcal/mol with 9, 5/5 basis set, from −0.509 to −4.518 kcal/mol in the one series of dimers, and from −0.531 to −7.248 kcal/mol with 9, 5/5 basis set, from −0.471 to −3.829 kcal/mol with 9, 5, 1/5, 1

Table 3. Ground state properties of the dimers formed between fluoromethanes and ammonia[a]

	CH4--NH3		CFH3--NH3		CF2H2--NH3		CF3H--NH3		Exp.
	9,5/5	9,5,1/5,1	9,5/5	9,5,1/5,1	9,5/5	9,5,1/5,1	9,5/5	9,5,1/5,1	
$r(C{-}N)$(Å)	4.2841	4.2297	3.7153	3.8405	3.4415	3.6100	3.2841	3.4713	
$r(C{-}H)$(Å)	1.0808	1.0824	1.0753	1.0794	1.0711	1.0764	1.0700	1.0738	
$\Delta r(C{-}H)$(Å)	-0.0005	-0.0005	-0.0013	-0.0017	-0.0002	-0.0022	-0.0050	-0.0012	
$r(C{-}X_1)$(Å)	1.0820	1.0835	1.4222	1.3655	1.0720	1.0764	1.3574	1.3142	
$r(C{-}X_2)$(Å)	1.0820	1.0835	1.0722	1.0817	1.3867	1.3371	1.3574	1.3142	
$r(N{-}H)$(Å)	3.2033	3.1473	2.6420	2.7611	2.3827	2.5449	2.2141	2.3975	
$r(N{-}H_2)$(Å)	0.9929	1.0006	0.9949	1.0011	0.9958	1.0011	0.9973	1.0015	
$r(N{-}H_8)$(Å)	0.9929	1.0006	0.9945	1.0010	0.9961	1.0013	0.9973	1.0015	
α_1(degree)	109.32	109.28	110.65	109.62	107.20	107.97	107.46	108.00	
α_2(degree)	109.32	109.28	109.43	109.27	107.58	108.19	107.46	108.00	
β_1(degree)	109.67	109.66	79.51	106.08	115.31	113.31	111.42	110.90	
β_2(degree)	109.67	110.22	80.80	106.44	112.70	111.64	111.42	110.90	
α_1'(degree)	115.01	108.10	114.00	107.96	113.09	107.72	106.34	107.69	
α_2'(degree)	115.01	108.10	113.98	107.93	113.14	107.78	106.34	107.69	
β_1'(degree)	103.19	110.79	85.64	92.07	116.02	122.25	116.00	111.20	
β_2'(degree)	103.15	110.80	96.90	103.38	109.48	115.29	116.00	111.40	
$<HCH$(degree)	179.96	180.00	175.89	176.47	169.62	170.13	180.00	180.00	
E(hartree)	-96.337107	-96.42121	-195.22308	-195.29379	-294.08693	-294.18515	-392.95425	-393.08643	
ΔE(kcal/mol)	-0.498	-0.509	-2.222	-1.694	-4.244	-2.910	-6.874	-4.518	
μ(debye)	1.70	1.98	3.34	3.08	4.09	3.56	4.92	4.25	
$\Delta\mu$(debye)	0.26	0.26	-0.77	0.77	-0.22	-0.40	0.0	0.66	
A(cm^{-1})	—	2.91	—	0.96	—	0.32	—	0.19	
B(cm^{-1})	—	0.11	—	0.08	—	0.08	—	0.07	1996.9
C(cm^{-1})	—	—	—	—	—	0.07	—	—	MHz
$f_{CH,CH}$(mdyn/Å)	—	5.778	—	5.875	—	6.020	—	6.198	
$\Delta f_{CH,CH}$(%)	—	2.9	—	6.9	—	7.8	—	2.7	
$f_{N{-}H,N{-}H}$(mdyn/Å)	—	0.008	—	0.029	—	0.058	—	0.093	0.066(2)

[a] For numbering of internal coordinates see *Fig.* 1. Here $\Delta r(C{-}H) = r(C{-}H)(dimers) - r(C{-}H)(fluoromethanes)$, $\Delta\mu = \mu(dimers) - (\mu(fluoromethanes) + \mu(NH_3))$, $\Delta E = E(dimers) - (E(fluoromethanes) + E(NH_3))$, $\Delta f_{CH,CH}(\%) = (f_{CH,CH}(dimers) - f_{CH,CH}(fluoromethanes)) \times 100$.

Table 4. Ground state properties of the dimers formed between fluoromethanes and water

	CH_4---OH_2		CFH_3---OH_2		CH_4---OH_2		CFH_3---OH_2	
	9, 5/5	9, 5, 1/5, 1	9, 5/5	9, 5, 1/5, 1	9, 5/5	9, 5, 1/5, 1	9, 5/5	9, 5, 1/5, 1
$r(\text{C--O})$(Å)	3.8917	3.9731	3.4827	3.6265	3.2621	3.4923	3.1074	3.3441
$r(\text{C-H})$(Å)	1.0806	1.0822	1.0744	1.0789	1.0700	1.0758	1.0679	1.0727
$\Delta r(\text{C-H})$(Å)	-0.0007	-0.0007	-0.0022	-0.0023	-0.0013	-0.0028	-0.0003	-0.0023
$r(\text{C-X}_4)$(Å)	1.0821	1.0834	1.4220	1.3648	1.0719	1.0789	1.3569	1.3132
$r(\text{C-X}_5)$(Å)	1.0822	1.0835	1.0771	1.0815	1.3867	1.3365	1.3574	1.3155
$r(\text{O--H})$(Å)	2.8111	2.8910	2.4641	2.6328	2.1925	2.4186	2.0419	2.2748
$r(\text{O-H}_7)$(Å)	0.9483	0.9431	0.9485	0.9433	0.9485	0.9436	0.9484	0.9436
α_1(degree)	109.25	109.26	110.64	109.64	107.22	108.01	107.47	108.08
α_2(degree)	109.27	109.28	109.44	109.31	107.59	108.24	107.44	108.09
β_1(degree)	109.59	109.65	108.56	108.03	117.49	118.29	111.51	112.52
β_2(degree)	109.60	109.65	109.59	108.24	115.02	116.68	111.40	112.46
α(degree)	112.56	106.32	112.40	106.27	112.47	106.32	112.51	106.50
β(degree)	117.12	114.70	115.53	113.18	115.95	111.25	117.10	114.75
<CHO(degree)	179.96	179.97	162.89	152.87	178.19	178.09	175.17	175.45
E(hartree)	-116.20241	-116.25860	-215.05480	-215.13111	-313.91898	-314.02235	-412.78614	-412.92310
ΔE(kcal/mol)	-0.531	-0.471	-2.496	-1.608	-4.718	-2.753	-7.248	-3.829
μ(debye)	2.78	2.37	4.47	3.85	4.462	3.30	5.618	4.52
$\Delta\mu$(debye)	0.28	0.23	-0.70	-0.42	-1.902	-1.08	0.70	0.51
A(cm^{-1})	—	3.90	—	0.19	—	0.33	—	0.19
B(cm^{-1})	—	0.12	—	0.07	—	0.08	—	0.07
C(cm^{-1})	—	—	—	—	—	0.07	—	—
$f_{\text{CH,CH}}$(mdyn/Å)	—	5.785	—	5.895	—	6.246	—	7.5
$\Delta f_{\text{CH,CH}}$(%)	—	3.6	—	8.9	—	9.9	—	7.5
$f_{\text{O--H,O--H}}$(mdyn/Å)	—	0.010	—	0.031	—	0.060	—	0.092

[a]For numbering of internal coordinates see *Fig.* 1. Here $\Delta r(\text{C-H}) = r(\text{C-H})(\text{dimers}) - r(\text{C-H})(\text{fluoromethanes})$, $\Delta\mu = \mu(\text{dimers}) - (\mu(\text{fluoromethanes}) + \mu(\text{OH}_2))$, $\Delta f_{\text{CH,CH}}(\%) = (f_{\text{CH,CH}}(\text{dimers}) - f_{\text{CH,CH}}(\text{fluoromethanes})) \times 100$. $\Delta E = E(\text{dimers}) - (E(\text{fluoromethanes}) + E(\text{OH}_2))$.

basis set in the other series of dimers. In cases of CH_4--NH_3, CFH_3--NH_3[6] and CFH_3--OH_2[7] ΔE's have been computed to -1.1, -7.6 and 6.58 kcal/mol respectively, applying a 4-31G level. These values without considering the basis set superposition errors are too large compared to ours. This trend is consistent with the general experience that the smaller basis set more overestimates the stabilization energies[28,29]. The strength of a hydrogen bond correlates with the basicity of the proton-acceptor and the acidity of the proton-donor molecule. These correlations are well established for the first row atoms N, O and F involved in hydrogen bonding[3]. It is generally known that as proton-donors NH_3 rather than H_2O makes a strong hydrogen bonding. As shown in *Table* 3 and 4 the stabilization energies in the two series of dimers show a conflicting result depending upon the size of the basis sets applied. The stabilization energies calculated using the smaller 9,5/5 basis set will be misunderstood that H_2O makes a stronger hydrogen bonding than NH_3. This is merely due to the overestimation of the dipole moment of H_2O monomer. However, the stabilization energies calculated using the larger 9,5,1/5,1 basis set involving polarization functions explicitly show that NH_3 is the stronger proton-acceptor. And this trend reveals the basis set depedence of the calculations.

Hydrogen bonds are usually characterized by the following two structural features[10]. The distances between the neighbouring atoms of the two functional groups (A-H--B) involved in the hydrogen bond are substantially smaller than the sum of thier van der Waals' radii: $R_{HB} < R^0_H + R^0_B$. And the AH bond length is increased upon hydrogen bond formation. The sum of the van der Waals' radii of C-(H--N) and C-(H--O) in the dimers of fluoromethanes with ammonia and water are given by 2.75 and 2.70 Å respectively. The van der Waals' radii used are as follows: H=1.20, N= 1.55 and O=1.5 Å. They are based on the values given by Bondi and Kitaigorodsky[31,32]. The calculated intermolecular distances using 9,5,1/5,1 basis set are 3.1473 Å on CH_4--NH_3, 2.7611 Å on CFH_3

--NH_3 and 2.8910 Å on CH_4--NH_3 respectively, larger than their van der Waals' radii. Therefore it may be thought that these dimers are van der Waals' complexes rather than hydrogen-bonded complexes. Those of CF_2H_2--NH_3, CF_3H--NH_3, CFH_3--OH_2, CF_2H_2--OH_2 and CF_3H--OH_2 are 2.5449, 2.3975, 2.6328, 2.4186 and 2.2748 Å respectively, substantially shorter than their van der Waals' radii. These dimers may be classified into the hydrogen-bonded complexes at least by their structural features. But, as shown in *Table* 3 and 4 at our level of calculation the C-H bond elongations with repect to monomers upon hydrogen bond formation are not observed on any of dimers. This does reflect again the systematic, methodical errors due to the use of the SCF approximation and the basis set dependence of the computed results.

Non-additive behaviour of dipole moments is a well known phenomenon in hydrogen bonding. The computed dipole moments of the dimers are expected to be too large as a consequence of the overestimated monomer moments. The polarities of hydrogen-bond donors increase upon bond formation, usually leading to larger dipole momenents of the complexes than expected from vectorial addition of the components. But, in the dimers CFH_3--NH_3, CF_2H_2--NH_3, CFH_3--OH_2 and CF_2H_2--OH_2 the directions of polarities of the subunits are quite different from those of the isolated monomers. Therfore their dipole moments decrease. In *Table* 3 and 4 the dipole moments μ's and the induced dipole moments $\Delta\mu$'s reflect well this behaviour.

CONCLUSIONS

The influence of most of the systematic, methodical errors due to the use of the SCF approximation and eventual deficiencies of the basis set applied, and the basis set dependence of the computed results are generally well characterized nowadays. So to get the results which have good agreement with experimental values large scale basis sets including electron correlation and full geome-

try optimization are required as a prerequisite.

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