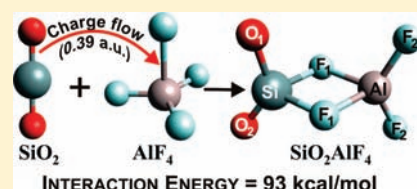


Moderately Reactive Molecules Forming Stable Ionic Compounds with Superhalogens[†]

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ABSTRACT: An explanation of the ability of selected moderately reactive molecules to form stable systems with superhalogens (AlF₄ and AlCl₄) is provided on the basis of theoretical considerations supported by *ab initio* calculations. It is demonstrated that even the molecules possessing high ionization potentials (such as SiO₂, NH₃, CHCl₃, CCl₂F₂) should form stable and strongly bound ionic compounds when combined with a properly chosen superhalogen system (acting as an oxidizing agent). The conclusion is supported by providing the structural parameters and interaction energies for the SiO₂AlF₄, NH₃AlF₄, CHCl₃AlF₄, CCl₂F₂AlF₄, SiO₂AlCl₄, and NH₃AlCl₄ compounds obtained at the CCSD(T)/6-311++G(d,p)//MP2/6-311++G(d,p) level. On the other hand, the AlF₄ and AlCl₄ superhalogens were found to be incapable of reacting with molecules whose ionization potentials (IP) exceed 13 eV (e.g., CO₂, CH₄). Finally, it is demonstrated that the competition between the electron binding energy of the superhalogen system and the IP of the molecule the superhalogen is combined with is a key factor for predicting the stability of certain species.



1. INTRODUCTION

Superhalogens are extraordinary inorganic compounds exhibiting enormously high electron affinities (spanning the 3.6–14 eV range).^{1–3} Their existence was predicted in 1981 by Boldyrev and Gutsev, who employed theoretical chemistry methods to support their hypothesis.¹ In addition, the simple MX_{k+1} formula was introduced¹ to describe one class of superhalogens, where M is a main group or transition metal atom, X is a halogen atom, and k is the maximal formal valence of atom M. Since the early 1980s, many other theoretical efforts have been undertaken to estimate the vertical electron detachment energies (VDE) of various anions having superhalogens as their neutral parents (see refs 4–12 and references cited therein). In 1999, dramatic progress was made in the investigation of superhalogen systems due to joined theoretical and experimental effort that resulted in an excellent report comprised of the first experimental photoelectron spectra of superhalogens (measured by the Wang's group) together with theoretical interpretations provided by Boldyrev and Simons.¹³ In particular, the photoelectron spectra of MX₂[−] (where M = Li, Na; X = Cl, Br, I) anions were obtained and assigned on the basis of *ab initio* outer-valence Green function (OVGF)^{14–22} calculations. Excellent agreement between experimentally and theoretically estimated VDE values has been achieved, and all of the anions have proven to be superhalogen-based species since their electron binding energies were found to be greater than 3.62 eV (see ref 13). Since then, many other superhalogen anions have been proposed, examined experimentally, and characterized theoretically, e.g., MX₃[−] (M = Be, Mg, Ca; X = Cl, Br),²³ the oxygen-based BO₂[−],²⁴ MCl₄[−] (M = Sc, Y, La),²⁵ and even larger species, such as [Na_nCl_{n+1}][−] (n = 1–4).²⁶ More recently, Pradhan et al. studied negatively charged MX_n clusters formed by the transition metal atom M (M = Sc, Ti, V) and containing up to seven halogen atoms X (X = F, Cl, Br).²⁷

Exploring various new superhalogen species is primarily focused on studying larger molecular clusters which are capable of forming strongly bound anions. The purpose of these efforts is to provide reliable data and predictions considering the possible use of such compounds as electron acceptors in the production of organic superconductors, as well as the role they can play in synthesis (e.g., in the oxidation of counterpart systems with high ionization potentials).^{28,29} The exploration of more unusual superhalogens (in which the central atom and/or halogen ligands are replaced with hydrogen atom and various functional groups, respectively) resulted in the determination that hydrogen atoms may play a central atom role in some superhalogen anions (HF₂[−], HCl₂[−], HBr₂[−], and HF₂[−])³⁰ while the extension of this study also covering larger [H_nF_{n+1}][−] species (n = 3–5, 7, 9, 12) resulted in the proposal of the enormously strongly bound anionic system H₁₂F₁₃[−], whose vertical electron binding energy approaches 14 eV.³ Recently, it was pointed out that the presence of halogen atoms in superhalogen species is not obligatory since the alternative ligands might be applied instead. Hence, it was demonstrated that the halogen ligands (F, Cl, Br, I) might be replaced with halogenoids (e.g., CN, SCN, OCN), and the electronic stabilities of the resulting anions may even exceed those obtained with the VII main group elements.³¹ According to recent findings, other alternative functional groups might also be exploited as ligands in superhalogen anions. Namely, the systems utilizing electrophilic substituents (i.e., NO₂, CF₃, CCl₃, SHO₃, and COOH)³² and acidic functional groups (i.e., ClO₄, ClO₃, ClO₂, ClO, NO₃, PO₃, H₂PO₄, HSO₄, HCO₃, SH)³³ as ligands were proposed and studied (see also a recent comprehensive review on molecular anions).³⁴

Received: May 6, 2011

Published: June 07, 2011

In our recent report,³⁵ we provided (on the basis of theoretical considerations supported by the *ab initio* calculations) an explanation of the hypothetical HAlCl_4 acid instability. In the course of our study, the existence of the corresponding salts (i.e., LiAlCl_4 , NaAlCl_4 , and KAlCl_4) was confirmed, whereas their parent acid (HAlCl_4) was identified as the $\text{HCl} \cdots \text{AlCl}_3$ adduct with the hydrogen chloride moiety tethered weakly to the quasi-planar aluminum chloride molecule. As we concluded, the electron affinity of the neutral superhalogen AlCl_4 molecule was the most important factor in determining the ability to form a stable MAlCl_4 compound ($M = \text{Li}, \text{Na}, \text{K}$). This finding was further confirmed in our most recent report,³⁶ in which we demonstrated that the competition between the IP and VDE values is indeed a key factor for predicting the stability of certain novel species (such as MgBX_5 , $X = \text{F}, \text{Cl}$). As we concluded, the reason why the MgBX_5 molecules (which might be considered as composed of the MgX and BX_4 fragments) are kinetically and thermodynamically stable is the proper balance between the IP of the MgX moiety and BX_4 's ability to accept an excess electron (manifested by the VDE of its anionic daughter).

Since the superhalogens are known to exhibit extremely large electron affinities, one should consider these species as potentially strong oxidizing agents as they are expected to act as effective electron acceptors. Therefore, in the present contribution, we decided to discuss the possibility of utilizing one of the superhalogen molecules as a strong electron acceptor capable of forming stable compounds with moderately reactive (i.e., chemically "inert") systems. In particular, our goal was to demonstrate that almost any neutral molecule (including those regarded as nearly nonreactive) might be assembled into a stable, strongly bound compound when combined with a properly designed superhalogen system. Moreover, we show that such a resulting compound exhibits partially ionic character as its stability is a consequence of the substantial electron density flow to the oxidizing agent used.

Our choice of superhalogen molecule was dictated primarily by the following premises: (i) the structural simplicity of the system and (ii) its strong ability to accept an excess electron. Hence, we decided to choose the AlF_4 superhalogen species as an electron acceptor since it consists of only five atoms and the electron binding energy of its corresponding anionic daughter (AlF_4^-) approaches 10 eV.³⁷ As far as the moderately reactive "test molecules" are concerned, we chose the following closed-shell neutral systems: methane, carbon dioxide, chloroform, silicon dioxide (SiO_2), ammonia, and dichlorodifluoromethane (Freon-12, CCl_2F_2); our choice of these particular molecules is explained and justified in the following sections, see section 3.

We believe that investigating basic issues such as the eventual stability (or lack thereof) of chemical compounds is important for the experimental community since recognizing the reasons for stability (or instability) of a designed novel compound seems crucial while planning and undertaking the actual synthesis.

2. METHODS

The equilibrium geometrical structures of the XAlF_4 ($X = \text{SiO}_2, \text{NH}_3, \text{CHCl}_3, \text{CCl}_2\text{F}_2, \text{CH}_4, \text{CO}_2$) and XAlCl_4 ($X = \text{SiO}_2, \text{NH}_3, \text{CHCl}_3$) systems and the corresponding harmonic vibrational frequencies were calculated by applying the second-order Møller–Plesset (MP2) perturbational method with the 6-311++G(d,p) basis set.^{38,39} The coupled-cluster method with single, double, and noniterative triple excitations (CCSD(T))⁴⁰ with the same 6-311++G(d,p) basis set was used to

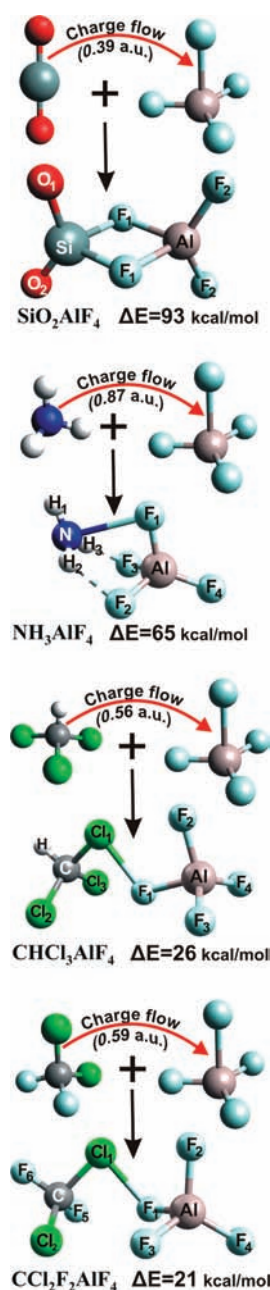


Figure 1. The equilibrium structures of the isolated SiO_2 , NH_3 , CHCl_3 , CCl_2F_2 , and AlF_4 molecules and the resulting SiO_2AlF_4 , NH_3AlF_4 , $\text{CHCl}_3\text{AlF}_4$, and $\text{CCl}_2\text{F}_2\text{AlF}_4$ compounds. The binding energy ΔE (i.e., the interaction between the constituting fragments) and the amount of the charge flow are also provided.

calculate the final energies of the species at their geometries obtained with the MP2 method. The ionization potentials for the neutral systems considered (i.e., SiO_2 , NH_3 , CHCl_3 , CCl_2F_2 , CH_4 , CO_2) were calculated by employing the outer-valence Green function OVGf method (B approximation).^{14–22} As a matter of fact, some of the earliest references²⁰ called the approach being developed "equations of motion (EOM)" rather than Green Function (GF). Since the OVGf approximation remains valid only for outer-valence ionizations for which the pole strengths (PS) are greater than 0.80–0.85,⁴¹ we verified that the PS values were sufficiently large to justify the use of the OVGf method for all states studied here (the smallest PS found for the states examined in this work was 0.901). The partial atomic charges (required for estimating

Table 1. The MP2 Geometrical Parameters and the Corresponding Harmonic Vibrational Frequencies (in cm^{-1}) for the XAlF_4 ($\text{X} = \text{SiO}_2, \text{NH}_3, \text{CHCl}_3, \text{CCl}_2\text{F}_2$) Species^a

species	geometrical parameters		vibrational frequencies		
SiO_2AlF_4	$\text{R}(\text{Al}-\text{F}_1) = 1.843$	$\alpha(\text{F}_1\text{AlF}_1) = 77.30$	$\nu_1(\text{a}') = 60$	$\nu_7(\text{a}'') = 280$	$\nu_{13}(\text{a}'') = 571$
	$\text{R}(\text{Al}-\text{F}_2) = 1.649$	$\alpha(\text{F}_2\text{AlF}_2) = 126.83$	$\nu_2(\text{a}'') = 107$	$\nu_8(\text{a}'') = 295$	$\nu_{14}(\text{a}') = 589$
	$\text{R}(\text{Si}-\text{F}_1) = 1.789$	$\alpha(\text{F}_1\text{SiF}_1) = 80.09$	$\nu_3(\text{a}') = 175$	$\nu_9(\text{a}') = 369$	$\nu_{15}(\text{a}') = 795$
	$\text{R}(\text{Si}-\text{O}_1) = 1.517$	$\alpha(\text{O}_1\text{SiO}_2) = 132.81$	$\nu_4(\text{a}') = 186$	$\nu_{10}(\text{a}') = 421$	$\nu_{16}(\text{a}') = 847$
	$\text{R}(\text{Si}-\text{O}_2) = 1.671$	$\omega(\text{F}_1\text{AlF}_1\text{F}_2) = 107.51$	$\nu_5(\text{a}'') = 213$	$\nu_{11}(\text{a}'') = 425$	$\nu_{17}(\text{a}') = 982$
		$\omega(\text{O}_1\text{SiAlF}_2) = 0.00$	$\nu_6(\text{a}') = 264$	$\nu_{12}(\text{a}') = 552$	$\nu_{18}(\text{a}') = 1297$
NH_3AlF_4	$\text{R}(\text{Al}-\text{F}_1) = 1.720$	$\alpha(\text{F}_1\text{AlF}_2) = 99.94$	$\nu_1(\text{a}) = 24$	$\nu_8(\text{a}) = 315$	$\nu_{15}(\text{a}) = 899$
	$\text{R}(\text{Al}-\text{F}_2) = 1.731$	$\alpha(\text{F}_3\text{AlF}_4) = 116.85$	$\nu_2(\text{a}) = 59$	$\nu_9(\text{a}) = 328$	$\nu_{16}(\text{a}) = 1033$
	$\text{R}(\text{Al}-\text{F}_3) = 1.749$	$\alpha(\text{AlF}_1\text{N}) = 83.16$	$\nu_3(\text{a}) = 187$	$\nu_{10}(\text{a}) = 362$	$\nu_{17}(\text{a}) = 1473$
	$\text{R}(\text{Al}-\text{F}_4) = 1.669$	$\alpha(\text{H}_1\text{NH}_2) = 120.99$	$\nu_4(\text{a}) = 197$	$\nu_{11}(\text{a}) = 485$	$\nu_{18}(\text{a}) = 1614$
	$\text{R}(\text{N}-\text{F}_1) = 2.555$	$\alpha(\text{H}_1\text{NH}_3) = 122.42$	$\nu_5(\text{a}) = 235$	$\nu_{12}(\text{a}) = 608$	$\nu_{19}(\text{a}) = 3062$
	$\text{R}(\text{H}_2-\text{F}_2) = 1.869$	$\omega(\text{F}_1\text{AlF}_3\text{F}_2) = 100.54$	$\nu_6(\text{a}) = 294$	$\nu_{13}(\text{a}) = 704$	$\nu_{20}(\text{a}) = 3387$
	$\text{R}(\text{H}_3-\text{F}_3) = 1.634$	$\omega(\text{AlF}_1\text{NH}_2) = 63.39$	$\nu_7(\text{a}) = 299$	$\nu_{14}(\text{a}) = 733$	$\nu_{21}(\text{a}) = 3672$
	$\text{R}(\text{N}-\text{H}_1) = 1.014$	$\omega(\text{H}_1\text{NH}_3\text{H}_2) = 160.22$			
	$\text{R}(\text{N}-\text{H}_2) = 1.031$				
	$\text{R}(\text{N}-\text{H}_3) = 1.049$				
$\text{CHCl}_3\text{AlF}_4$	$\text{R}(\text{Al}-\text{F}_1) = 1.855$	$\alpha(\text{F}_1\text{AlF}_2) = 95.77$	$\nu_1(\text{a}) = 3$	$\nu_9(\text{a}) = 268$	$\nu_{17}(\text{a}) = 697$
	$\text{R}(\text{Al}-\text{F}_2) = 1.698$	$\alpha(\text{F}_3\text{AlF}_4) = 117.72$	$\nu_2(\text{a}) = 27$	$\nu_{10}(\text{a}) = 279$	$\nu_{18}(\text{a}) = 798$
	$\text{R}(\text{Al}-\text{F}_3) = 1.676$	$\alpha(\text{AlF}_1\text{Cl}_1) = 110.33$	$\nu_3(\text{a}) = 62$	$\nu_{11}(\text{a}) = 284$	$\nu_{19}(\text{a}) = 852$
	$\text{R}(\text{Al}-\text{F}_4) = 1.676$	$\alpha(\text{Cl}_1\text{CCl}_2) = 110.62$	$\nu_4(\text{a}) = 66$	$\nu_{12}(\text{a}) = 311$	$\nu_{20}(\text{a}) = 866$
	$\text{R}(\text{F}_1-\text{Cl}_1) = 2.136$	$\alpha(\text{HCCl}_3) = 109.71$	$\nu_5(\text{a}) = 112$	$\nu_{13}(\text{a}) = 383$	$\nu_{21}(\text{a}) = 891$
	$\text{R}(\text{C}-\text{Cl}_1) = 1.822$	$\omega(\text{F}_1\text{AlF}_2\text{F}_3) = 108.59$	$\nu_6(\text{a}) = 166$	$\nu_{14}(\text{a}) = 434$	$\nu_{22}(\text{a}) = 1267$
	$\text{R}(\text{C}-\text{Cl}_2) = 1.739$	$\omega(\text{F}_2\text{AlF}_4\text{F}_3) = 141.93$	$\nu_7(\text{a}) = 176$	$\nu_{15}(\text{a}) = 586$	$\nu_{23}(\text{a}) = 1276$
	$\text{R}(\text{C}-\text{Cl}_3) = 1.739$	$\omega(\text{AlCCl}_1\text{F}_1) = 0.02$	$\nu_8(\text{a}) = 259$	$\nu_{16}(\text{a}) = 625$	$\nu_{24}(\text{a}) = 3163$
	$\text{R}(\text{C}-\text{H}) = 1.090$	$\omega(\text{HCCl}_1\text{Cl}_2) = 116.33$			
		$\omega(\text{Cl}_1\text{CCl}_3\text{Cl}_2) = 125.44$			
$\text{CCl}_2\text{F}_2\text{AlF}_4$	$\text{R}(\text{Al}-\text{F}_1) = 1.846$	$\alpha(\text{F}_1\text{AlF}_2) = 97.33$	$\nu_1(\text{a}) = 25$	$\nu_9(\text{a}) = 274$	$\nu_{17}(\text{a}) = 594$
	$\text{R}(\text{Al}-\text{F}_2) = 1.693$	$\alpha(\text{F}_3\text{AlF}_4) = 117.89$	$\nu_2(\text{a}) = 41$	$\nu_{10}(\text{a}) = 284$	$\nu_{18}(\text{a}) = 674$
	$\text{R}(\text{Al}-\text{F}_3) = 1.687$	$\alpha(\text{AlF}_1\text{Cl}_1) = 108.54$	$\nu_3(\text{a}) = 52$	$\nu_{11}(\text{a}) = 306$	$\nu_{19}(\text{a}) = 726$
	$\text{R}(\text{Al}-\text{F}_4) = 1.673$	$\alpha(\text{Cl}_1\text{CCl}_2) = 110.98$	$\nu_4(\text{a}) = 78$	$\nu_{12}(\text{a}) = 317$	$\nu_{20}(\text{a}) = 842$
	$\text{R}(\text{F}_1-\text{Cl}_1) = 2.135$	$\alpha(\text{F}_5\text{CF}_6) = 109.62$	$\nu_5(\text{a}) = 105$	$\nu_{13}(\text{a}) = 393$	$\nu_{21}(\text{a}) = 892$
	$\text{R}(\text{C}-\text{Cl}_1) = 1.870$	$\omega(\text{F}_1\text{AlF}_2\text{F}_3) = 104.83$	$\nu_6(\text{a}) = 159$	$\nu_{14}(\text{a}) = 422$	$\nu_{22}(\text{a}) = 998$
	$\text{R}(\text{C}-\text{Cl}_2) = 1.708$	$\omega(\text{F}_2\text{AlF}_4\text{F}_3) = 141.05$	$\nu_7(\text{a}) = 196$	$\nu_{15}(\text{a}) = 452$	$\nu_{23}(\text{a}) = 1162$
	$\text{R}(\text{C}-\text{F}_5) = 1.311$	$\omega(\text{AlCCl}_1\text{F}_1) = 25.56$	$\nu_8(\text{a}) = 246$	$\nu_{16}(\text{a}) = 482$	$\nu_{24}(\text{a}) = 1160$
	$\text{R}(\text{C}-\text{F}_6) = 1.326$	$\omega(\text{Cl}_1\text{CCl}_2\text{F}_6) = 114.72$			
	$\omega(\text{Cl}_2\text{CF}_5\text{F}_6) = 127.12$				

^a Bond lengths (R) in Å, valence angles (α) and dihedral angles (ω) in degrees.

the charge flow values) were fitted to the electrostatic potential according to the Merz–Singh–Kollman scheme.⁴²

Since the methods we used for the odd-electron systems are based on an unrestricted Hartree–Fock starting point (using the single-determinant reference wave function), it is important to ensure that little, if any, artificial spin contamination enters into the final wave functions. We computed the expectation value $\langle S^2 \rangle$ for the species studied in this work and found values of 0.753–0.772 in all radical (doublet) cases; hence, we are certain that spin contamination is not large enough to affect our findings significantly.

All calculations were performed with the Gaussian 03 software package.⁴³ In order to avoid erroneous results from the default direct SCF calculations, the keyword SCF=NoVarAcc was used, and the two-electron integrals were evaluated (without prescreening) to a tolerance of 10^{-20} au. The optimizations of the geometries were performed using relatively tight convergence thresholds (i.e., 10^{-5} hartree/bohr (or radian) for the root-mean-square first derivative).

3. RESULTS

Since our main goal was to demonstrate the use of the AlF_4 neutral molecule as an effective and strong electron acceptor, we decided to investigate its ability to ionize a few arbitrarily chosen representative molecules. However, our choice of these molecules was dictated by the necessity of fulfilling the following conditions: (i) the molecular systems were intended to be common, closed-shell neutral molecules; (ii) the molecules chosen were expected to be either nearly chemically inert or moderately reactive and to exhibit large ionization potentials. Such prerogatives led us to six neutral, closed-shell molecules (i.e., $\text{CO}_2, \text{CH}_4, \text{SiO}_2, \text{NH}_3, \text{CHCl}_3$, and CCl_2F_2) which are both moderately reactive and difficult to ionize (their IP values span the 10–15 eV range). We believe that the results we present show the ability of the AlF_4 superhalogen system to ionize even the molecules that are not commonly considered to act as the

reducers (i.e., electron donors). In other words, we demonstrate the unusual properties of the AlF_4 molecule as an enormously strong oxidizing agent (i.e., electron acceptor) capable of forming

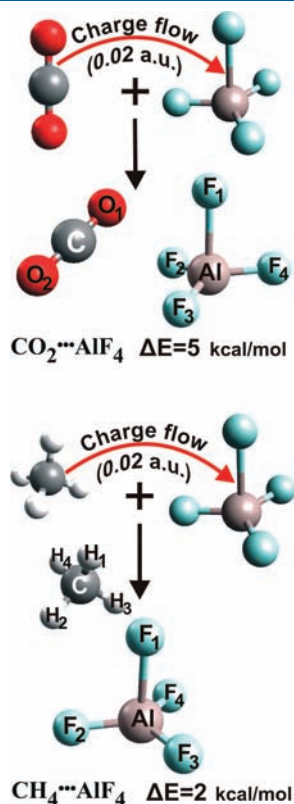


Figure 2. The equilibrium structures of the isolated CO_2 , CH_4 , and AlF_4 molecules and the resulting $[\text{CO}_2 \cdots \text{AlF}_4]$ and $[\text{CH}_4 \cdots \text{AlF}_4]$ weakly bound complexes. The binding energy ΔE (i.e., the interaction between the constituting fragments) and the amount of the charge flow are also provided.

stable compounds even when combined with moderately reactive chemical systems.

3.1. Stable Compounds Involving SiO_2 , NH_3 , CHCl_3 , and CCl_2F_2 . We begin our discussion with describing the results obtained for the AlF_4 interacting with the SiO_2 , NH_3 , CHCl_3 , and CCl_2F_2 molecules. According to our findings, the AlF_4 superhalogen forms a stable compound with the SiO_2 molecule, and the resulting equilibrium structure of the SiO_2AlF_4 system corresponds to the bidentate form with the silicon atom linked to the AlF_4 moiety through two fluorine (F_1) atoms (see Figure 1). The AlF_4 was also found to be capable of forming stable molecules with the NH_3 , CHCl_3 , and CCl_2F_2 systems. Namely, the ammonia binds to the AlF_4 through one N–F bonding interaction and two $\text{H} \cdots \text{F}$ bonds (the latter resembling typical hydrogen bonds), whereas chloroform and CCl_2F_2 (dichlorodifluoromethane, Freon-12) molecules are linked with the AlF_4 through one F–Cl bonding interaction. The resulting structures depicted in Figure 1 show that the AlF_4 fragment adopts a quasi-tetrahedral configuration in NH_3AlF_4 , $\text{CHCl}_3\text{AlF}_4$, and $\text{CCl}_2\text{F}_2\text{AlF}_4$ compounds. Since the isolated AlF_4 neutral system is known to adopt the C_s -symmetry structure with the three fluorine atoms surrounding the central aluminum atom in a quasi-planar AlF_3 configuration and the fourth (most distant) F atom tethered weakly to the Al atom,¹⁰ whereas the corresponding AlF_4^- anion is tetrahedral (T_d symmetry), we conclude that the AlF_4 fragment adopts an anionic rather than a neutral geometrical configuration while assembled into SiO_2AlF_4 , NH_3AlF_4 , $\text{CHCl}_3\text{AlF}_4$, and $\text{CCl}_2\text{F}_2\text{AlF}_4$ molecules. This conclusion is additionally supported by four similar Al–F bond lengths observed in each of these species; namely, the differences in the Al–F distances do not exceed 0.20, 0.08, 0.18, and 0.17 Å in SiO_2AlF_4 , NH_3AlF_4 , $\text{CHCl}_3\text{AlF}_4$, and $\text{CCl}_2\text{F}_2\text{AlF}_4$, respectively (see Table 1).

Such anionic character in the AlF_4 moiety has to be the result of a significant electron density flow from the associated SiO_2 , NH_3 , CHCl_3 , or CCl_2F_2 counterpart molecule. Indeed, the population analysis performed (based on the partial atomic charges fitted according to the Merz–Singh–Kollman scheme to reproduce the electrostatic potential) indicates the substantial

Table 2. The MP2 Geometrical Parameters and the Corresponding Harmonic Vibrational Frequencies (in cm^{-1}) for the $[\text{CO}_2 \cdots \text{AlF}_4]$ and $[\text{CH}_4 \cdots \text{AlF}_4]$ Species^a

species	geometrical parameters			vibrational frequencies		
$\text{CO}_2 \cdots \text{AlF}_4$	$R(\text{Al}-\text{F}_1) = 2.192$	$\alpha(\text{F}_1\text{AlF}_2) = 99.39$	$\nu_1(\text{a}) = 20$	$\nu_7(\text{a}) = 141$	$\nu_{13}(\text{a}) = 652$	
	$R(\text{Al}-\text{F}_2) = 1.660$	$\alpha(\text{F}_3\text{AlF}_4) = 119.61$	$\nu_2(\text{a}) = 44$	$\nu_8(\text{a}) = 180$	$\nu_{14}(\text{a}) = 672$	
	$R(\text{Al}-\text{F}_3) = 1.665$	$\alpha(\text{O}_1\text{CO}_2) = 179.00$	$\nu_3(\text{a}) = 56$	$\nu_9(\text{a}) = 239$	$\nu_{15}(\text{a}) = 923$	
	$R(\text{Al}-\text{F}_4) = 1.663$	$\alpha(\text{AlF}_1\text{O}_1) = 84.79$	$\nu_4(\text{a}) = 83$	$\nu_{10}(\text{a}) = 241$	$\nu_{16}(\text{a}) = 934$	
	$R(\text{C}-\text{O}_1) = 1.174$	$\omega(\text{F}_1\text{AlF}_3\text{F}_2) = 105.07$	$\nu_5(\text{a}) = 94$	$\nu_{11}(\text{a}) = 302$	$\nu_{17}(\text{a}) = 1338$	
	$R(\text{C}-\text{O}_2) = 1.165$	$\omega(\text{F}_2\text{AlF}_4\text{F}_3) = 164.25$	$\nu_6(\text{a}) = 123$	$\nu_{12}(\text{a}) = 650$	$\nu_{18}(\text{a}) = 2436$	
	$R(\text{Al}-\text{C}) = 3.697$					
	$\text{CH}_4 \cdots \text{AlF}_4$	$R(\text{Al}-\text{F}_1) = 2.232$	$\alpha(\text{F}_1\text{AlF}_2) = 97.19$	$\nu_1(\text{a}) = 15$	$\nu_9(\text{a}) = 163$	$\nu_{17}(\text{a}) = 1364$
		$R(\text{Al}-\text{F}_2) = 1.663$	$\alpha(\text{F}_3\text{AlF}_4) = 119.70$	$\nu_2(\text{a}) = 49$	$\nu_{10}(\text{a}) = 237$	$\nu_{18}(\text{a}) = 1371$
		$R(\text{Al}-\text{F}_3) = 1.661$	$\alpha(\text{AlF}_1\text{H}_1) = 110.33$	$\nu_3(\text{a}) = 53$	$\nu_{11}(\text{a}) = 240$	$\nu_{19}(\text{a}) = 1572$
$R(\text{Al}-\text{F}_4) = 1.661$		$\alpha(\text{H}_1\text{CH}_2) = 110.35$	$\nu_4(\text{a}) = 72$	$\nu_{12}(\text{a}) = 299$	$\nu_{20}(\text{a}) = 1586$	
$R(\text{C}-\text{H}_1) = 1.092$		$\alpha(\text{H}_3\text{CH}_4) = 108.81$	$\nu_5(\text{a}) = 89$	$\nu_{13}(\text{a}) = 674$	$\nu_{21}(\text{a}) = 3063$	
$R(\text{C}-\text{H}_2) = 1.091$		$\omega(\text{F}_1\text{AlF}_2\text{F}_3) = 89.76$	$\nu_6(\text{a}) = 96$	$\nu_{14}(\text{a}) = 931$	$\nu_{22}(\text{a}) = 3193$	
$R(\text{C}-\text{H}_3) = 1.091$		$\omega(\text{F}_2\text{AlF}_4\text{F}_3) = 167.57$	$\nu_7(\text{a}) = 111$	$\nu_{15}(\text{a}) = 934$	$\nu_{23}(\text{a}) = 3203$	
$R(\text{C}-\text{H}_4) = 1.090$		$\omega(\text{H}_1\text{CH}_2\text{H}_3) = 116.33$	$\nu_8(\text{a}) = 124$	$\nu_{16}(\text{a}) = 1362$	$\nu_{24}(\text{a}) = 3206$	
$R(\text{Al}-\text{C}) = 3.770$		$\omega(\text{H}_2\text{CH}_4\text{H}_3) = 120.05$				
		$\omega(\text{AlF}_1\text{CH}_1) = 177.65$				

^a Bond lengths (R) in Å; valence angles (α) and dihedral angles (ω) in degrees.

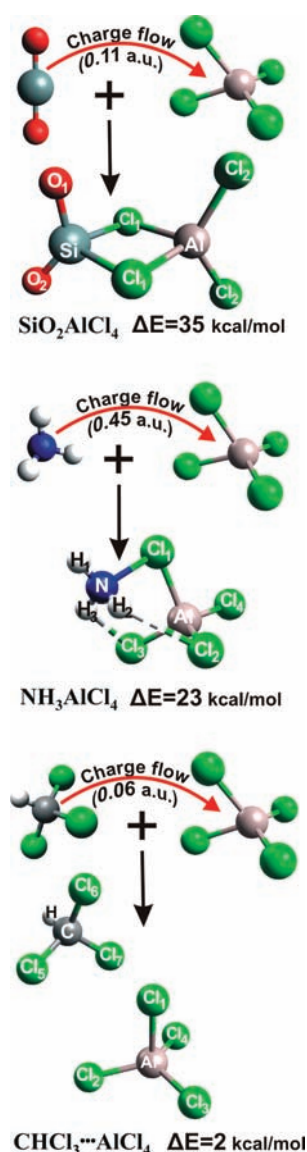


Figure 3. The equilibrium structures of the isolated SiO₂, NH₃, CHCl₃, and AlCl₄ molecules and the resulting SiO₂AlF₄, NH₃AlF₄, and [CHCl₃···AlCl₄] species. The binding energy ΔE (i.e., the interaction between the constituting fragments) and the amount of the charge flow are also provided.

charge flow (Δq) occurring when the XAlF₄ molecules are formed (where X stands for SiO₂, NH₃, CHCl₃ or CCl₂F₂). Namely, the Δq values were calculated to be equal to 0.39 au (for SiO₂AlF₄), 0.87 au (for NH₃AlF₄), 0.56 au (for CHCl₃AlF₄), and 0.59 au (for CCl₂F₂AlF₄) and should be interpreted as the amount of electron density transferred from the electron donor (X) to the acceptor (AlF₄) in each case. Such a significant charge flow observed for the SiO₂AlF₄, NH₃AlF₄, CHCl₃AlF₄, and CCl₂F₂AlF₄ systems may suggest their partially ionic character. This assumption is further confirmed by the relatively large values of the calculated binding energies (ΔE) for these species (by the “binding energy”, we mean the interaction energy between the donor X and the acceptor AlF₄ in the XAlF₄ system⁴⁴). The estimated ΔE values span the 21–93 kcal/mol range (see Figure 1), which indicates rather strong interactions between the X and AlF₄ fragments in XAlF₄ molecules (particularly in the case of SiO₂AlF₄ and NH₃AlF₄ systems,

for which the interaction energy reads 93 and 65 kcal/mol, respectively). In addition, our supposition concerning the ionic character of the SiO₂AlF₄, NH₃AlF₄, CHCl₃AlF₄, and CCl₂F₂AlF₄ compounds may be supported by the observation that each of these four donor molecules X (i.e., SiO₂, NH₃, CHCl₃, CCl₂F₂) is subject to substantial geometric changes when assembled with the AlF₄ acceptor into the XAlF₄ molecule, and most importantly, the predicted structural modifications of X resemble those observed when the isolated molecule X is ionized. The most striking example confirming this observation is the NH₃ molecule, which becomes more planar when bound to the AlF₄ (the H₁NH₃H₂ dihedral angle reads 160.2°, see Table 1) while the corresponding values for the isolated neutral (NH₃) and ionized (NH₃⁺) ammonia read 115.0° and 180.0°, respectively, as calculated at the same theory level. Hence, the structure of the NH₃ changes considerably when assembled into the NH₃AlF₄ and the direction of these changes is consistent with the structural modifications observed for the NH₃→NH₃⁺ process. Even though the changes in the structures of the SiO₂, CHCl₃, and CCl₂F₂ molecules are not as significant as those observed for NH₃, one may notice that the predicted minor modifications of the bond lengths and valence angles are also consistent with the structural transformations characteristic for the ionization processes.

Therefore, we conclude that each of the SiO₂AlF₄, NH₃AlF₄, CHCl₃AlF₄, and CCl₂F₂AlF₄ compounds should be considered as an ionic molecule consisting of the X⁺ cation (i.e., SiO₂⁺, NH₃⁺, CHCl₃⁺, or CCl₂F₂⁺) interacting with the AlF₄⁻ anion. Our conclusion is supported by the following observations: (i) the significant charge flow between the constituting X and AlF₄ fragments, (ii) large values of the interaction (binding) energy between X and AlF₄ in the resulting XAlF₄ species, and (iii) the tetrahedral-like structure of the AlF₄ moiety (resembling the isolated AlF₄⁻) and the modified structure of the X fragment (resembling the X⁺) when assembled into the XAlF₄.

3.2. Weakly Bound [CO₂···AlF₄] and [CH₄···AlF₄] Complexes. The CO₂ and CH₄ molecules tend to interact differently with the AlF₄ system than any of the SiO₂, NH₃, CHCl₃, and CCl₂F₂ compounds described in the preceding section. First of all, the resulting XAlF₄ structures (X = CO₂, CH₄) seem to resemble the weakly bound complexes (adducts) of two fragments, i.e., the neutral AlF₄ system and the methane or carbon dioxide molecule, which is manifested primarily by the relatively large CO₂···AlF₄ and CH₄···AlF₄ distances separating the two interacting moieties in the CO₂AlF₄ and CH₄AlF₄ species (see Figure 2 and Table 2). In addition, the analysis of the AlF₄ subunit geometrical structures in CO₂AlF₄ and CH₄AlF₄ clearly reveals that one of its fluorine atoms is more weakly bound to the Al central atom than the remaining F atoms (three Al–F bond lengths in CO₂AlF₄ span the 1.660–1.665 Å range, while the fourth Al–F distance is larger by ca. 0.53 Å; similarly, the three Al–F bonds in CH₄AlF₄ are in the 1.661–1.663 Å range, whereas the fourth Al–F separation is larger by ca. 0.57 Å, see Table 2). Moreover, the three fluorine atoms (labeled F₂, F₃, and F₄ in Figure 2 and Table 2) are localized in a quasi-planar configuration around the central Al atom (the deviation from planarity is 16° and 12° for the CO₂AlF₄ and CH₄AlF₄, respectively, as indicated by the F₂AlF₄F₃ dihedral angles), which suggests that the AlF₄ fragments in the CO₂AlF₄ and CH₄AlF₄, albeit slightly deformed, resemble the structure of the isolated neutral AlF₄ molecule rather than the tetrahedral AlF₄⁻ anion. Accordingly, the structures of the CO₂ and CH₄ subunits in CO₂AlF₄ and CH₄AlF₄ are similar to those observed for the isolated CO₂ and CH₄ systems rather than to the CO₂⁺ and CH₄⁺ cations.

Table 3. The MP2 Geometrical Parameters and the Corresponding Harmonic Vibrational Frequencies (in cm^{-1}) for the XAlCl_4 ($\text{X} = \text{SiO}_2, \text{NH}_3, \text{CHCl}_3$) Species^a

species	geometrical parameters			vibrational frequencies		
$\text{SiO}_2\text{AlCl}_4$	$R(\text{Al}-\text{Cl}_1) = 2.272$	$\alpha(\text{Cl}_1\text{AlCl}_1) = 89.30$	$\nu_1(\text{a}') = 27$	$\nu_7(\text{a}'') = 236$	$\nu_{13}(\text{a}') = 403$	
	$R(\text{Al}-\text{Cl}_2) = 2.066$	$\alpha(\text{Cl}_2\text{AlCl}_2) = 123.67$	$\nu_2(\text{a}'') = 86$	$\nu_8(\text{a}') = 248$	$\nu_{14}(\text{a}'') = 468$	
	$R(\text{Si}-\text{Cl}_1) = 2.220$	$\alpha(\text{Cl}_1\text{SiCl}_1) = 91.98$	$\nu_3(\text{a}') = 112$	$\nu_9(\text{a}'') = 257$	$\nu_{15}(\text{a}') = 523$	
	$R(\text{Si}-\text{O}_1) = 1.674$	$\alpha(\text{O}_1\text{SiO}_2) = 132.29$	$\nu_4(\text{a}') = 138$	$\nu_{10}(\text{a}') = 297$	$\nu_{16}(\text{a}') = 656$	
	$R(\text{Si}-\text{O}_2) = 1.522$	$\omega(\text{Cl}_1\text{AlCl}_1\text{Cl}_2) = 110.57$	$\nu_5(\text{a}'') = 143$	$\nu_{11}(\text{a}') = 349$	$\nu_{17}(\text{a}') = 819$	
		$\omega(\text{O}_1\text{SiAlCl}_2) = 0.00$	$\nu_6(\text{a}') = 196$	$\nu_{12}(\text{a}'') = 403$	$\nu_{18}(\text{a}') = 1274$	
	$\omega(\text{AlCl}_1\text{SiCl}_1) = 5.30$					
NH_3AlCl_4	$R(\text{Al}-\text{Cl}_1) = 2.314$	$\alpha(\text{Cl}_1\text{AlCl}_4) = 102.75$	$\nu_1(\text{a}) = 68$	$\nu_8(\text{a}) = 186$	$\nu_{15}(\text{a}) = 608$	
	$R(\text{Al}-\text{Cl}_2) = 2.116$	$\alpha(\text{Cl}_2\text{AlCl}_3) = 111.86$	$\nu_2(\text{a}) = 86$	$\nu_9(\text{a}) = 320$	$\nu_{16}(\text{a}) = 1156$	
	$R(\text{Al}-\text{Cl}_3) = 2.116$	$\alpha(\text{AlCl}_1\text{N}) = 87.85$	$\nu_3(\text{a}) = 101$	$\nu_{10}(\text{a}) = 376$	$\nu_{17}(\text{a}) = 1600$	
	$R(\text{Al}-\text{Cl}_4) = 2.090$	$\alpha(\text{H}_1\text{NH}_2) = 111.88$	$\nu_4(\text{a}) = 119$	$\nu_{11}(\text{a}) = 422$	$\nu_{18}(\text{a}) = 1625$	
	$R(\text{N}-\text{Cl}_1) = 2.320$	$\alpha(\text{H}_1\text{NH}_3) = 111.88$	$\nu_5(\text{a}) = 144$	$\nu_{12}(\text{a}) = 518$	$\nu_{19}(\text{a}) = 3500$	
	$R(\text{H}_2-\text{Cl}_2) = 2.762$	$\omega(\text{Cl}_1\text{AlCl}_2\text{Cl}_3) = 107.90$	$\nu_6(\text{a}) = 165$	$\nu_{13}(\text{a}) = 521$	$\nu_{20}(\text{a}) = 3654$	
	$R(\text{H}_3-\text{Cl}_3) = 2.762$	$\omega(\text{Cl}_2\text{AlCl}_4\text{Cl}_3) = 138.52$	$\nu_7(\text{a}) = 168$	$\nu_{14}(\text{a}) = 569$	$\nu_{21}(\text{a}) = 3678$	
	$R(\text{N}-\text{H}_1) = 1.014$	$\omega(\text{AlH}_1\text{NCl}_1) = 0.01$				
	$R(\text{N}-\text{H}_2) = 1.016$	$\omega(\text{H}_1\text{NH}_2\text{H}_3) = 125.80$				
	$R(\text{N}-\text{H}_3) = 1.016$	$\omega(\text{NCl}_1\text{Cl}_4\text{Al}) = 0.00$				
	$\text{CHCl}_3 \cdots \text{AlCl}_4$	$R(\text{Al}-\text{Cl}_1) = 2.425$	$\alpha(\text{Cl}_1\text{AlCl}_2) = 102.88$	$\nu_1(\text{a}) = 20$	$\nu_9(\text{a}) = 147$	$\nu_{17}(\text{a}) = 604$
$R(\text{Al}-\text{Cl}_2) = 2.087$		$\alpha(\text{Cl}_3\text{AlCl}_4) = 118.58$	$\nu_2(\text{a}) = 26$	$\nu_{10}(\text{a}) = 155$	$\nu_{18}(\text{a}) = 608$	
$R(\text{Al}-\text{Cl}_3) = 2.096$		$\alpha(\text{AlCl}_1\text{Cl}_5) = 71.13$	$\nu_3(\text{a}) = 29$	$\nu_{11}(\text{a}) = 167$	$\nu_{19}(\text{a}) = 696$	
$R(\text{Al}-\text{Cl}_4) = 2.091$		$\alpha(\text{Cl}_3\text{CCL}_6) = 110.65$	$\nu_4(\text{a}) = 40$	$\nu_{12}(\text{a}) = 246$	$\nu_{20}(\text{a}) = 796$	
$R(\text{C}-\text{Cl}_5) = 1.756$		$\alpha(\text{HCCl}_7) = 105.91$	$\nu_5(\text{a}) = 50$	$\nu_{13}(\text{a}) = 279$	$\nu_{21}(\text{a}) = 831$	
$R(\text{C}-\text{Cl}_6) = 1.761$		$\omega(\text{Cl}_1\text{AlCl}_3\text{Cl}_2) = 105.68$	$\nu_6(\text{a}) = 73$	$\nu_{14}(\text{a}) = 283$	$\nu_{22}(\text{a}) = 1270$	
$R(\text{C}-\text{Cl}_7) = 1.782$		$\omega(\text{Cl}_2\text{AlCl}_3\text{Cl}_4) = 150.67$	$\nu_7(\text{a}) = 86$	$\nu_{15}(\text{a}) = 392$	$\nu_{23}(\text{a}) = 1275$	
$R(\text{C}-\text{H}) = 1.086$		$\omega(\text{AlCCl}_3\text{Cl}_1) = 27.21$	$\nu_8(\text{a}) = 101$	$\nu_{16}(\text{a}) = 395$	$\nu_{24}(\text{a}) = 3206$	
$R(\text{Al}-\text{C}) = 4.972$		$\omega(\text{Cl}_3\text{CHCl}_6) = 121.42$				
		$\omega(\text{Cl}_3\text{CCL}_7\text{Cl}_6) = 124.64$				

^a Bond lengths (R) in Å; valence angles (α) and dihedral angles (ω) in degrees.

Table 4. The Ionization Potentials (IP) Obtained Theoretically (at the OVGf/6-311++G(3df,3pd) Level) and Experimentally for the $\text{SiO}_2, \text{NH}_3, \text{CHCl}_3, \text{CCl}_2\text{F}_2, \text{CO}_2,$ and CH_4 Molecules; Interaction Energies (ΔE) and Charge Flows (Δq) for the Resulting Compounds^a

X molecule	IP_{OVGF}	IP_{exp}	X/ AlF_4 or X/ AlCl_4	interaction energy (ΔE)	charge flow (Δq)	
SiO_2	13.29	12.60 ± 0.05^{45}	$\text{SiO}_2 / \text{AlF}_4$	93.41	(0.39)	strongly bound
NH_3	10.87	10.19 ± 0.01^{46}	$\text{NH}_3 / \text{AlF}_4$	64.65	(0.87)	strongly bound
CHCl_3	11.51	11.50 ± 0.01^{47}	$\text{CHCl}_3 / \text{AlF}_4$	26.24	(0.56)	strongly bound
CCl_2F_2	12.22	12.06 ± 0.2^{48}	$\text{CCl}_2\text{F}_2 / \text{AlF}_4$	21.39	(0.59)	strongly bound
CO_2	13.83	13.78 ± 0.01^{49}	$\text{CO}_2 / \text{AlF}_4$	5.28	(0.02)	weakly bound
CH_4	14.35	14.40^{50}	$\text{CH}_4 / \text{AlF}_4$	2.41	(0.02)	weakly bound
SiO_2	13.29	12.60 ± 0.05^{45}	$\text{SiO}_2 / \text{AlCl}_4$	34.90	(0.11)	strongly bound
NH_3	10.87	10.19 ± 0.01^{46}	$\text{NH}_3 / \text{AlCl}_4$	22.99	(0.45)	strongly bound
CHCl_3	11.51	11.50 ± 0.01^{47}	$\text{CHCl}_3 / \text{AlCl}_4$	2.20	(0.06)	weakly bound

^a IPs in eV; ΔE in kcal/mol; Δq in au. $\text{VDE}(\text{AlF}_4) = 9.789$ eV, $\text{VDE}(\text{AlCl}_4) = 7.016$ eV

The interaction energies (ΔE) between X ($\text{X} = \text{CO}_2$ or CH_4) and AlF_4 estimated for the CO_2AlF_4 and CH_4AlF_4 species are substantially smaller than those observed for the $\text{SiO}_2, \text{NH}_3, \text{CHCl}_3,$ and CCl_2F_2 molecules interacting with the AlF_4 . Namely, the ΔE calculated for the CO_2/AlF_4 was 5 kcal/mol, while a value of only 2 kcal/mol was found for the CH_4/AlF_4 . These small interaction energies seem to be consistent with the observation of hardly any charge flow ($\Delta q = 0.02$ au in both cases) between the CO_2 and

AlF_4 in CO_2AlF_4 and between the CH_4 and AlF_4 in CH_4AlF_4 . Such negligible charge flow values indicate the inability of the AlF_4 system to ionize either the carbon dioxide or methane molecule, which seems consistent with the fact that the IP values of both CO_2 and CH_4 systems (13.83 and 14.35 eV, respectively) significantly exceed the vertical electron binding energy of the AlF_4^- anion (9.79 eV).³⁷

Therefore, we conclude that neither the CO_2 nor the CH_4 molecule is capable of forming strongly bound ionic compounds

while interacting with the AlF_4 superhalogen system. Instead, weakly bound $[\text{CO}_2 \cdots \text{AlF}_4]$ and $[\text{CH}_4 \cdots \text{AlF}_4]$ complexes are generated in which the slightly structurally modified neutral (i.e., nonionized) CO_2 or CH_4 fragments can be distinguished. Our conclusion is also supported by the negligible charge flow between the constituting CO_2 (or CH_4) and AlF_4 fragments and small values of the interaction (binding) energy between CO_2 (or CH_4) and AlF_4 in the resulting $[\text{CO}_2 \cdots \text{AlF}_4]$ and $[\text{CH}_4 \cdots \text{AlF}_4]$ species.

3.3. $\text{SiO}_2\text{AlCl}_4$, NH_3AlCl_4 , and $[\text{CHCl}_3 \cdots \text{AlCl}_4]$ Species. Since the results described in the preceding sections seemed to indicate that the most important factor responsible for the stability of the XAlF_4 compounds ($\text{X} = \text{SiO}_2, \text{NH}_3, \text{CHCl}_3, \text{CCl}_2\text{F}_2, \text{CO}_2, \text{CH}_4$) is the ability of the AlF_4 system to ionize the X molecule, we decided to verify this observation by extending our studies to cover three arbitrarily chosen additional compounds (i.e., $\text{SiO}_2\text{AlCl}_4, \text{NH}_3\text{AlCl}_4$, and $\text{CHCl}_3\text{AlCl}_4$) in which the AlF_4 was replaced with the AlCl_4 . As we reported in the past, the AlCl_4 superhalogen is a weaker excess electron acceptor than AlF_4 . Namely, the vertical electron detachment energy of the AlCl_4^- was 7.02 eV, whereas that of the AlF_4^- was estimated to approach 10 eV (9.79 eV).³⁷ Hence, AlCl_4 is expected to form less stable compounds than AlF_4 when combined with any of the moderately reactive $\text{SiO}_2, \text{NH}_3$, or CHCl_3 molecules.

Indeed, the replacement of AlF_4 with AlCl_4 leads to the $\text{SiO}_2\text{AlCl}_4, \text{NH}_3\text{AlCl}_4$, and $\text{CHCl}_3\text{AlCl}_4$ (see Figure 3 and Table 3) compounds in which the interaction energy ΔE values are significantly smaller than those calculated for the corresponding $\text{SiO}_2\text{AlF}_4, \text{NH}_3\text{AlF}_4$, and $\text{CHCl}_3\text{AlF}_4$ molecules. In particular, the ΔE for the $\text{SiO}_2\text{AlCl}_4$ was 35 kcal/mol, while the interaction energy for the analogous SiO_2AlF_4 was found to be 93 kcal/mol (see Table 4). The ΔE values for NH_3AlCl_4 and NH_3AlF_4 were 23 and 65 kcal/mol, respectively, and we found the same pattern for the $\text{CHCl}_3\text{AlCl}_4$ ($\Delta E = 2$ kcal/mol) and $\text{CHCl}_3\text{AlF}_4$ ($\Delta E = 26$ kcal/mol) compounds. In the case of each $\text{XAlCl}_4/\text{XAlF}_4$ pair considered ($\text{X} = \text{SiO}_2, \text{NH}_3$, or CHCl_3), the decrease in the interaction energy is accompanied with a charge flow decrease (see Table 4). In particular, the Δq value describing the charge flow between SiO_2 and AlCl_4 in $\text{SiO}_2\text{AlCl}_4$ (0.11 au) is considerably smaller than the Δq of 0.39 au representing the charge flow between SiO_2 and AlF_4 in SiO_2AlF_4 ; analogously, Δq 's of 0.45 and 0.87 au are predicted for NH_3AlCl_4 and NH_3AlF_4 , respectively. Finally, a negligibly small charge flow of 0.06 au is calculated for the CHCl_3 and AlCl_4 in $\text{CHCl}_3\text{AlCl}_4$, whereas $\Delta q = 0.56$ au was estimated for CHCl_3 and AlF_4 in the corresponding $\text{CHCl}_3\text{AlF}_4$, see Table 4.

As far as the equilibrium geometries are concerned, $\text{SiO}_2\text{AlCl}_4$ forms a bidentate structure with the silicon atom linked to the AlCl_4 moiety through two chlorine atoms (labeled Cl_1 in Figure 3) resembling the equilibrium structure of SiO_2AlF_4 (see Figure 1). NH_3AlCl_4 also mimics the corresponding NH_3AlF_4 with its one $\text{N}-\text{Cl}$ bonding interaction and two hydrogen $\text{H} \cdots \text{Cl}$ bonds, as depicted in Figure 3. The most striking difference, however, we observe while comparing the $\text{CHCl}_3\text{AlCl}_4$ and $\text{CHCl}_3\text{AlF}_4$, as the latter is a relatively strongly bound system (see the preceding sections), whereas the former seems to correspond to the weakly bound complex. The $\text{CHCl}_3\text{AlCl}_4$ species should be viewed as the $[\text{CHCl}_3 \cdots \text{AlCl}_4]$ complex primarily because of its small interaction energy (2 kcal/mol). However, the important observation is that the $\text{CHCl}_3\text{AlF}_4$ system loses its ionic character when the fluorine atoms are replaced with chlorine atoms, which is manifested by both (i) the negligibly small charge flow (0.06 au) and

(ii) the geometry of the AlCl_4 subunit resembling the neutral AlCl_4 molecule rather than the tetrahedral AlCl_4^- anion.

Hence, we conclude that AlCl_4 , as a weaker electron acceptor than AlF_4 , forms XAlCl_4 compounds exhibiting smaller interaction energies between the X and AlCl_4 fragments than was observed in the case of analogous systems involving AlF_4 .

4. SUMMARY AND CONCLUSIONS

On the basis of our ab initio CCSD(T)/6-311++G(d,p) calculations on the XAlF_4 ($\text{X} = \text{SiO}_2, \text{NH}_3, \text{CHCl}_3, \text{CCl}_2\text{F}_2, \text{CO}_2, \text{CH}_4$) molecules (whose geometries were optimized at the MP2/6-311++G(d,p) level), we provided (i) the interaction energy between the X and AlF_4 fragments for each XAlF_4 compound, (ii) the charge flow between the X and AlF_4 (which might be viewed as the amount of electron density transferred from the X molecule to the electron acceptor AlF_4), and (iii) the equilibrium geometrical structure of each XAlF_4 system. In addition, we also studied similar XAlCl_4 ($\text{X} = \text{SiO}_2, \text{NH}_3, \text{CHCl}_3$) species (at the same theory level) in which a weaker (AlCl_4) electron acceptor was used.

The analysis of these results reveals the strong dependence between the first ionization potential of the X molecule and the electron binding energy of the electron acceptor utilized (either AlF_4 or AlCl_4) on the stability of the resulting XAlF_4 or XAlCl_4 system. Namely, the NH_3 (IP = 10.87 eV), CHCl_3 (IP = 11.51 eV), CCl_2F_2 (IP = 12.22 eV), and SiO_2 (IP = 13.29 eV) closed-shell neutral molecules form stable, strongly bound compounds (exhibiting partially ionic character) with AlF_4 (whose vertical electron binding energy is 9.79 eV), see Table 4. The ionic nature of the XAlF_4 ($\text{X} = \text{SiO}_2, \text{NH}_3, \text{CHCl}_3, \text{CCl}_2\text{F}_2$) compounds is confirmed by the large values of the interaction energy (21–93 kcal/mol) and substantial charge flow (0.39–0.87 au) between the two constituting X and AlF_4 fragments.

However, AlF_4 forms only weakly bound complexes when combined with either CO_2 or CH_4 since these molecules possess larger IP values (13.83 and 14.35 eV, respectively). Hence, the resulting species do not exhibit ionic character, as the corresponding interaction energies are small (2–5 kcal/mol) and the charge flow values are negligible (0.02 au) and therefore should be viewed as the weakly bound $[\text{CO}_2 \cdots \text{AlF}_4]$ and $[\text{CH}_4 \cdots \text{AlF}_4]$ complexes.

The results obtained for the three systems involving AlCl_4 (instead of AlF_4) as an electron acceptor confirmed our conclusions considering the key role of the electron acceptor strength in forming stable compounds with the $\text{SiO}_2, \text{NH}_3$, and CHCl_3 molecules. In particular, the interaction energies and the charge flow values for the resulting XAlCl_4 species were found to be considerably smaller than those estimated for the corresponding XAlF_4 compounds (see Table 4), which is clearly caused by the smaller excess electron binding energy of AlCl_4 (VDE = 7.02 eV) in comparison to AlF_4 (VDE = 9.79 eV).

Therefore, we conclude that the AlF_4 molecule might be utilized as a strong oxidizing agent, as it is capable of combining with even moderately reactive molecules exhibiting IP values approaching 13 eV (such as silicon dioxide (SiO_2), chloroform (CHCl_3), ammonia (NH_3), and dichlorodifluoromethane (Freon-12, CCl_2F_2)) to form strongly bound ionic compounds. As the electron binding energy of the AlF_4 system was found to be the most important factor determining its ability to combine with other molecules, we postulate that AlF_4 should be capable of forming strongly bound species when combined with practically any molecules whose IPs do not exceed ca. 13 eV (due to AlF_4 's

ability to partially ionize even the molecules that are not commonly considered to act as reducers).

We believe that designing even stronger electron acceptors (whose electron affinities exceed 10 eV) in the near future will allow one to oxidize molecules exhibiting very large ionization potentials (e.g., CO₂, CH₄). Although such oxidizing agents have already been proposed by our group (for example, the H₁₂F₁₃ system whose excess electron binding energy approaches 14 eV),³ their structural complexity makes them inconvenient for experimental chemists, as the eventual synthesis thereof is anticipated to be problematic. Therefore, the designing of the novel electron acceptors that would be both structurally simple and capable of oxidizing chemical systems exhibiting high ionization potentials still remains an important challenge for theoretical chemists.

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ACKNOWLEDGMENT

This work was supported by the Polish National Science Center (NCN) Grant No. N N204 201740 and partially by the NCN Grant No. DS/8371-4-0137-1. The computer time provided by the Academic Computer Center in Gdańsk (TASK) is also gratefully acknowledged.

DEDICATION

[†]This manuscript is dedicated to Professor Alexander Boldyrev on the occasion of his 60th birthday

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