

Investigation of the possibility of interaction between lithium fluoride clusters and boron using LDI MS

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Abstract: It is known that the “superalkali” cluster Li_2F can significantly improve the hydrogen storage capabilities in carbon materials; boron compounds play a similar role. However, the possibility of interactions of lithium fluoride clusters with boron and hydrogen has not been investigated so far. In this work, a laser desorption/ionization mass spectrometry (LDI MS) was used for this purpose. Preliminary results showed that the interaction between the “superalkali” Li_3F cluster, boron and six hydrogen atoms is possible; the ion $\text{Li}_3\text{FBH}_6^+$ was detected. Non-stoichiometric clusters of lithium fluoride can also combine with boron and hydrogen in the following manner: $\text{Li}_5\text{F}_2\text{BH}_5^+$, $\text{Li}_5\text{F}_3\text{BH}_2^+$, $\text{Li}_4\text{F}_5\text{BH}_4^+$, $\text{Li}_6\text{F}_2\text{B}_6\text{H}^+$, and $\text{Li}_8\text{F}_6\text{H}^+$.

Keywords: “superalkali” clusters, LDI MS, hydrogen storage, boron

1. Introduction

The search for alternative energy sources that do not have a negative impact on environmental pollution is one of the most important issues for humanity today. Hydrogen is recognized as a new economic energy model [1-4]. However, there are many problems that must be overcome to make hydrogen available as a fuel (hydrogen extraction, hydrogen is a highly flammable fuel source, high cost of a unit of hydrogen fuel cell power, regulatory issues related to the framework that defines commercial deployment models, cost of feedstock, new infrastructure). In the area of basic research, hydrogen storage should be first.

Theoretical and experimental studies have shown that various materials can be used as hydrogen storage, such as nanostructured carbon clusters, boron-based materials,

hydrides and liquid organic carriers, zeolites, clathrates, and others [5-10]. Previous studies have also shown that metal-decorated carbon fullerenes and their boron-substituted nanostructures could be good candidates for the storage of H₂ molecules. For example, it has been discovered that lithium-doped fullerenes, Li_x-C₆₀, with x= 6, 9, 12 efficiently reversibly adsorb H₂. It was also shown that the reversible hydrogen storage of C₆₀ and C₄₈B₁₂ coated with transition metals can be as high as 9 wt%. Additions to the fullerene play a crucial role in the interaction with H₂. The electrostatic interaction between Li (with low ionization energy of 5.39 eV) and H₂ is believed to play an important role in this process [11-13]. Compounds that have lower ionization energy than lithium are "superalkali" clusters of the Li_nF_m type. "Superalkali" clusters are successfully obtained by evaporation of LiF salt in mass spectrometers of various types. Thanks to their low ionization energy, the electrostatic interaction between "superalkali" clusters and hydrogen is expected to be stronger than that of alkali metals [14]. In accordance with that theoretical studies have shown that fullerene doped with Li₂F-type "superalkali" clusters (10.86 wt%) is more efficient than Li_x-C₆₀ in hydrogen storage [15]. On the other hand, lithium-decorated diborene and diboryne clusters can trap H₂ molecules by ion-quadrupole and ion-induced dipole interactions, making these systems well suited for hydrogen storage [16]. However, the interaction between "superalkali" clusters, B and hydrogen has not yet been studied. Therefore, in this work we have investigated the LiF/B system using the LDI MS.

2. Experimental

Results were obtained using a commercially available matrix-assisted laser desorption/ionization mass spectrometer (MALDI MS), Voyager- DE PRO (Sciex, USA) equipped with a time-of-flight (TOF) mass analyzer and operating in linear or reflector mode as standard. A nitrogen laser (with 20 Hz pulse frequency, a wavelength of 337 nm, and pulse duration of 3 ns) was installed in this mass spectrometer. Other instrumental parameters were: Accelerating voltage 25000 V, grid voltage 85%, laser intensity 3300 a.u. and number of laser beats 200, with a delayed extraction time of 100 ns. Mass spectra were recorded in positive reflectron mode.

The sample was a suspension of LiF:B (1:5 ratio) in 50 µl of deionized water; 1 µl of the sample was applied directly to a stainless steel plate and dried at room temperature before being introduced to the mass spectrometer. No additional hydrogen source was used in these experimental conditions.

3. Results and discussion

The LDI mass spectrum of LiF/B in positive mode is shown in Figure 1. The identification of the peaks recorded in Figure 1 was done in the following way: *m/z* 55.17, 56.17, 57.17 correspond to Li₃FBH₆⁺ (calculated 55.10, 56.11, 57.10); *m/z* 87.15 88.17, 89.17 correspond to Li₅F₂BH₅⁺ (calculated 87.13, 88.12, 89.12); *m/z* 103.13, 104.13, 105.13

correspond to $\text{Li}_5\text{F}_3\text{BH}_2^+$ (calculated 103.10, 104.10, 105.10); m/z 136.13, 137.12, 138.12 correspond to $\text{Li}_4\text{F}_5\text{BH}_4^+$ (calculated 136.10, 137.10, 138.10), m/z 144.17, 145.17, 146.17, 147.17, correspond to $\text{Li}_6\text{F}_2\text{B}_6\text{H}^+$ (calculated 144.16, 145.16, 146.16, 147.16); m/z 169.22, 170.18, 171.18 correspond to $\text{Li}_8\text{F}_6\text{H}^+$ (calculated 169.13, 170.13, 171.13).

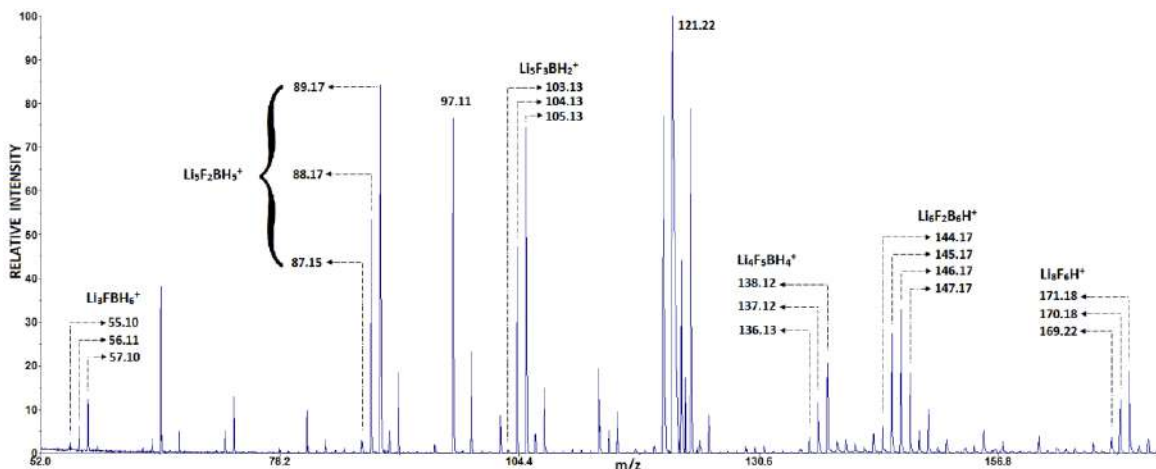


Figure 1. The positive mod LDI mass spectrum of LiF/B.

Preliminary results show that an interaction can occur between the “superalkali” Li_3F cluster and a boron atom and 6 hydrogen atoms. Other lithium fluoride clusters such as Li_5F_2 , Li_5F_3 , and Li_4F_5 also interact with a boron atom and a different number of hydrogen atoms. The Li_6F_2 cluster interacts with 6 boron atoms, while the Li_8F_6 cluster interacts directly with one hydrogen atom.

4. Conclusions

The LDI MS was used to investigate possibilities interaction between clusters lithium fluoride with boron and hydrogen. In this work clusters are detected: $\text{Li}_3\text{FBH}_6^+$, $\text{Li}_5\text{F}_2\text{BH}_3^+$, $\text{Li}_5\text{F}_3\text{BH}_2^+$, $\text{Li}_4\text{F}_5\text{BH}_4^+$, $\text{Li}_6\text{F}_2\text{B}_6\text{H}^+$, and $\text{Li}_8\text{F}_6\text{H}^+$. The results show that “superalkali” clusters Li_3F and non-stoichiometric lithium fluoride clusters can interact with boron and hydrogen atoms.

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