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Charge-Transfer Complexes between the Amines $(CH_3)_nNH_{3-n}$ ($n = 0-3$) and the ClF Molecule: An ab Initio and Density Functional Study on the Intermolecular Interaction

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The intermolecular interactions between the amines NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$ and the ClF molecule were investigated with the aid of ab initio calculations performed at different levels of Møller−Plesset perturbation theory and coupled cluster expansions. In addition, three density functional theory approaches were probed. Medium-sized to extended polarized basis sets were applied. Distinct and very systematic differences occur for the calculated complex properties in this series when applying different electron correlation methods. In these four complexes, the computed intramolecular ClF distance is substantially widened relative to that of the isolated ClF molecule by about 0.07−0.15 Å, whereas the calculated intermolecular N···Cl distance is substantially contracted by about 0.2−0.3 Å upon going from H_3N···ClF to $(CH_3)_3N$···ClF, in agreement with the experimentally observed trend. Computed dipole moments range from about 5.7 D in H_3N···ClF to about 7.6 D in $(CH_3)_3N$···ClF, indicating an increasingly polar structure. Successive methyl substitution modifies the interaction energy between the amine and ClF systematically from about −9 kcal mol^{-1} in H_3N···ClF to about −20 kcal mol^{-1} in the $(CH_3)_3N$···ClF complex. These complexes can be described best as charge-transfer complexes with modest intramolecular structure relaxations in the amine and with an important contribution originating from a significant stretching of the ClF molecule.

1. Introduction

In recent rotational spectroscopic investigations,[1,2] the structures of the *prereactive* complexes of ClF with NH_3 and of ClF with $(CH_3)_3N$ were reported. In the complex with ammonia the experimental data were interpreted in terms of a small contribution of the ionic structure $[H_3NCl]^+$···F^- to the valence bond description of H_3N···ClF.[1] The structure of the complex with trimethylamine, on the other hand, was interpreted with the ionic form $[(CH_3)_3NCl]^+$···F^- being the main contributor to its valence bond description.[2] Rotational spectroscopic data on the methylamine-ClF and dimethylamine-ClF complexes are not available yet. Gas-phase infrared spectra of these four intermolecular complexes have not been observed so far. Only a single infrared investigation in cryogenic Ar and N_2 matrices is available for the NH_3 and $(CH_3)_3N$ complexes with ClF.[3]

Amine-ClF complexes were treated previously in ab initio self-consistent field (SCF) calculations.[4−6] The structure and the vibrational spectra of the ammonia-ClF[7−11] and methylamine-ClF[8] complexes were studied with the aid of different ab initio methods including electron correlation. So far, theoretical studies including electron correlation on $(CH_3)_2HN$···ClF and $(CH_3)_3N$···ClF are not available.

In the previous works of this series, the complexes of amines with the F_2 molecule have been investigated systematically,[12] and the methodical requirements to achieve a reliable description of the interactions of the halogens F_2, ClF, and Cl_2 with the NH_3 molecule have been considered in greater detail.[13,14] In this contribution, the three complexes CH_3H_2N···ClF, $(CH_3)_2HN$···ClF, and $(CH_3)_3N$···ClF are studied systematically and the results are compared with the previously treated case of H_3N···ClF.[14] The main goals of this investigation are (i) to assist in the interpretation of the experimentally derived structure for the $(CH_3)_3N$···ClF complex[2] and (ii) to obtain sufficiently reliable and useful predictions for the structures and other properties of the CH_3H_2N···ClF and the $(CH_3)_2HN$···ClF complexes before experimental investigations.

Apart from the expected effects of incomplete basis set saturation, a striking sensitivity of the computed equilibrium structures and interaction energies to the level of electron correlation applied had been observed in the H_3N···halogen complexes.[13,14] While the use of extended basis sets was affordable even for the higher-order correlations methods in those cases, this kind of detailed methodical investigation was only possible with medium-sized basis sets in the methyl-substituted amines. In most of the extended basis set calculations on the complexes of ClF with the methyl-substituted amines, the Møller−Plesset second order (MP2) method[15] and several density functional theory (DFT) approaches were applied. The results of the higher-order electron correlation calculations as obtained with the medium-sized basis sets, in combination with the trends observed in the extended basis set MP2 and DFT calculations, could, however, be used to extrapolate toward the desired high-quality data. The trends in the computed equilibrium structures, interaction energies, dipole moments, electric field gradients, and selected vibrational spectroscopic data are reported.

2. Method of Calculation

All quantum chemical calculations were performed with the Gaussian 98 suite of programs.[16] Based on the experience gained from the previous investigations on H_3N···ClF,[14] four basis sets were used: 6-31++G(d,p), 6-311++G(2d,2p), 6-311++G-

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(3df,2p),[17−22] and aug-cc-pVTZ.[23−25] With these four basis sets, the structures of the complexes were optimized at the MP2 level and with three DFT methods (B3LYP,[26−29] PW91PW91,[30] and BH&HLYP as implemented in Gaussian 98). This choice was motivated by the previously observed acceptable performance of B3LYP for the methylated amine$\cdots$$F_2$ complexes,[12] by a recent use of PW91PW91 in the pure van der Waals system $(N_2)_2$,[31] and by a recent study[32] of the charge-transfer complexes of NH_3 with BrCl and Br_2 in which the use of the BH&HLYP method was recommended. The counterpoise (CP) correction[33] to the basis set superposition error (BSSE) including the contribution of geometry relaxation was computed in all cases at the conventionally optimized complex equilibrium geometries. Harmonic vibrational frequencies and zero point energy (ZPE) corrections were calculated for all four complexes. In a few cases, where this surpassed the available computing resources, the ZPE corrections were taken over from the smaller basis set calculations.

In the previous studies on $H_3N\cdots ClF$[14] and $H_3N\cdots F_2$[13,14] the computed complex properties were very sensitive to the level of electron correlation chosen. Methods that include the influence of triple substitutions led to substantially different results than those that do not. Moreover, the calculated equilibrium structure was also significantly dependent on whether the CP correction was added as a mere energy correction at the conventionally optimized geometries, or whether it was taken into account directly in the course of the geometry optimization.

To achieve a reasonable estimate of the effect of higher-order electron correlation effects on the computed equilibrium geometries, point-wise scans of the 2D energy surfaces were executed, with the two distances R(Cl−F) and R(N$\cdots$Cl) as variable parameters, thereby freezing the amines at their MP2-optimized structures in the respective complexes. The justification for this approach lies in the very modest structure relaxations of the amines taking place upon complex formation as found in the full MP2 and DFT structure optimizations. In these 2D scans, Møller−Plesset perturbation theory calculations up to MP4(SDTQ)[34] and coupled cluster calculations at CCSD and CCSD(T)[35−39] levels were performed for the three methylated-amine$\cdots$ClF complexes with the 6-31++G(d,p) basis and for the $CH_3H_2N\cdots ClF$ complex also with the 6-311++G(2d,2p) basis. Larger basis set MP4(SDTQ) or CCSD(T) calculations for the $(CH_3)_2HN\cdots ClF$ and $(CH_3)_3N\cdots ClF$ complexes were prohibitive. At each point on these 2D energy surfaces, the CP corrections were computed, thus allowing also determination of the CP-corrected equilibrium structures.

3. Results

3.1. The Monomers. Calculated equilibrium distances, dipole moments, harmonic vibrational frequencies, and infrared intensities of the ClF molecule as obtained at selected methodical levels are compiled in Table 1. The MP2 and CCSD(T) results with all four basis sets were already reported in ref 14, but are included for completeness. The trends observed are quite uniform. To approach the experimental values, very extended basis sets are necessary. Even the aug-cc-pVTZ calculations lead to equilibrium distances that are somewhat too large. This slow convergence with respect to basis set extension has already been noted in earlier investigations.[41,42] The MP2, MP4(SDQ), and CCSD results for the equilibrium distance are very similar; the MP4(SDTQ) and CCSD(T) are both larger by about 0.01 Å. As far as the DFT methods are concerned, we observe that the B3LYP results are bracketed by the PW91PW91 and BH&HLYP data and are, in general, very close to the MP2 numbers. The BH&HLYP equilibrium distance is considerably shorter than all the others, accompanied by a substantially higher harmonic vibrational frequency. Table 2 contains selected structural parameters and dipole moments of the four amines as obtained with the 6-311++G(3df,2p) basis at the MP2 level as representative examples. The agreement between theoretical and experimental structures is satisfactory. Computed bond distances and bond angles are, with a few exceptions, within

TABLE 1: Computed Equilibrium Distances, R(Cl−F), Dipole Moments, μ, Harmonic Vibrational Frequencies, ν, and Infrared Intensities, A, of the ClF Molecule[a]

basis set	method	R(ClF)	μ	ν	A
6-31++G(d)	MP2	1.670	1.28	779	23
	B3LYP	1.670	1.19	773	23
	PW91PW91	1.682	1.12	747	21
	BH&HLYP	1.638	1.22	840	30
	MP4(SDQ)	1.672	1.32	770	23
	MP4(SDTQ)	1.682			
	CCSD	1.669			
	CCSD(T)	1.679			
6-311++G(2d)	MP2	1.664	1.098	751	25
	B3LYP	1.664	1.068	758	28
	PW91PW91	1.677	0.983	737	25
	BH&HLYP	1.632	1.088	818	35
	MP4(SDQ)	1.664	1.13	745	24
	MP4(SDTQ)	1.679			
	CCSD	1.662			
	CCSD(T)	1.675			
6-311++G(3df)	MP2	1.633	0.913	796	29
	B3LYP	1.641	0.904	786	30
	PW91PW91	1.654	0.830	762	27
	BH&HLYP	1.610	0.923	849	38
	MP4(SDQ)	1.633	0.853	793	29
	MP4(SDTQ)	1.647			
	CCSD	1.630			
	CCSD(T)	1.643			
aug-cc-pVTZ	MP2	1.639	0.916	800	27
	B3LYP	1.649	0.925	787	29
	PW91PW91	1.660	0.839	765	26
	BH&HLYP	1.615	0.940	854	36
	MP4(SDQ)	1.637			
	MP4(SDTQ)	1.652			
	CCSD	1.634			
	CCSD(T)	1.646			
aug-cc-pVQZ	MP2	1.630	0.886		
	experiment	1.632[b], 1.628[c]	0.888[c]	786[c]	

[a] R(Cl−F) in Å, μ in D, ν in cm^{-1}, A in km mol^{-1}. [b] Calculated from experimental B_0 value as reported in ref 1. [c] Ref 40.

TABLE 2: Selected MP2 Calculated Structural Parameters and Dipole Moments of NH_3 and the Methylated Amines as Obtained with the 6-311++G(3df,2p) Basis Set[a]

molecule		MP2	experiment
NH_3	R(N−H)	1.011	1.016[b]
	∠(HNH)	107.1	107.3[b]
	μ	1.55	1.47[c]
CH_3NH_2	R(N−H)	1.013	1.010[d]
	R(C−N)	1.464	1.471
	∠(HNH)	108.6	107.1
	∠(HNC)	112.4	110.2
	μ	1.37	1.29[c]
$(CH_3)_2NH$	R(N−H)	1.016	1.019[e]
	R(C−N)	1.461	1.462
	∠(HNC)	110.9	108.9
	∠(CNC)	113.7	112.2
	μ	1.09	1.03[c]
$(CH_3)_3N$	R(C−N)	1.463	1.451[f]
	∠(CNC)	111.7	110.9
	μ	0.68	0.63[c]

[a] Bond distances in Å, bond angles in degrees and dipole moments in D. [b] ref 43. [c] ref 44. [d] ref 45. [e] ref 46. [f] ref 47.

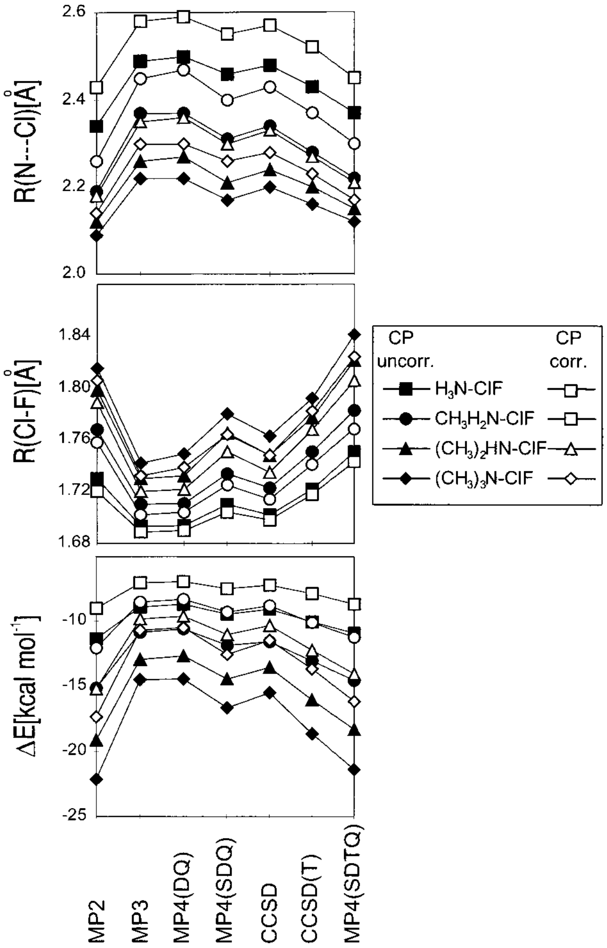

Figure 1. Calculated trends in the intermolecular R(N···Cl) distance, the intramolecular R(Cl−F) distance, and in the interaction energy Δ*E* of amine-ClF complexes as obtained with the 6-31++G(d,p) basis, with different electron correlation methods, and with and without applying the CP correction in the course of geometry optimization.

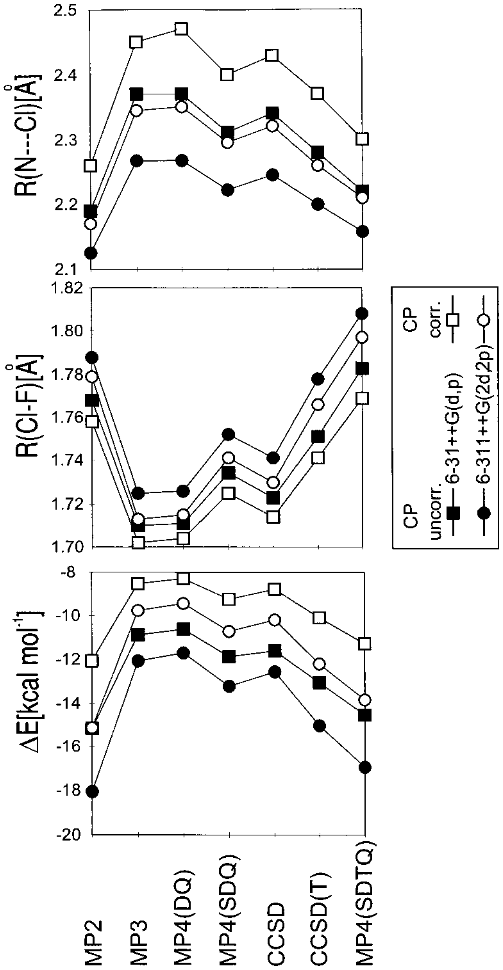

Figure 2. Calculated trends in the intermolecular R(N···Cl) distance, the intramolecular R(Cl−F) distance, and in the interaction energy Δ*E* of the methylamine-ClF complex as obtained with the 6-31++G(d,p) and 6-311++G(2d,2p) basis sets, with different electron correlation methods, and with and without applying the CP correction in the course of geometry optimization.

0.01 Å and 2° of the experimental numbers. Dipole moments are also well reproduced. The structural and other properties of the amines as calculated with higher-order correlation methods or with the other DFT methods are not substantially different and are therefore not reported.

3.2. The Complexes. *3.2.1. Structure and Energetics. 3.2.1.1. The Effect of Higher-order Electron Correlations and of the CP Correction.* Before discussing the results for the individual complexes in greater detail an overview of the systematic features to be expected in the series of $(CH_3)_nH_{3-n}N-ClF$ complexes is provided. The trends in the calculated equilibrium distances, R(N···Cl) and R(Cl−F), and in the stabilization energies for the four amine-ClF complexes as obtained with different electron correlation methods, when applying the 6-31++G(d,p) basis, are shown in Figure 1. Results as obtained with and without including the CP corrections in the course of the 2D geometry optimization are compared. The 6-31++G(d,p) and the corresponding 6-311++G(2d,2p) results for the methylamine-ClF complex are confronted in Figure 2.

Figure 1 clearly demonstrates that in this series higher-order electron correlation effects are very systematic indeed. For each of the methods the interaction energy becomes more negative, the intermolecular R(N···Cl) distance is contracted and the intramolecular R(Cl−F) distance is elongated upon increasing the number of methyl groups. For all four amines the methodical trends observed are essentially the same. The MP2-computed intermolecular distance, R(N···Cl), is consistently shorter than the CCSD(T) and MP4(SDTQ) values, whereas the other four electron correlation methods lead to even larger values. The MP2-calculated intramolecular distance, R(Cl−F), is close to the CCSD(T) and MP4(SDTQ) results, the other four methods lead to shorter distances. The pattern for the calculated interaction energies closely follows that for R(N···Cl). MP2-calculated values are below their CCSD(T) and MP4(SDTQ) counterparts. Comparing CCSD with CCSD(T) and MP4(SDQ) with MP4(SDTQ) results, one observes that the inclusion of triple substitutions has a strong influence. We also infer that the inclusion of the CP correction does not at all modify the differences between the various electron correlation methods. It has, however, a sizable quantitative effect, despite the sets of diffuse and polarization functions already included in the 6-31++G(d,p) basis. The CP correction to the interaction energy and to the reduction of R(Cl−F) increases with an increasing degree of methylation, whereas the CP correction to the intermolecular R(N···Cl) distance decreases. The latter two trends can be easily explained because the intramolecular degree of freedom becomes softer upon successive methylation, whereas the intermolecular potential becomes steeper.

Figure 2 clearly shows that the methodical trends are also quite independent of the basis set used. With the larger basis set, however, the methylamine-ClF complex becomes more strongly bound, accompanied by a shorter R(N···Cl) and a

TABLE 3: MP2- and DFT-Calculated Stabilization Energies of the H_3N-ClF Complex as Obtained with Different Basis Sets (kcal mol^{-1})

basis set	method	ΔE	ΔE(ZPE)	ΔE(CP)	ΔE(ZPE + CP)
6-31++G(d,p)	MP2[a]	−11.4	−9.4	−9.0	−7.1
	B3LYP	−14.7	−12.4	−13.7	−11.3
	PW91PW91	−20.3	−17.8	−19.1	−16.6
	BH&HLYP	−11.7	−9.5	−10.8	−8.5
	CCSD(T)[a]	−10.1		−7.9	
	MP4(SDTQ)[a]	−10.9		−8.7	
6-311++G(2d,2p)	MP2[a]	−12.4	−10.1	−10.5	−8.2
	B3LYP	−14.4	−12.1	−13.7	−11.3
	PW91PW91	−20.1	−17.6	−19.3	−16.9
	BH&HLYP	−11.3	−9.1	−10.7	−8.5
6-311++G(3df,2p)	MP2[a]	−12.0	−9.8	−10.3	−8.1
	B3LYP	−13.0	−10.7	−12.4	−10.2
	PW91PW91	−18.5	−16.1	−18.0	−15.6
	BH&HLYP	−10.1	−8.0	−9.7	−7.6
aug-cc-pVTZ	MP2[a]	−11.8	−9.6	−11.0	−8.7
	B3LYP	−12.6	−10.3	−12.5	−10.1
	PW91PW91	−18.0	−15.6	−17.9	−15.5
	BH&HLYP	−9.7	−7.6	−9.5	−7.5
	CCSD(T)[a]	−10.1		−9.4	

[a] Data taken from ref 14.

TABLE 4: Selected MP2- and DFT-Calculated Structural Parameters and the Dipole Moment of the H_3N-ClF Complex as Obtained with Different Basis Sets[a]

basis set	method	R(ClF)	ΔR(ClF)[b]	R(N···Cl)	μ
6-31++G(d,p)	MP2[c]	1.730	0.060	2.34	5.7
	MP2 (CP)[c,d]	1.720	0.050	2.43	
	B3LYP	1.753	0.083	2.29	6.4
	PW91PW91	1.790	0.102	2.23	7.0
	BH&HLYP	1.689	0.051	2.36	5.5
	CCSD(T)[c]	1.722	0.043	2.43	
	CCSD(T) (CP)[c,d]	1.718	0.039	2.52	
	MP4(SDTQ)*c*	1.751	0.069	2.37	
	MP4(SDTQ) (CP)[c,d]	1.743	0.061	2.45	
6-311++G(2d,2p)	MP2[c]	1.747	0.083	2.24	6.0
	B3LYP	1.757	0.093	2.25	6.4
	PW91PW91	1.793	0.116	2.19	6.9
	BH&HLYP	1.693	0.061	2.31	5.6
6-311++G(3df,2p)	MP2[c]	1.710	0.077	2.23	5.7
	B3LYP	1.728	0.087	2.26	6.0
	PW91PW91	1.765	0.111	2.19	6.6
	BH&HLYP	1.664	0.054	2.33	5.1
aug-cc-pVTZ	MP2[c]	1.714	0.075	2.24	5.7
	MP2 (CP)[c,d]	1.712	0.077	2.26	
	B3LYP	1.734	0.085	2.27	6.0
	PW91PW91	1.770	0.110	2.20	6.5
	BH&HLYP	1.668	0.053	2.34	5.1
	CCSD(T)[c]	1.705	0.059	2.32	
	CCSD(T) (CP)[c,d]	1.702	0.056	2.35	

[a] Bond distances in Å and dipole moments in D. [b] Increase relative to the ClF monomer. [c] Data taken from ref 14. [d] CP-corrected.

longer R(Cl−F). The CP correction to the stabilization energies and the structural parameters is still sizable and only slightly smaller with the 6-311++G(2d,2p) basis.

The most important points from this section may be summarized as follows: (i) MP2-calculated numbers are closer to the results of those electron correlation methods that take account of triple substitutions than to those that do not. (ii) MP2-calculated intermolecular distances are too short by about 0.1 or 0.03 Å when compared with CCSD(T) or MP4(SDTQ) results, respectively. It appears that these findings are quite independent of the basis set applied, similar to the experience gained from investigations on other $H_3N\cdots$halogen complexes.[13,14] With increasing methyl substitution, CP corrections to the intermolecular distance slightly decrease, whereas they become slightly larger for the intramolecular R(Cl−F) distance and the intermolecular interaction energy. Thus, even with the aug-cc-pVTZ basis, one has to expect CP corrections of about +0.03 Å for R(N···Cl), −0.003 Å for R(Cl−F), and 0.8 kcal mol^{-1}, as found for the H_3N-ClF complex,[14] for the methyl-substituted amine-ClF complexes as well, with a tendency as described above when increasing the number of methyl groups.

3.2.1.2. H_3N-ClF. A very detailed discussion of MP2, CCSD(T), and other higher-order correlation energy results on this complex, including the influence of applying the CP correction in the course of geometry optimization, has already been given (see Tables 6−9 of ref 14). Therefore, in Tables 3 and 4, the DFT results on stabilization energies, on R(Cl−F) and R(N···Cl), and on dipole moments as obtained in this work are compared only with the MP2 results. However, CCSD(T) (6-31++G(d,p), aug-cc-pVTZ), and MP4(SDTQ) [6-31++G(d,p)] results stemming from the 2D scans described above are also included.

With the two larger basis sets the MP2 values for ΔE(CP) and ΔE(ZPE + CP) and for the structural parameters and the dipole moments are bracketed by the B3LYP and BH&HLYP numbers, with B3LYP showing the signature of a slightly

TABLE 5: Calculated Stabilization Energies of the $(CH_3)_3N{-}ClF$ Complex as Obtained with Different Methods and Basis Sets (kcal mol^{-1})

basis set	method	ΔE	ΔE(ZPE)	ΔE(CP)	ΔE(ZPE+CP)
6-31++G(d,p)	MP2	−22.1	−20.2	−17.2	−15.3
	B3LYP	−20.3	−18.2	−19.4	−17.3
	PW91PW91	−27.5	−25.4	−26.4	−24.3
	BH&HLYP	−16.0	−14.0	−15.1	−13.1
	CCSD(T)	−18.6		−13.7	
	MP4(SDTQ)	−21.4		−16.2	
6-311++G(2d,2p)	MP2	−25.1	−23.4	−21.0	−19.4
	B3LYP	−21.1	−18.9	−19.9	−17.7
	PW91PW91	−28.1	−25.9	−26.8	−24.6
	BH&HLYP	−16.9	−14.8	−15.5	−13.4
6-311++G(3df,2p)	MP2	−24.9	−22.9	−21.2	−19.2
	B3LYP	−19.3	−17.2	−18.2	−16.1
	PW91PW91	−26.3	−24.2	−25.1	−23.0
	BH&HLYP	−15.3	−13.3	−14.2	−12.2
aug-cc-pVTZ	MP2	−24.0[a]	−22.0[a]	−22.2[a]	−20.2[a]
	B3LYP	−21.4	−19.3[b]	−21.1	−19.0[b]
	PW91PW91	−25.1	−23.0[b]	−24.7	−22.6[b]
	BH&HLYP	−14.1	−12.1[b]	−13.8	−11.8[b]

[a] Estimated. [b] ZPE corrections taken from calculations with the 6-311++G(3df,2p) basis.

TABLE 6: Selected MP2- and DFT-Calculated Structural Parameters and the Dipole Moment of the $(CH_3)_3N{-}ClF$ Complex as Obtained with Different Methods and Basis Sets[a]

basis set	method	R(ClF)	ΔR(ClF)[b]	R(N···Cl)	μ
6-31++G(d,p)	MP2	1.815	0.145	2.09	7.8
	MP2 (CP)[c]	1.806	0.136	2.14	
	B3LYP	1.802	0.132	2.18	7.4
	PW91PW91	1.839	0.157	2.15	7.8
	BH&HLYP	1.732	0.094	2.19	6.5
	CCSD(T)	1.792	0.113	2.17	
	CCSD(T) (CP)[c]	1.782	0.103	2.23	
	MP4(SDTQ)	1.841	0.159	2.12	
	MP4(SDTQ) (CP)[c]	1.824	0.142	2.17	
6-311++G(2d,2p)	MP2	1.822	0.158	2.07	7.9
	B3LYP	1.805	0.141	2.16	7.4
	PW91PW91	1.836	0.159	2.13	7.7
	BH&HLYP	1.742	0.110	2.15	6.7
6-311++G(3df,2p)	MP2	1.788	0.155	2.04	7.6
	B3LYP	1.776	0.135	2.15	7.0
	PW91PW91	1.806	0.152	2.13	7.3
	BH&HLYP	1.707	0.097	2.16	6.2
aug-cc-pVTZ	MP2	1.792[d]	0.153[d]	2.05[d]	7.6[d]
	B3LYP	1.781	0.132	2.17	7.0
	PW91PW91	1.812	0.152	2.14	7.3
	BH&HLYP	1.711	0.096	2.18	6.1

[a] Bond distances in Å and dipole moments in D. [b] Increase relative to the ClF monomer. [c] CP-corrected. [d] Estimated.

stronger intermolecular interaction and BH&HLYP that of a slightly weaker intermolecular interaction. The PW91PW91 results, on the other hand, are quite far outside this region in the direction of a grossly overestimated intermolecular interaction. With all DFT approaches, the CP correction is practically negligible (about 0.1 kcal mol^{-1}), when using the aug-cc-pVTZ basis set. The BH&HLYP/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ CP-corrected interaction energies are actually surprisingly close. The experimentally determined value of 2.37 Å[1] for the intermolecular R(N···Cl) distance is in good agreement with the CP-corrected CCSD(T) and the BH&HLYP values of 2.35 and 2.34 Å, respectively, as obtained with the aug-cc-pVTZ basis, whereas the MP2, B3LYP, and PW91PW91 values of 2.26, 2.27, and 2.20 Å are all considerably too short.

3.2.1.3. $(CH_3)_3N{-}ClF$. The calculated interaction energies for the trimethylamine-ClF complex are collected in Table 5. The optimized structural parameters R(Cl−F) and R(N···Cl) and the calculated dipole moments are shown in Table 6. Quite independent of the method applied, the structure of the trimethylamine moiety remains largely unchanged. Only the CNC bond angles are widened by about 2°. Turning first to the stabilization energies, we observe a significantly more attractive interaction in the $(CH_3)_3N{-}ClF$ complex than in the $H_3N{-}ClF$ complex at all levels of approximation. At MP2 and B3LYP levels, $(CH_3)_3N{-}ClF$ is stronger bound by about a factor of 2 when compared with $H_3N{-}ClF$, whereas this enhancement factor is smaller for the other two DFT approaches. The MP2/aug-cc-pVTZ (estimated) and B3LYP/aug-cc-pVTZ values for ΔE(ZPE + CP) are close to −20 kcal mol^{-1}, whereas the BH&HLYP/aug-cc-pVTZ amounts to about −12 kcal mol^{-1}. On the basis of the trends observed with the 6-31++G(d,p) basis and the experience with the CCSD(T) basis set dependence in the $H_3N{-}ClF$ complex, one could extrapolate to a hypothetical CCSD(T)/aug-cc-pVTZ stabilization energy of -14 ± 2 kcal mol^{-1}.

In contrast to the previously discussed $H_3N{-}ClF$ complex, the 6-31++G(d,p) calculated values for R(N···Cl) span a much narrower range in $(CH_3)_3N{-}ClF$. For $(CH_3)_3N{-}ClF$ the 6-31++G(d,p)-calculated DFT values for R(N···Cl) are (i) with 2.18, 2.15, and 2.19 Å for B3LYP, PW91PW91, and BH&HLYP, respectively, much more similar, and (ii) they are bracketed by the CP-corrected MP2 (2.14 Å) and CCSD(T) (2.23 Å) values.

TABLE 7: Selected Calculated CP-Corrected Stabilization Energies, Optimized Structural Parameters, and the Dipole Moment of the $CH_3H_2N{-}ClF$ Complex as Obtained with Different Methods and Basis Sets[a]

basis set	method	Δ*E*(CP)	R(ClF)	ΔR(ClF)[b]	R(N···Cl)	*μ*
6-31++G(d,p)	MP2[c]	−12.1	1.758	0.088	2.26	6.9
	CCSD(T)[c]	−10.1	1.741	0.062	2.37	
	MP4(SDTQ)[c]	−11.3	1.769	0.087	2.30	
6-311++G(2d,2p)	MP2[c]	−14.7	1.775	0.111	2.18	7.1
	CCSD(T)[c]	−11.5	1.762	0.087	2.27	
	MP4(SDTQ)[c]	−13.1	1.793	0.114	2.22	
6-311++G(3df,2p)	MP2	−14.7	1.750	0.155	2.11	6.8
	B3LYP	−15.8	1.754	0.113	2.19	6.7
	PW91PW91	−22.2	1.788	0.134	2.15	7.1
	BH&HLYP	−12.1	1.687	0.077	2.23	5.8
aug-cc-pVTZ	MP2	−15.4	1.753	0.114	2.11	6.8
	B3LYP	−15.6	1.759	0.110	2.20	6.7
	PW91PW91	−22.0	1.794	0.134	2.16	7.1
	BH&HLYP	−11.8	1.690	0.075	2.24	5.8

[a] Stabilization energies in kcal mol^{-1}, bond distances in Å, and dipole moments in D. [b] Increase relative to the ClF monomer. [c] CP-corrected structures.

TABLE 8: Selected Calculated CP-Corrected Stabilization Energies, Structural Parameters, and the Dipole Moment of the $(CH_3)_2HN{-}ClF$ Complex as Obtained with Different Methods and Basis Sets[a]

basis set	method	Δ*E*(CP)	R(ClF)	ΔR(ClF)*b*	R(N···Cl)	*μ*
6-31++G(d,p)	MP2[c]	−15.0	1.789	0.119	2.18	7.6
	CCSD(T)[c]	−12.3	1.768	0.089	2.15	
	MP4(SDTQ)[c]	−14.1	1.806	0.127	2.30	
6-311++G(3df,2p)	MP2	−18.6	1.775	0.142	2.05	7.4
	B3LYP	−16.6	1.770	0.129	2.15	7.0
	PW91PW91	−24.6	1.802	0.148	2.13	7.4
	BH&HLYP	−13.7	1.702	0.092	2.18	6.2
aug-cc-pVTZ	MP2	−19.5[d]	1.778[d]	0.139[d]	2.05[d]	6.8[d]
	B3LYP	−15.6	1.773	0.110	2.17	6.7
	PW91PW91	−22.0	1.806	0.134	2.14	7.1
	BH&HLYP	−11.8	1.704	0.075	2.20	5.8

[a] Stabilization energies in kcal mol^{-1}, bond distances in Å, and dipole moments in D. [b] Increase relative to the ClF monomer. [c] CP-corrected structures. [d] Estimated.

The basis set dependence of the computed intermolecular distance is also considerably weaker than for the $H_3N{-}ClF$ complex. Applying a correction of +0.02 Å for the remaining BSSE error, and of +0.09 Å for the difference between MP2 and CCSD(T) optimized structures, together with the knowledge of the small differences between aug-cc-pVTZ and 6-311++G-(3df,2p) results, one arrives at estimates for CP-corrected MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ values for R(N···Cl) close to 2.07 and 2.16 Å, respectively. The former value is in acceptable agreement with the experimentally derived 2.09 Å[2]; the latter value, although preferable on theoretical grounds, is, somewhat disappointingly, distinctly larger. The three calculated DFT R(N···Cl) values are all close to the CCSD(T) estimate. The MP2-calculated widening of the intramolecular R(Cl−F) in $(CH_3)_3N{-}ClF$ relative to the ClF monomer is, quite independent of the basis set, close to 0.15 Å. Again, the MP2-calculated value is surprisingly close to the experimental value of 0.15 Å, whereas, this widening is calculated to be 0.10 Å only at the CCSD(T) level. B3LYP and PW91PW91 values for this widening are close to the MP2 results, whereas BH&HLYP is closer to the CCSD(T) answer.

The MP2-calculated dipole moment of $(CH_3)_3N{-}ClF$ amounts to 7.6 D, about 2 D larger than that of $H_3N{-}ClF$, although the dipole moment of ammonia is almost 1 D larger than that of trimethylamine. At the DFT levels, the corresponding dipole moment increase is smaller and close to 1 D. The optimized structures of the $H_3N{-}ClF$ and $(CH_3)_3N{-}ClF$ complexes have both C_{3v} symmetry, as verified with the aid of vibrational analysis.

3.2.1.4. $CH_3H_2N{-}ClF$ and $(CH_3)_2HN{-}ClF$. To date, there are no experimental data available for these two complexes. The theoretical data presented here, however, could help to bridge the gap between the ammonia and the trimethylamine complex with ClF in a systematic manner and to make predictions useful for future experiments. The calculated CP-corrected stabilization energies, the equilibrium distances R(Cl−F) and R(N···Cl), and the dipole moments of $CH_3H_2N{-}ClF$ and $(CH_3)_2HN{-}ClF$, as obtained at different methodical levels, are compiled in Tables 7 and 8. The few bond angles that characterize the orientation of the ClF molecule to the amine are collected in Table 9. Only MP2 and DFT results as obtained with the aug-cc-pVTZ basis set are displayed.

$CH_3H_2N{-}ClF$ and $(CH_3)_2HN{-}ClF$ have both C_s symmetry, again verified by vibrational analysis. The N···Cl−F bond angle is very close to linearity (see Table 9). The structural properties and stabilization energies of these two complexes are best discussed when comparing them to $H_3N{-}ClF$ and $(CH_3)_3N{-}ClF$. The trends observed with successive methyl substitution appear to be highly regular. This is illustrated in Figure 3, where the MP2- and DFT-calculated values for R(N···Cl), R(Cl−F), and Δ*E*(CP), as obtained with the 6-311++G(3df,2p) and aug-cc-pVTZ basis sets, are depicted for the four amine-ClF complexes. The variation of R(N···Cl) and R(Cl−F) and of Δ*E*(CP) in this series is perfectly smooth. The somewhat sharper property change, as obtained at the MP2 level, when compared with the DFT trends, has also been observed already for the interaction of F_2 with the same four amines.[12] This comparatively simple behavior allows one to estimate the CCSD(T)/aug-cc-pVTZ and also the experimental values for the intermolecular distance R(N···Cl). Accepting the experimental R(N···Cl) values of 2.37 and 2.09 Å, respectively, for $H_3N{-}ClF$ and $(CH_3)_3N{-}ClF$, one arrives at 2.19 ± 0.02 and 2.12 ±

TABLE 9: Selected MP2- and DFT-Calculated Bond Angles of the CH_3H_2N-ClF and $(CH_3)_2HN-ClF$ Complexes as Obtained with the Aug-cc-pVTZ Basis Set (degrees)

complex	bond angle	B3LYP	PW91PW91	BH&HLYP	MP2
CH_3H_2N-ClF	∠FClN	179.7	179.5	179.3	178.6
	∠ClNC	112.5	111.9	111.7	109.8
	∠ClNH	105.0	104.6	106.2	107.1
	∠CNH	112.6	113.1	112.1	112.2
	∠HNH	108.6	109.0	108.1	108.3
$(CH_3)_2HN-ClF$	∠FClN	179.2	179.3	179.1	178.8[a]
	∠ClNC	109.2	108.9	109.1	108.4[a]
	∠ClNH	101.8	101.4	103.1	104.2[a]
	∠CNH	110.7	111.1	110.5	110.9[a]
	∠HNH	114.5	114.6	114.0	113.7[a]

[a] 6-311++G(3df,2p) results.

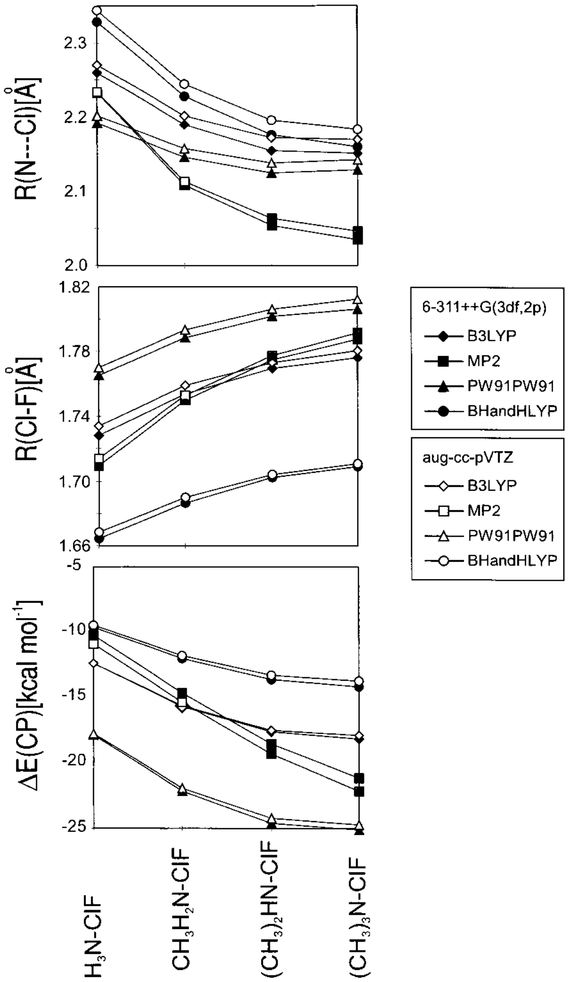

Figure 3. Calculated trends in the intermolecular R(N···Cl) distance, the intramolecular R(Cl−F) distance, and in the interaction energy Δ*E*(CP) of amine-ClF complexes as obtained with the 6-311++G-(3df,2p) and aug-cc-pVTZ basis sets. Grey squares: Estimated MP2/aug-cc-pVTZ values.

TABLE 10: MP2- and DFT-Computed Electric Field Gradients of ClF, NH_3, and $(CH_3)_3N$ Molecules and of the Complexes H_3N-ClF and $(CH_3)_3N-ClF$ as Obtained with the 6-311++G(3df,2p) Basis (a.u.)

method	MP2	B3LYP	PW91PW91	BH&HLYP
ClF				
Cl	−7.066	−7.339	−7.151	−7.395
F	−4.039	−4.316	−4.296	−4.284
NH_3				
N	0.823	0.910	0.855	0.933
$(CH_3)_3N$				
N	1.100	1.239	1.178	1.262
NH_3ClF				
N	0.589	0.628	0.533	0.728
Cl	−7.009	−7.130	−6.608	−7.523
F	−3.200	−3.384	−3.208	−3.551
$(CH_3)_3NClF$				
N	0.506	0.662	0.583	0.769
Cl	−6.367	−6.737	−6.152	−7.304
F	−2.623	−3.025	−2.929	−3.134

TABLE 11: Comparison of Computed and Experimental $\chi(^{14}N)$ and $\chi(^{35}Cl)$ Nuclear Quadrupole Coupling Constants for ClF, NH_3, $(CH_3)_3N$ Molecules and the Complexes NH_3-ClF and $(CH_3)_3N-ClF$ as Obtained with the 6-311++G(3df,2p) Basis (MHz)

method	MP2	B3LYP	PW91PW91	BH&HLYP	experiment
ClF					
Cl	−135.6	−140.8	−137.2	−141.9	−145.87[a]
NH_3					
N	−3.93	−4.32	−4.06	−4.43	−4.09[b]
$(CH_3)_3N$					
N	−5.22	−5.88	−5.59	−5.99	−5.50[c]
NH_3ClF					
N	−2.80	−2.89	−2.53	−3.46	−2.948[d]
Cl	−134.46	−136.78	−126.77	−144.33	−145.88[d]
$(CH_3)_3NClF$					
N	−2.40	−3.14	−2.77	−3.65	−3.095[e]
Cl	−129.3	−122.2	−118.0	−140.1	−136.29[e]

[a] Ref 49. [b] Ref 50. [c] Ref 51. [d] Ref 1. [e] Ref 2.

0.02 Å for R(N···Cl) in CH_3H_2N-ClF and $(CH_3)_2HN-ClF$. The estimated CCSD(T)/aug-cc-pVTZ values are with 2.23 ± 0.02 and 2.17 ± 0.02 Å distinctly larger. Overall, the DFT approaches perform quite well in this series, providing a reasonably consistent description of the structural and energetic trends in these complexes.

3.2.2. Electric Field Gradients. In Table 10, computed electric field gradients (efg's) are compiled for the monomers NH_3, ClF, and $(CH_3)_3N$, and for the H_3N-ClF and $(CH_3)_3N-ClF$ complexes, because experimental values of nuclear quadrupole coupling constants have been reported for these two complexes.[1,2] All efg's were computed with the 6-311++G(3df,2p) basis at the respective MP2- and DFT-optimized structures. Computed efg's may be converted to nuclear quadrupole constants in megaHertz by multiplication with a constant[48] (−4.746 for ^{14}N, and 19.185 for ^{35}Cl). Calculated and experimental nuclear quadrupole coupling constants $\chi(^{14}N)$ and $\chi(^{35}Cl)$ are presented in Table 11. The calculation of very accurate efg's probably requires more advanced theoretical methods than the MP2 and DFT methods applied in this work. Moreover, averaging over intermolecular large-amplitude modes could complicate the comparison in the complexes. From the calculations presented here, therefore, one should only expect to obtain a reasonably correct description of the trends. Turning first to $\chi(^{35}Cl)$, we observe that the calculated values are mostly greater than the experimental ones.

TABLE 12: B3LYP- and MP2-Computed ν(Cl−F) and ν(N···Cl) Harmonic Stretching Frequencies and Infrared Intensities in Amine−ClF Complexes[a]

	method/basis set			
	B3LYP/ 6-311++G(2d,2p)	MP2/ 6-311++G(2d,2p)	B3LYP/ 6-311++G(3df,2p)	MP2/ 6-311++G(3df,2p)
ClF				
ν(Cl−F)	758 (28)[b]	751 (25)	786 (30)	796 (29)
H_3N−ClF				
ν(Cl−F)	587 (251)	591 (230)	601 (250)	619 (237)
ν(N···Cl)	268 (69)	252 (112)	254 (66)	232 (104)
CH_3H_2N−ClF				
ν(Cl−F)	552 (307)	549 (298)	561 (307)	564 (299)
ν(N···Cl)[c]	257 (28) 351 (61)	278 (49) 377 (106)	255 (35) 345 (57)	277 (73) 374 (96)
$(CH_3)_2HN$−ClF				
ν(Cl−F)	533 (356)	533 (378)	539 (353)	
ν(N···Cl)[c]	219 (18) 403 (65)	244 (15) 425 (20) 453 (84)	216 (19) 396 (76)	
$(CH_3)_3N$−ClF				
ν(Cl−F)	523 (383)	528 (501)	529 (371)	
ν(N···Cl)	207 (19)	240 (13)	205 (21)	

[a] Frequencies in cm^{-1}, infrared intensities in km mol^{-1}. [b] Infrared intensities in parentheses. [c] The N···Cl stretching appears in two or three modes as a consequence of coupling to the F−Cl−N and ClNC bendings.

This is already known for the ClF monomer. There is almost no change in the experimental $\chi(^{35}Cl)$ value upon going from ClF to H_3N−ClF, wheras a significant change occurs in $(CH_3)_3N$−ClF. Although significantly higher than the experimental values, this feature is best represented by the MP2-calculated $\chi(^{35}Cl)$, whereas the DFT methods are less successful. For the $\chi(^{14}N)$ efg's, on the other hand, the DFT methods follow the experimental trends more faithfully than the MP2 numbers. The origin for this behavior is probably not so much an erronous description of the complex properties, but occurs already at the stage of the trimethylamine molecule and then simply persists in the complex.

3.2.3. Restricted Vibrational Analysis. The computed complete vibrational spectra and the assignments will be discussed in more detail elsewhere. Here, only the data pertinent to the intra- and intermolecular stretching degrees of freedom r(Cl−F) and r(N···Cl) which are changed most in these of complexes are inspected more closely. In Table 12, the computed harmonic stretching frequencies and their infrared intensities are collected. The ClF stretching frequencies in the complexes are systematically red-shifted upon successive methyl substitution. The calculated shifts [B3LYP/6-311++G(3df,2p)] of −185 and −257 cm^{-1} for the Cl−F stretching frequencies in H_3N−ClF and $(CH_3)_3N$−ClF agree quite well with the experimentally (Ar-matrix) determined shifts of about −170 and −265 cm^{-1}, respectively.[3] The calculated intermolecular stretching frequency, on the other hand, is also successively red-shifted upon methylation, despite the increase of the corresponding force constant, an effect of the concomitant increase of the molecular mass in the amine. The high polarity of the complexes is also visible in the sizable infrared intensities, in particular, that of the Cl−F stretching mode. For example, the infrared intensity of the Cl−F stretching frequency in $(CH_3)_3N$−ClF is calculated to be enhanced by more than a factor of 10 relative to that of the free ClF molecule.

Summary and Conclusions

A large-scale systematic study of the structures, the stabilization energies, and other properties of the complexes of ClF with the simple amines, NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$, has been presented. In agreement with rotational spectroscopic data, the calculations show a strongly increased ionic character of the trimethylamine-ClF complex as compared with the H_3N−ClF complex. The trends upon successive methylation of the amine, that is, the decrease of the intermolecular distance R(N···Cl), the progressive widening of R(Cl−F), and the increase of the stabilization energy, are well described qualitatively by the DFT and MP2 approaches. The large systematic differences between various higher-order correlation methods, already observed for H_3N−halogen interactions, persist for the methylated amine-ClF interactions as well. Therefore, the theoretical prediction of the intermolecular distance, R(N···Cl), in the methylated amine-ClF complexes (accurate to a few hundredth of an Å), is still a challenging problem. Eventually, more advanced multireference configuration interaction calculations including size-consistency corrections will be necessary.

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