



Editor's choice

The acid strength of the datively bound complexes involving AlF_3 lone pair acceptor and various lone pair donors

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ABSTRACT

The acid strength of the datively bound $\text{X} \rightarrow \text{AlF}_3$ complexes ($\text{X} = \text{HF}, \text{HCl}, \text{H}_2\text{S}, \text{AsH}_3, \text{PH}_3, \text{NF}_2\text{H}, \text{NFH}_2, \text{NH}_3, \text{and H}_2\text{O}$) is evaluated on the basis of theoretical calculations employing ab initio methods. Significant enhancement of the X acidity upon the formation of X/AlF_3 compounds is predicted. It is demonstrated that even the non-acidic molecules X (e.g., $\text{H}_2\text{O}, \text{NH}_3$) combined with AlF_3 are expected to form the $\text{X} \rightarrow \text{AlF}_3$ complexes characterized by the acid strength comparable or larger than that of H_2SO_4 .

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1. Introduction

The term "superacid" appeared in the literature for the very first time in the work of Hall and Conant published in 1927 [1]. A few decades later it was proposed to define superacids as the compounds whose acidity is stronger than that of 100% sulfuric acid which means that their Hammett acidity function (H_0) is smaller than -12 [2,3]. However, the superacid chemistry has only become a widespread area when Olah and Hogeveen published their reports on the stability of carbocations [4–9]. These studies triggered the continuing theoretical [10–15] and experimental [16–23] investigations concerning various superacids' properties, such as structures, stabilities and acid strengths. Our group contributed to these studies by (i) providing the evaluation of the acid strength of a series of aluminum-based Lewis–Brønsted superacids (HF/AlF_3 (HAlF_4), $\text{HF}/\text{Al}_2\text{F}_6$ (HAl_2F_7), $\text{HF}/\text{Al}_3\text{F}_9$ ($\text{HAl}_3\text{F}_{10}$), and $\text{HF}/\text{Al}_4\text{F}_{12}$ ($\text{HAl}_4\text{F}_{13}$)) [24] and the similar superacids containing In, Sn, and Sb ($\text{HIn}_n\text{F}_{3n+1}$, $\text{HSn}_n\text{F}_{4n+1}$, and $\text{HSb}_n\text{F}_{5n+1}$ ($n = 1-3$)) [25], as well as Ti and Ge ($\text{HTi}_n\text{F}_{4n+1}$ and $\text{HGe}_n\text{F}_{4n+1}$ ($n = 1-3$)) [26]; (ii) determining that the protonation of superhalogen anions [27–29] might be considered as the route to superacids' formation in selected cases [30,31]; (iii) emphasizing the importance of microsolvation effects on the acidity of the systems containing the excess of either Brønsted acid component (i.e., $n\text{HF}/\text{AlF}_3$ and $n\text{HF}/\text{GeF}_4$ ($n = 1-6$)) [32] or Lewis acid component ($\text{HClO}_4/n(\text{AlF}_3)$ and $\text{HClO}_4/n(\text{SbF}_5)$ ($n = 1-3$)) [33]; and (iv) demonstrating that certain hydrogenation

reactions (e.g., carbon monoxide hydrogenation yielding formaldehyde) might be catalyzed by either HAlF_4 or HSbF_6 superacid [34,35].

The binary Lewis–Brønsted superacids are commonly prepared by mixing Brønsted acid (B) and strong Lewis acid (L), hence the structure of the representative building block consists of a pair of B and L molecules held together by mutual interactions. The most important feature of such a building block is the presence of a $\text{B} \rightarrow \text{L}$ dative bond. For example, the structure of HAlF_4 should be written as $\text{HF} \rightarrow \text{AlF}_3$ which illustrates that the fluorine electron lone pair of the HF Brønsted acid molecule is being donated to the empty $3p$ aluminum orbital of the Lewis acid molecule. Moreover, the whole $\text{HF} \rightarrow \text{AlF}_3$ system is additionally stabilized by the hydrogen bond [36]. The presence of the dative bond in the Lewis–Brønsted superacids is crucial as it strongly affects the resulting distribution of the electron density in the system, namely, the electron density is moved toward the Lewis acid component (e.g., AlF_3) which usually increases the polarity of the $\text{B} \rightarrow \text{L}$ complex. As a consequence, the Brønsted acid component (e.g., HF) exhibits electron density deficit which in turn weakens the $\text{H}-\text{F}$ bond and thus increases the acid strength.

Earlier studies on many Lewis–Brønsted superacids revealed that their acidity (manifested by the Gibbs free energies of the superacid deprotonation reactions ($\Delta G_{\text{acid}}^{298}$)) may vary to span approximately 230–303 kcal/mol range (where $\Delta G_{\text{acid}}^{298}$ of 303 kcal/mol is the limiting value for superacids as it corresponds to the Gibbs free deprotonation energy of the sulfuric acid as measured by Viggiano et al. [37] and confirmed by theoretical calculations [11]). In particular, the strongest Lewis–Brønsted superacid

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proposed thus far (HSb₃F₁₆) is characterized by $\Delta G_{acid}^{298} = 230$ kcal/mol [25] while the values predicted for other systems are somewhat larger (e.g., 240 kcal/mol for HAu₃F₁₆ [31], 265 kcal/mol for HGaCl₄ [30], 272 kcal/mol for HBeCl₃ [13], 281 kcal/mol for HPF₆ [13]). Clearly, the acid strength of the Lewis–Brønsted superacid strongly depends on the choice of both L and B components that a given acid consists of. Despite a large number of superacids investigated thus far, this issue has not been systematically addresses yet. Therefore, in this contribution, we describe our studies on the **X**/AlF₃ (**X** → AlF₃) compounds, where **X** is the neutral closed-shell molecule capable of acting as electron lone pair donor. In order to provide the results covering the cases where the efficiency of the predicted electron density flow (from **X** to AlF₃) varies, we chose the set of commonly known molecules to act as lone pair donors whose acidity is either apparent (e.g., HF, HCl, H₂S) or almost negligible (e.g., H₂O, NH₃). We hope that the results we provide will help the experimental chemists in designing novel Lewis–Brønsted superacids exhibiting the desired acid strength.

2. Methods

The **X**/AlF₃ (**X** = HF, HCl, H₂S, AsH₃, PH₃, NF₂H, NFH₂, NH₃, and H₂O) closed-shell neutral systems (i.e., complexes consisting of the AlF₃ Lewis acid forming dative bond with **X** molecule) and their corresponding anions (i.e., negatively charged closed-shell species formed by deprotonation thereof) were investigated using theoretical quantum chemistry methods. In particular, the equilibrium geometries and harmonic vibrational frequencies were calculated using the quadratic configuration interaction method with single and double excitations (QCISD) [38–40] with the aug-cc-pVDZ basis set [41] (for H, F, Cl, N, P, As, O, and S) and the aug-cc-pV(D + d)Z basis set [42] (for Al).

The Gibbs free energies of the deprotonation reactions (ΔG_{acid}^{298}) concerning the isolated **X** molecules (HF, HCl, H₂S, AsH₃, PH₃, NF₂H, NFH₂, NH₃, and H₂O) and their complexes with AlF₃ were evaluated using the electronic energies, zero-point energy corrections, thermal corrections and entropy contributions (at T = 298.15 K) estimated with the QCISD method and the same basis sets. In each case the Gibbs free energy of the proton was also accounted for.

The gas-phase basicity (also called absolute or intrinsic basicity) of each **X** molecule (ΔG_{base}^{298}) was calculated as the negative of the Gibbs free energy change associated with the $\mathbf{X} + \text{H}^+ \rightarrow \mathbf{XH}^+$ reaction (with the Gibbs free energy of the proton accounted for). Such defined ΔG_{base}^{298} values were evaluated using the electronic energies, zero-point energy corrections, thermal corrections and entropy contributions (at T = 298.15 K) estimated with the QCISD method and the same aug-cc-pVDZ/aug-cc-pV(D + d)Z basis sets.

In order to verify the reliability of the QCISD/aug-cc-pVDZ theory level applied, we refined our calculations (including geometry optimizations and harmonic vibrational frequency calculations) for two **X**/AlF₃ complexes (we chose the most weakly bound and the most strongly bound systems, namely HCl/AlF₃ and NH₃/AlF₃ whose binding energies are equal to 10.5 and 40.7 kcal/mol, respectively) at the more advanced CCSD(T)/aug-cc-pVTZ level. We found that the Gibbs free deprotonation energies evaluated for these two complexes by using the CCSD(T) method and the aug-cc-pVTZ basis set differ from those predicted by employing the QCISD method and the aug-cc-pVDZ basis set by less than 1 kcal/mol. Therefore, we are confident that the theory level applied in this contribution (i.e., QCISD/aug-cc-pVDZ/aug-cc-pV(D + d)Z) is adequate and reliable.

The partial atomic charges were evaluated by the Natural Bond Orbital (NBO) analysis scheme [43–45] using the QCISD electron densities.

All calculations were performed using the GAUSSIAN16 (Rev. B.01) package [46].

3. Results

The equilibrium structures of the HF/AlF₃, HCl/AlF₃, H₂S/AlF₃, AsH₃/AlF₃, PH₃/AlF₃, NF₂H/AlF₃, NFH₂/AlF₃, NH₃/AlF₃, and H₂O/AlF₃ systems and their corresponding deprotonation products are presented and described in this section whereas the Cartesian coordinates of all systems studied are provided in the Supporting Information (see Table S1). All systems analyzed correspond to energetic minima (as confirmed by frequency analysis).

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.cplett.2018.06.059>.

3.1. Equilibrium structures of the **X**/AlF₃ systems and their deprotonated forms

While designing our **X**/AlF₃ systems we have chosen the set of structurally simple closed-shell molecules **X** which contain both (i) at least one hydrogen atom (needed to assure that the resulting **X**/AlF₃ compound may act as a system capable of donating a proton) and (ii) electron lone pair that could be donated to the empty 3p Al orbital of AlF₃ (see the hybrid compositions presented in Table S2 in the Supporting Information). In addition, while choosing the **X** molecules we wanted to include the systems whose acidity/basicity varies. Therefore, each of the systems we have chosen is capable of acting as a proton donor (i.e., Brønsted acid) and as an electron lone pair donor (i.e., Lewis base).

The equilibrium structures of the NH₃/AlF₃, (NH₂/AlF₃)[−], H₂O/AlF₃, (HO/AlF₃)[−], NFH₂/AlF₃, and (NFH/AlF₃)[−] are presented in Fig. 1, the structures of PH₃/AlF₃, (PH₂/AlF₃)[−], NF₂H/AlF₃, (NF₂/AlF₃)[−], AsH₃/AlF₃, and (AsH₂/AlF₃)[−] are shown in Fig. 2, whereas those of the H₂S/AlF₃, (HS/AlF₃)[−], HCl/AlF₃, (Cl/AlF₃)[−], HF/AlF₃, and (F/AlF₃)[−] are depicted in Fig. 3 (all structures presented correspond to energetic minima, as confirmed by frequency analysis).

In general, the structures of the neutral **X**/AlF₃ systems contain the non-planar AlF₃ fragment and the **X** molecule tethered to it via the dative bond (see the dashed lines in Figs. 1–3). In most cases considered, the hydrogen atoms of the **X** systems form the H-bonds with the fluorine ligands connected to the Al atom (see the dotted lines in Figs. 1–3) which provides the additional stabilization. As a consequence, the binding energies (BE) predicted for the **X**/AlF₃ complexes are positive and span the 10.5–40.7 kcal/mol range, see Table 1 (binding energy for each **X**/AlF₃ complex was calculated by subtracting the energies of the isolated and relaxed (i.e., separately optimized) **X** and AlF₃ species from that of the **X**/AlF₃ compound). The positive values of the Gibbs free fragmentation energies (with respect to the $\mathbf{X}/\text{AlF}_3 \rightarrow \mathbf{X} + \text{AlF}_3$ process) also support the stability of all systems considered, see Table 1.

As expected, the length of the **X** → Al dative bond strongly depends on the choice of the **X** component, namely, the shortest separation (1.968 Å) was found for H₂O/AlF₃ whereas the longest dative bond length (2.613 Å) was predicted for AsH₃/AlF₃. In all neutral cases the AlF₃ fragment adopts pyramidal structure (i.e., it is deformed from its planar D_{3h}-symmetry structure exhibited by the isolated aluminum trifluoride) with the Al–F bond lengths spanning the relatively narrow 1.653–1.674 Å range. The lengths of the hydrogen bonds in the **X**/AlF₃ systems are related to both (i) the separations between **X** and AlF₃ fragments (which in turn is caused by the differences in atomic radii of N, P, As, O, S, Cl, and F atoms) and (ii) the mutual orientation of the **X** and AlF₃ subunits. The shortest H-bonds (i.e., 2.237 Å in HF/AlF₃, 2.564 Å in HCl/AlF₃, 2.603 Å in H₂O/AlF₃, 2.779 Å in NH₃/AlF₃) are predicted

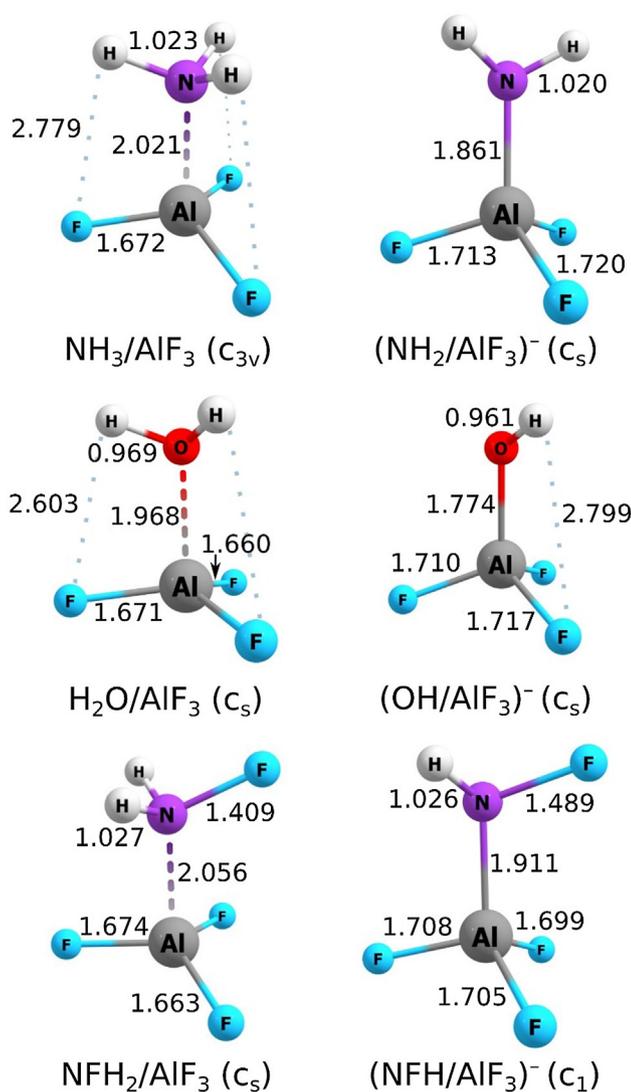


Fig. 1. The structures of the X/AlF_3 neutral compounds ($X = \text{NH}_3$, H_2O , NFH_2) and their corresponding deprotonated systems. Selected bond lengths are provided in Å. Dative bonds and hydrogen bonds are represented by the dashed and dotted lines, respectively. All structures presented correspond to energetic minima.

for the systems whose X component involves either the first row atoms or halogen atoms.

It seems important to notice the structural changes in the X/AlF_3 compounds upon their deprotonation. First of all, we would like to point out that each of these deprotonated systems corresponds to the relatively strongly bound anion. One of these anions, i.e., $(\text{AlF}_4)^-$, was studied in the past and classified as strongly electronically bound species having its vertical electron detachment energy equal to 9.79 eV [47,48] whereas the remaining $(\text{HS}/\text{AlF}_3)^-$, $(\text{Cl}/\text{AlF}_3)^-$, $(\text{NH}_2/\text{AlF}_3)^-$, $(\text{HO}/\text{AlF}_3)^-$, $(\text{AsH}_2/\text{AlF}_3)^-$, $(\text{PH}_2/\text{AlF}_3)^-$, $(\text{NF}_2/\text{AlF}_3)^-$, and $(\text{NFH}/\text{AlF}_3)^-$ anions also represent the negatively charged systems containing four ligands bound to the central aluminum atom and thus their excess electron binding energies are expected to be substantial. Once a proton is detached from any of the X/AlF_3 species, the quasi-tetrahedral ligand orientation around the Al center is adopted, the excess negative charge becomes delocalized among four ligands and the $X-\text{AlF}_3$ bond shortens. Indeed, the $\text{N}-\text{Al}$ distance shortens by 0.145–160 Å, whereas the $\text{O}-\text{Al}$, $\text{S}-\text{Al}$, $\text{P}-\text{Al}$, and $\text{As}-\text{Al}$ separations decrease by 0.194, 0.206, 0.114, and 0.102 Å, respectively (see Figs. 1–3). The most profound shortenings of the $X-\text{Al}$ bond lengths (by

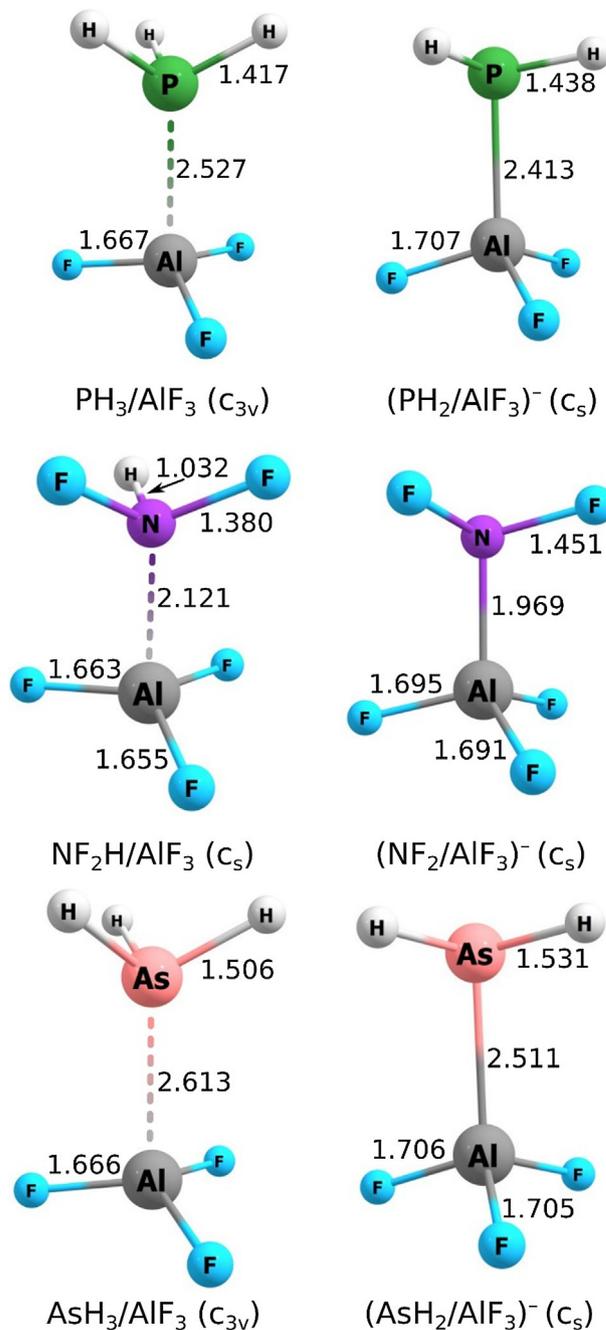


Fig. 2. The structures of the X/AlF_3 neutral compounds ($X = \text{PH}_3$, NF_2H , AsH_3) and their corresponding deprotonated systems. Selected bond lengths are provided in Å. Dative bonds are represented by the dashed lines. All structures presented correspond to energetic minima.

0.300–0.334 Å) are observed when the HF/AlF_3 and HCl/AlF_3 compounds are compared to their deprotonated $(\text{F}/\text{AlF}_3)^-$ and $(\text{Cl}/\text{AlF}_3)^-$ forms. This is caused by the fact that for $X = \text{HF}$ and $X = \text{HCl}$ the deprotonation process leads to the anions whose all four ligands are halogen atoms which allows for an effective delocalization of the excess electron density. Moreover, due to the fact that the AlF_3 system is arbitrarily assumed to play the Lewis acid role in all X/AlF_3 complexes investigated, the $X = \text{HF}$ case is special because withdrawing a proton from HF/AlF_3 produces the anion whose all four ligands are the same which renders its shape perfectly tetrahedral as the excess negative charge is delocalized evenly among all fluorine atoms surrounding the central Al atom. As revealed by the earlier studies [49,50], such symmetrical

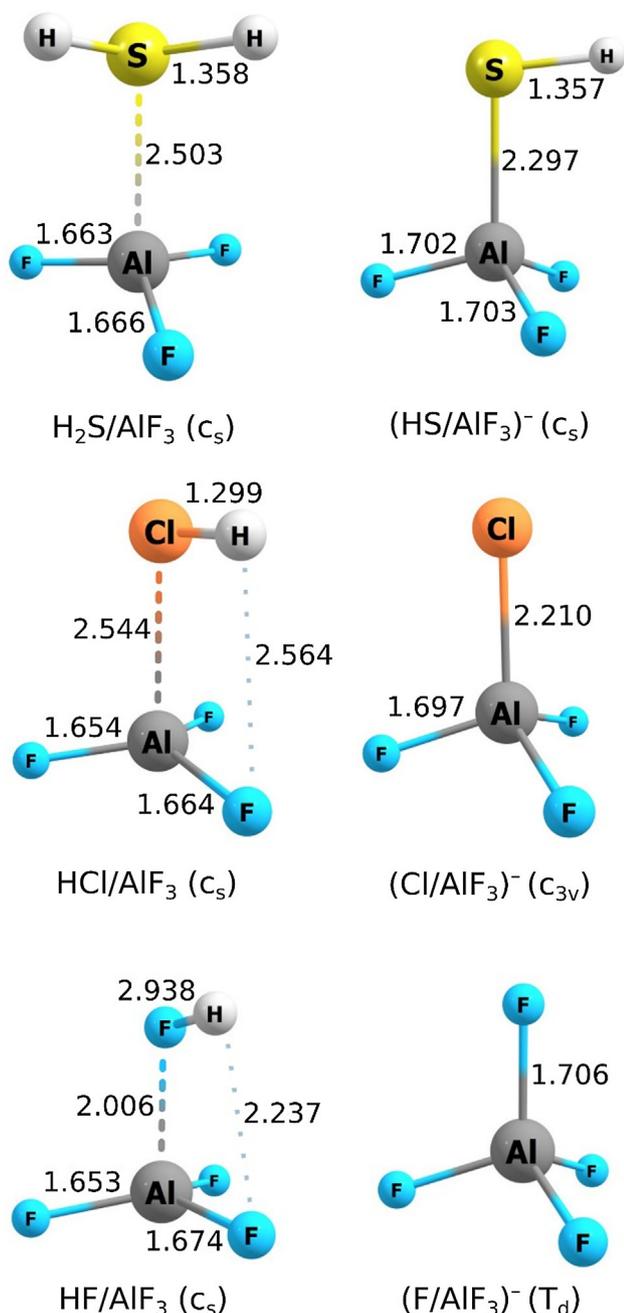


Fig. 3. The structures of the X/AlF_3 neutral compounds ($X = \text{H}_2\text{S}, \text{HCl}, \text{HF}$) and their corresponding deprotonated systems. Selected bond lengths are provided in Å. Dative bonds and hydrogen bonds are represented by the dashed and dotted lines, respectively. All structures presented correspond to energetic minima.

Table 1

The Gibbs free deprotonation energies (ΔG_{acid}^{298} in kcal/mol) of X molecules and X/AlF_3 compounds, intrinsic basicities of X (ΔG_{base}^{298} in kcal/mol), the binding energies (BE in kcal/mol) and the Gibbs free fragmentation energies at $T = 298.15$ K (ΔG_{frag}^{298}) of X/AlF_3 systems.

X	Symmetry	Gas-phase basicity $\Delta G_{base}^{298}(X)$	Gibbs free deprotonation energy $\Delta G_{acid}^{298}(X)$	(X/AlF_3)	Symmetry	Gibbs free deprotonation energy $\Delta G_{acid}^{298}(X/\text{AlF}_3)$	BE	ΔG_{frag}^{298}
HF	$C_{\infty v}$	107.5	362.7	HF/AlF_3	C_s	265.9	16.6	7.2
HCl	$C_{\infty v}$	126.8	326.4	HCl/AlF_3	C_s	265.6	10.5	1.9
H_2O	C_{2v}	156.3	382.6	$\text{H}_2\text{O}/\text{AlF}_3$	C_s	296.8	30.2	19.3
H_2S	C_{2v}	161.9	344.1	$\text{H}_2\text{S}/\text{AlF}_3$	C_s	288.5	18.9	9.0
NF_2H	C_s	162.2	352.9	$\text{NF}_2\text{H}/\text{AlF}_3$	C_s	292.2	20.0	8.4
NFH_2	C_s	185.8	374.2	$\text{NFH}_2/\text{AlF}_3$	C_s	308.3	30.6	18.8
AsH_3	C_{3v}	187.2	352.6	$\text{AsH}_3/\text{AlF}_3$	C_{3v}	299.2	18.0	7.4
PH_3	C_{3v}	188.6	361.5	PH_3/AlF_3	C_{3v}	303.3	19.7	6.5
NH_3	C_{3v}	208.0	395.7	NH_3/AlF_3	C_{3v}	322.6	40.7	29.3

structures are favored while various strongly bound anions are formed, as they assure maximizing their electronic stabilities. The exceptional character of the HF/AlF_3 system (among the compounds investigated in this work) due to its very stable anionic (i.e., deprotonated) form is also important for its acidity which we discuss in the following section.

3.2. The acidity of the X/AlF_3 systems

As it was indicated in the preceding section, each X molecule contains at least one hydrogen atom and an electron lone pair which makes it capable of acting as both a proton donor (i.e., Brønsted acid) and an electron lone pair donor (i.e., Lewis base). Even though the acidity and basicity of X systems might be evaluated independently (by calculating the ΔG_{acid}^{298} and ΔG_{base}^{298} value, respectively), it should be stressed that these features of X molecules are coupled with each other when the resulting X/AlF_3 systems are concerned. Namely, the acidity of X (i.e., its ability to donate a proton manifested by the ΔG_{acid}^{298} value predicted for the isolated X) changes when X forms a dative bond by donating its electron lone pair to AlF_3 . The formation of the $X \rightarrow \text{Al}(3p)\text{F}_3$ bond results in the negative charge flow toward the AlF_3 component and its efficiency is related to the basicity of the X component (manifested by the ΔG_{base}^{298} value predicted for the isolated X). The consequence of this change in the electron density distribution (due to the $X \rightarrow \text{AlF}_3$ bond formation) is larger acidity of X/AlF_3 in comparison to X (expressed in terms of Gibbs free deprotonation energies as $\Delta G_{acid}^{298}(X/\text{AlF}_3) < \Delta G_{acid}^{298}(X)$). Hence, the resulting ΔG_{acid}^{298} values predicted for the X/AlF_3 systems should be related to both the acidity and basicity of their corresponding isolated X components.

The acidities of X and X/AlF_3 systems (represented by their ΔG_{acid}^{298} values) are gathered in Table 1 while the differences between $\Delta G_{acid}^{298}(X)$ and $\Delta G_{acid}^{298}(X/\text{AlF}_3)$ for each X are depicted in Fig. 4. As it turns out, the acidity growth upon the formation of the X/AlF_3 complex is large when the species X exhibiting very weak acidity are concerned, i.e., NH_3 , H_2O . In these cases, the acidity increases by 73 and 86 kcal/mol for $\Delta G_{acid}^{298}(\text{NH}_3)$ vs. $\Delta G_{acid}^{298}(\text{NH}_3/\text{AlF}_3)$ and for $\Delta G_{acid}^{298}(\text{H}_2\text{O})$ vs. $\Delta G_{acid}^{298}(\text{H}_2\text{O}/\text{AlF}_3)$, respectively (see the vertical lines in Fig. 4). The analogous acidity growth upon the formation of the X/AlF_3 complex is less profound (yet substantial, as it spans the 53–66 kcal/mol range) for the remaining X systems excluding HF. Not surprisingly, the difference between $\Delta G_{acid}^{298}(X)$ and $\Delta G_{acid}^{298}(X/\text{AlF}_3)$ is the largest for $X = \text{HF}$ and it equals to 97 kcal/mol, see Table 1 and Fig. 4. As we have already explained (see the preceding section), the HF/AlF_3 system differs from the other compounds investigated in this work due to its very stable deprotonated (i.e., anionic) form, namely the $(\text{AlF}_4)^-$ anion, having four equivalent ligands and thus characterized by the most effective excess negative charge delocalization.

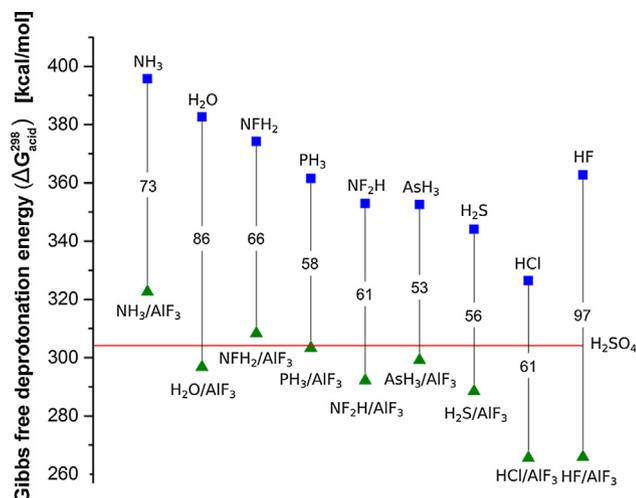


Fig. 4. The Gibbs free deprotonation energies (ΔG_{acid}^{298} in kcal/mol) of the **X** (blue squares) and **X/AlF₃** (green triangles) neutral compounds (**X** = NH₃, H₂O, NFH₂, PH₃, NF₂H, AsH₃, H₂S, HCl, and HF). The differences in ΔG_{acid}^{298} between **X** and the corresponding **X/AlF₃** ($\Delta G_{acid}^{298}(X) - \Delta G_{acid}^{298}(X/AlF_3)$) inserted into the vertical lines are given in kcal/mol. The red horizontal line corresponds to the ΔG_{acid}^{298} of H₂SO₄ = 303 kcal/mol (Gibbs free deprotonation energy for the sulfuric acid) [11,37]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The values of ΔG_{acid}^{298} predicted for various **X/AlF₃** systems indicate that even the molecules which are not commonly recognized as acids (although are potentially capable of donating a proton), i.e., NH₃ and H₂O, should behave as such when combined with the strong Lewis acid (AlF₃). Namely, the resulting acidity of the NH₃/AlF₃ (322.6 kcal/mol) is substantial and much larger than the acidity of pure hydrogen fluoride (whose ΔG_{acid}^{298} is larger by ca. 40 kcal/mol, see Table 1) whereas the acidity of H₂O/AlF₃ (296.8 kcal/mol) exceeds that of 100% sulfuric acid. In general, the ΔG_{acid}^{298} values of most systems studied (HF/AlF₃, HCl/AlF₃, H₂S/AlF₃, AsH₃/AlF₃, PH₃/AlF₃, NF₂H/AlF₃, and H₂O/AlF₃) are smaller than 303 kcal/mol (ΔG_{acid}^{298} of H₂SO₄ [11,37]) and hence these compounds might be classified as superacids, whereas the ΔG_{acid}^{298} 's of two remaining NFH₂/AlF₃ and NH₃/AlF₃ systems are small enough to treat these compounds as relatively strong acids.

Since we expected that the ability of the **X** system to donate its electron lone pair to AlF₃ should be related to the intrinsic basicity of **X** ($\Delta G_{base}^{298}(X)$), we estimated the ΔG_{base}^{298} values of all **X** molecules considered and compared them to the corresponding $\Delta G_{acid}^{298}(X/AlF_3)$ values, see Table 1 and Fig. 5. Indeed, the data points plotted in Fig. 5 reveal a satisfactory correlation between these quantities. Namely, nearly linear dependence of $\Delta G_{acid}^{298}(X/AlF_3)$ on $\Delta G_{base}^{298}(X)$ can be noticed, as the correlation coefficient of 0.95707 was found during the linear regression procedure employed. Hence, the analysis of the results presented in Fig. 5 indicates that the **X** compounds characterized by small ΔG_{base}^{298} values are expected to form strong acids when combined with AlF₃.

Finally, we would like to point out that all systems investigated in this contribution (i.e., HF/AlF₃, HCl/AlF₃, H₂S/AlF₃, AsH₃/AlF₃, PH₃/AlF₃, NF₂H/AlF₃, NFH₂/AlF₃, NH₃/AlF₃, and H₂O/AlF₃) and designed by combining the neutral closed-shell **X** molecule (containing at least one H atom and capable of donating an electron lone pair) with the strong Lewis acid (AlF₃) represent the datively bound **X** → Al(3p)F₃ compounds exhibiting substantial acid strength. Hence, the molecules whose acidity in isolated form is not substantial (e.g., H₂O, H₂S, AsH₃, NF₂H) may still play the Brønsted acid role in binary Lewis-Brønsted superacids.

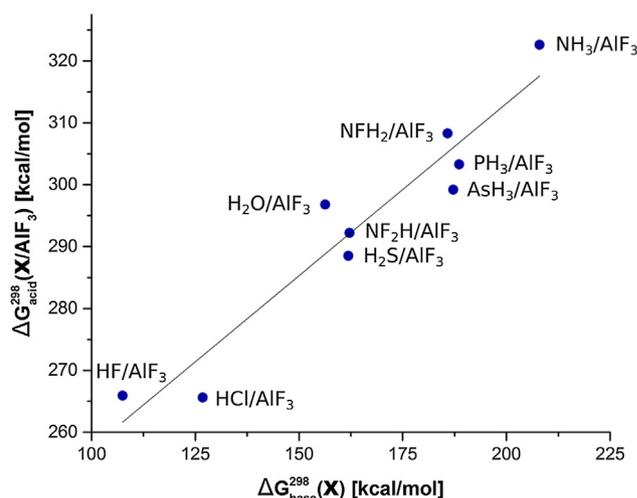


Fig. 5. The dependence of the Gibbs free deprotonation energy of the **X/AlF₃** compound ($\Delta G_{acid}^{298}(X/AlF_3)$) on the intrinsic basicity of **X** ($\Delta G_{base}^{298}(X)$). The correlation coefficient corresponding to the linear regression approximation applied (see the solid line) was calculated to be 0.95707.

4. Conclusions

On the basis of our quantum chemical calculations performed with the QCISD method and the aug-cc-pVDZ (for H, F, Cl, N, P, As, O, and S) and aug-cc-pV(D+d)Z (for Al) basis sets for the **X/AlF₃** (**X** = HF, HCl, H₂S, AsH₃, PH₃, NF₂H, NFH₂, NH₃, and H₂O) and their corresponding anions (i.e., negatively charged systems formed by deprotonation of the **X/AlF₃** systems) we formulated the following conclusions:

- The minimum energy **X/AlF₃** structures correspond to the datively bound **X** → AlF₃ complexes additionally stabilized by the hydrogen bonds whereas their deprotonated forms are stable negatively charged systems adopting quasi-tetrahedral arrangement of four ligands around the Al atom.
- The acid strength of **X** molecules is significantly enhanced upon the formation of the **X/AlF₃** compounds which is manifested by the decrease of the Gibbs free deprotonation energy ($\Delta G_{acid}^{298}(X/AlF_3) < \Delta G_{acid}^{298}(X)$).
- The acidity increase caused by the formation of the **X/AlF₃** compounds is large enough to turn even the non-acidic molecules **X** (such as H₂O or NH₃) into very strong acids **X/AlF₃** characterized by the acid strength comparable or larger than that of 100% H₂SO₄.
- The acidity of the **X/AlF₃** compounds studied (most of which correspond to the binary Lewis-Brønsted superacids) manifested by their Gibbs free deprotonation energy ($\Delta G_{acid}^{298}(X/AlF_3)$) is related to both the acidity of **X** (given by the Gibbs free deprotonation energy of **X** ($\Delta G_{acid}^{298}(X)$)) and the intrinsic basicity of **X** (given by $\Delta G_{base}^{298}(X)$).

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References

- [1] N.F. Hall, J.B. Conant, *J. Am. Chem. Soc.* 49 (1927) 3047.
- [2] R.J. Gillespie, T.E. Peel, *Adv. Phys. Org. Chem.* 9 (1971) 1.
- [3] R.J. Gillespie, T.E. Peel, *J. Am. Chem. Soc.* 95 (1973) 5173.
- [4] G.A. Olah, J. Lukas, *J. Am. Chem. Soc.* 89 (1967) 2227.
- [5] A.F. Bickel, C.J. Gaasbeek, H. Hogeveen, J.M. Oelderik, J.C. Platteeuw, *J. Chem. Soc. Chem. Commun.* 13 (1967) 634.
- [6] H. Hogeveen, A.F. Bickel, *J. Chem. Soc. Chem. Commun.* 13 (1967) 635.
- [7] G.A. Olah, R.H. Schlosberg, *J. Am. Chem. Soc.* 90 (1968) 2726.
- [8] H. Hogeveen, A.F. Bickel, *Recl. Trav. Chim. Pays-Bas* 88 (1969) 371.
- [9] G.A. Olah, Y. Halpern, J. Shen, Y.K. Mo, *J. Am. Chem. Soc.* 93 (1971) 1251.
- [10] A.H. Otto, T. Steiger, S. Schrader, *Chem. Commun.* 3 (1998) 391.
- [11] I.A. Koppel, P. Burk, I. Koppel, I. Leito, T. Sonoda, M. Mishima, *J. Am. Chem. Soc.* 122 (2000) 5114.
- [12] K.E. Gutowski, D.A. Dixon, *J. Phys. Chem. A* 110 (2006) 12044.
- [13] A.K. Srivastava, N. Misra, *Polyhedron* 102 (2015) 711.
- [14] S. Senger, L. Radom, *J. Phys. Chem. A* 104 (2000) 7375.
- [15] G. Zhong, B. Chan, L. Radom, *Org. Lett.* 11 (2009) 749.
- [16] J. Axhausen, C. Ritter, K. Lux, A. Kornath, *Z. Anorg. Allg. Chem.* 639 (2013) 65.
- [17] C. Bour, R. Guillot, V. Gandon, *Chem. Eur. J.* 21 (2015) 6066.
- [18] G.A. Olah, G.K. Prakash, J. Sommer, *Science* 206 (1979) 13.
- [19] D. Touiti, R. Jost, J. Sommer, *J. Chem. Soc. Perkin Trans. 2* (1986) 1793.
- [20] R. Jost, J. Sommer, *Rev. Chem. Intermed.* 9 (1988) 171.
- [21] J. Axhausen, K. Lux, A. Kornath, *Angew. Chem. Int. Ed.* 53 (2014) 3720.
- [22] M. Nava, I.V. Stoyanova, S. Cummings, E.S. Stoyanov, C.A. Reed, *Angew. Chem. Int. Ed.* 53 (2014) 1131.
- [23] S. Cummings, H.P. Hratchian, C.A. Reed, *Angew. Chem. Int. Ed.* 55 (2016) 1382.
- [24] M. Czapla, P. Skurski, *Chem. Phys. Lett.* 630 (2015) 1.
- [25] M. Czapla, P. Skurski, *J. Phys. Chem. A* 119 (2015) 12868.
- [26] I. Anusiewicz, S. Freza, P. Skurski, *Polyhedron* 144 (2018) 125.
- [27] G.L. Gutsev, A.I. Boldyrev, *Chem. Phys.* 56 (1981) 277.
- [28] X.B. Wang, C.F. Ding, L.S. Wang, A.I. Boldyrev, J. Simons, *J. Chem. Phys.* 110 (1999) 4763.
- [29] C. Sikorska, P. Skurski, *Inorg. Chem.* 50 (2011) 6384.
- [30] M. Czapla, I. Anusiewicz, P. Skurski, *Chem. Phys.* 465–466 (2016) 46.
- [31] M. Czapla, P. Skurski, *Int. J. Quant. Chem.* 118 (2018) e25494.
- [32] M. Czapla, I. Anusiewicz, P. Skurski, *RSC Adv.* 6 (2016) 29314.
- [33] J. Brzeski, I. Anusiewicz, P. Skurski, *Theor. Chem. Acc.* 137 (2018) 57.
- [34] O. Rybacka, M. Czapla, P. Skurski, *Phys. Chem. Chem. Phys.* 19 (2017) 18047.
- [35] O. Rybacka, M. Czapla, P. Skurski, *Theor. Chem. Acc.* 136 (2017) 140.
- [36] M. Czapla, P. Skurski, *Phys. Chem. Chem. Phys.* 17 (2015) 19194.
- [37] A.A. Viggiano, M.J. Henchman, F. Dale, C.A. Deakne, J.F. Paulson, *J. Am. Chem. Soc.* 114 (1992) 4299.
- [38] J.A. Pople, M. Head-Gordon, K. Raghavachari, *J. Chem. Phys.* 87 (1987) 5968.
- [39] J. Gauss, D. Cremer, *Chem. Phys. Lett.* 150 (1988) 280.
- [40] E.A. Salter, G.W. Trucks, R.J. Bartlett, *J. Chem. Phys.* 90 (1989) 1752.
- [41] R.A. Kendall, T.H. Dunning Jr, R.J. Harrison, *J. Chem. Phys.* 96 (1992) 6796.
- [42] T.H. Dunning Jr, K.A. Peterson, A.K. Wilson, *J. Chem. Phys.* 114 (2001) 9244.
- [43] J.P. Foster, F. Weinhold, *J. Am. Chem. Soc.* 102 (1980) 7211.
- [44] A.E. Reed, F. Weinhold, *J. Chem. Phys.* 78 (1983) 4066.
- [45] A.E. Reed, R.B. Weinstock, F. Weinhold, *J. Chem. Phys.* 83 (1985) 735.
- [46] Gaussian 16, Revision B.01, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A.V. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V. Ortiz, A.F. Izmaylov, J.L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V.G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M.J. Bearpark, J.J. Heyd, E.N. Brothers, K.N. Kudin, V.N. Staroverov, T.A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A.P. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, J.M. Millam, M. Klene, C. Adamo, R. Cammi, J.W. Ochterski, R.L. Martin, K. Morokuma, O. Farkas, J.B. Foresman, D.J. Fox, Gaussian, Inc., Wallingford CT, 2016.
- [47] C. Sikorska, S. Smuczyńska, P. Skurski, I. Anusiewicz, *Inorg. Chem.* 47 (2008) 7348.
- [48] C. Sikorska, P. Skurski, *Chem. Phys. Lett.* 536 (2012) 34.
- [49] D. Wileńska, P. Skurski, I. Anusiewicz, *J. Fluorine Chem.* 168 (2014) 99.
- [50] S. Smuczyńska, P. Skurski, *Chem. Phys. Lett.* 452 (2008) 44.