

**Summary of the PhD thesis of Marcin Czaplak entitled:
"Evaluation of the acid strength and stability of selected Lewis-Brønsted superacids by
using theoretical methods"**

Superacids have been thoroughly investigated since 1927, however, they were properly defined in the second half of 20th century as chemical compounds stronger than 100% sulfuric acid (H₂SO₄). Due to their unusual properties, the superacids are capable of protonating even very weak bases such as carbonyl compounds and hydrocarbons. Thus, these compounds are mainly useful in organic chemistry in which they play the catalyst role. The most frequently used in scientific laboratories superacid is the fluoroantimonic acid (HF/SbF₅ or HSbF₆ in a different notation) belonging to the mixed Lewis-Brønsted superacids. The HSbF₆ is also commonly considered as the strongest liquid superacid known, however, some theoretical investigations concerning the gas phase properties of superacids showed that even stronger acids might likely exist. Hence, it seems justified to undertake the search for novel superacidic systems that could be characterized by the higher acidity than the substances recognized thus far.

The classical preparation method that is being employed to obtain the mixed superacids mentioned above consists of combining together the strong Lewis acid (e.g., SbF₅, AsF₅, BCl₃) and Brønsted acid (e.g., HF, HCl), however, the Lewis-Brønsted superacids can also be considered as superhalogen anions (such as (SbF₆)⁻, (AsF₆)⁻, and (BCl₄)⁻) neutralized by the additional proton. Therefore, it can be assumed that the search for novel Lewis-Brønsted superacids should be conducted by considering the well-known superhalogen systems that represent their natural precursors. The connection between superacids and superhalogens may also be used to develop alternative methods of superacid synthesis, which in turn could render the preparation of such compounds possible (with respect to those systems that cannot be synthesized using classical techniques, e.g., superacids containing gold atoms).

Superhalogens (recognized as the natural Lewis-Brønsted superacids precursors) represent the group of chemical compounds described by the general MX_{k+1} formula (where M means a central atom, X is the halogen atom, while k stands for the maximal formal valence of M). Superhalogens are characterized by the enormous values of electron affinity (EA) which are usually significantly higher than 3.62 eV (EA of the chlorine atom). Thus, superhalogens form very strongly valence-bound $(MX_{k+1})^-$ superhalogen anions whose vertical electron

detachment energies may approach 14 eV in certain cases. Due to their properties, superhalogens are used, among other applications, as negatively charged components in ionic liquids or lithium-ion batteries. On the other hand, the neutral superhalogen systems can also be utilized as effective oxidizers with respect to the compounds characterized by very high ionization potential values (such as water, benzene, and carbon dioxide).

The main goal of this doctoral project was to evaluate the acid strength and stability of selected Lewis-Brønsted superacids. This objective was accomplished by the design and description of superacidic systems characterized by the general formulas: $\text{HAl}_n\text{F}_{3n+1}$ ($n=1-4$), $\text{HIn}_n\text{F}_{3n+1}$, $\text{HSn}_n\text{F}_{4n+1}$, $\text{HSb}_n\text{F}_{5n+1}$, and $\text{HAu}_n\text{F}_{5n+1}$ ($n=1-3$), which were obtained by the protonation of their corresponding superhalogen anions. Additionally, the following issues were verified: (i) the hypothesis concerning the possibility of obtaining superacidic system by using any superhalogen precursor, (ii) the dependence of increasing the number of Brønsted acid molecules surrounding Lewis acid on the acidity of the superacidic system investigated, (iii) the effect of an excess electron attachment to the neutral HAlF_4 superacid. All the studies were performed theoretically, by employing quantum chemistry computational methods (*DFT* and *ab initio*). The acid strength of the systems investigated was determined by evaluating their deprotonation energies (*DE*) and Gibbs free energies of deprotonation (ΔG_{acid}), whereas their geometrical and thermodynamic stability was verified by calculating the elimination energies (*EE*) and Gibbs free elimination energies with respect to the Brønsted acid molecule loss.

The results obtained in my doctoral project unambiguously indicate that Lewis-Brønsted superacids should indeed be treated as the superhalogen anions combined with the additional proton. Therefore, it was confirmed that the investigations of superacids, as well as the alternative methods of their synthesis, can be based on the superhalogen systems described previously. It should also be stressed that all systems investigated (i.e., $\text{HAl}_n\text{F}_{3n+1}$ ($n=1-4$), $\text{HIn}_n\text{F}_{3n+1}$, $\text{HSn}_n\text{F}_{4n+1}$, $\text{HSb}_n\text{F}_{5n+1}$, and $\text{HAu}_n\text{F}_{5n+1}$ ($n=1-3$)) exhibit strong acidic properties. Additionally, it has been proven that the acid strength of the Lewis-Brønsted superacids strongly depends on the vertical electron detachment energies of their corresponding superhalogen anions (the *VDE* energy increase correlates with the increase of superacid strength). By examining a number of other systems containing the elements from 1st, 2nd, 13rd and 14th main groups of the periodic table, it was also shown that the protonation of superhalogen anions does not always lead to strong Lewis-Brønsted superacids. Namely, it was

concluded that, in order to obtain the systems with the superacidic properties, the superhalogen anions characterized by the sufficiently high excess electron binding energy should be used.

Furthermore, the results of my research indicate that the use of excess of Brønsted acid (with respect to the Lewis acid) causes the increase of the resulting system acidity. Thus, the studies, which are aimed to provide the exact evaluation of the acidity of Lewis-Brønsted superacids should take into account the microsolvation effects occurring in superacid solutions (in theoretical studies it means that at least five Brønsted acid molecules surrounding each Lewis acid system should be considered). Additionally, due to their polarity the Lewis-Brønsted superacids are capable of an excess electron binding which results in the formation of electronically stable dipole-bound anionic states. However, these systems are geometrically unstable and undergo spontaneous fragmentation which leads to the formation of very strongly bound superhalogen anion and hydrogen atom. The mentioned susceptibility to the dissociative electron attachment process is probably the distinctive feature of Lewis-Brønsted superacids.