

## PRODUCTION OF HETEROGENEOUS SUPERALKALI CLUSTERS $\text{Li}_n\text{F}$ ( $n=2-6$ ) BY KNUDSEN – CELL MASS SPECTROMETRY

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The superalkali clusters are important because they can be considered as potential building block for the assembly of novel nanostructured materials with unique structural, electronic, optical, magnetic, and thermodynamic properties. We have modified and used the Knudsen cell mass spectrometer in order to obtain and measurement of the ionization potentials of the superalkali clusters. In this work the clusters  $\text{Li}_n\text{F}$  ( $n = 2 - 6$ ) have produces in the vapor over a mixture of lithium fluoride and lithium iodide by means of Knudsen cell which is placed into ionization chamber of the magnetic sector mass spectrometer. The simultaneous production and mass spectrometric detection of the ionic of clusters provide information on the conditions of formation and the distribution of these ion species. It is observed that the ions of clusters with an even numbered of lithium atoms are more stable than the ions of clusters with an odd numbered of lithium atoms. The clusters  $\text{Li}_5\text{F}$  and  $\text{Li}_6\text{F}$  were detected experimentally for the first time with their ionization energies of  $(4.29 \pm 0.25)$  eV, and  $(4.24 \pm 0.25)$  eV, respectively.

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### 1. Introduction

The field of cluster physics has gained immense importance due to the potential of designing nanomaterials with predecided characteristics. Khanna et al. have revealed that atomic clusters with suitable size and composition could be designed to mimic the chemistry of atoms in the Periodic Table and that such clusters could be described as superatoms. The superatom clusters represent potential building blocks for the new cluster assebled materials, whose desired properties may be tailored through selection of size and composition. Researches on superatoms thus promote the development of nanoscale and supramolecular chemistry, and materials science [1-15].

The superatom compounds are formed by combining superalkalies within superhalogens. The first theoretical evidence of existence of superalkalies presented by Boldirev et al. Superalkalies characterized by lower ionization potentials (IPs) than the ionization potentials of alkali – metal atoms (5.39 – 3.89 eV) [16-18]. The first experimentally confirmation of this kind of clusters is the  $\text{Li}_3\text{O}$  cluster, which was discovered by Wu et al. [19].

Generally, lithium and lithium-based clusters continue to attract attention because of their interesting physical and chemical properties. Lithium is the simplest metal, with three electrons and their clusters are considered as models for other metallic clusters. A large number of studies on the stabilities, bonding nature, spectroscopic parameters, and ionization potential and electron affinities of the bare lithium clusters have been reported using various experimental and theoretical methods. The  $\text{Li}_n$ , (where  $n=2-6$ ) clusters belongs to the group of the superalkali [20-28]. The addition of an impurity to the bare lithium clusters can initiate fundamental changes in their geometries, energy properties, and bonding nature, leading to new materials. The interaction of

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atom with lithium metal clusters is a subject of interest for applications in field corrosion of metals and nuclear reactor and hot fusion technologies.

The very small heterogeneous clusters of the type  $\text{Li}_n\text{F}$  ( $n = 2-6$ ) have nine or more valence electrons and they are of particular importance because they have exhibited a unique behavior, such as nonmetallic character, or increased stability and extreme in other parameters such as ionization potentials, electron affinities, etc. These clusters with “excess” valence electrons violate the octet rule, at least formally, and can be regarded as hypervalent molecules or clusters [29]. Hypervalent species are possible intermediates in metal cluster and metal surface reactions which can affect the catalytic and electronic properties of a metal; they also reveal fundamental information about the relationship between hypervalency and stability [30].

In a class of fluorine – doped lithium clusters of  $\text{Li}_n\text{F}$  ( $n > 1$ ) type, the smallest clusters  $\text{Li}_2\text{F}$  was extensively studied either theoretically [17, 18, 29, 31-35] and experimentally [30, 36 - 45]. The theoretical calculations by Schleyer et al. have shown that the clusters with “excess” electron are thermodynamically more stable than octet molecules with eight valence electrons like  $\text{Li}_2\text{O}$ ,  $\text{Li}_2\text{S}$  and  $\text{Li}_4\text{C}$ . They consider that  $\text{Li}_2\text{F}$  cluster is not stable toward angular deformation to give shorter Li- Li distances and better lithium atomic orbital (AO) overlap. The “excess” electron delocalizes over the all lithium atoms forming a lithium “cage” or network of positive charge ( $\text{Li}_2^+$ ). On the other hand the F atoms possess nearly maximum anionic charges ( $\text{F}^-$ ). The stability of the neutral clusters of the type  $\text{Li}_2\text{F}$  is due both to the attractive electrostatic interactions between  $\text{Li}_2^+$  cations and the  $\text{F}^-$  and the covalent interactions between the lithium atoms in the “cage”. The  $\text{Li}_2\text{F}^+$  cation is linear ( $D_{\infty h}$  symmetry). The stability of the  $\text{Li}_2\text{F}^+$  is due to the electrostatic attraction of the  $\text{Li}^+$  cations to the negative charged F atom. The Li - F bonds in all these cations are essentially fully ionic [17, 29].

The latest investigation indicates that the hypervalent clusters represent a new kind of compound with potential the nonlinear optical properties due to their nature of the chemical bonding. [46].

Furthermore, Hebant and Picard have theoretical predicted the structures and thermodynamic stability of the clusters such as  $\text{M}_2\text{X}$ , where M is Li, Na, K or Rb, and X is F, Cl, Br or I. They named these clusters subhalides. Also, they have revealed that the solubility of the metal in their halides can be explained in some cases by the formation of the subhalides. Generally, reactivity of metals with their halides is a crucial point in many industrial processes such as electrowinning or electrorefining and extraction systems [32, 47, 48].

Honea et al. have proposed the classification of clusters with “excess” valent electrons, using information obtained from the measured ionization potentials, abundance mass spectra and from theoretical studies of structural and other properties. According to classifications, clusters  $\text{Li}_2\text{F}$  belong to the class of the type F-centers clusters. The F-centers have high abundances, high electron binding energies, and optical absorption bands characteristic of a nearly filled cubic lattice with an electron localized in an anion vacancy, for which ionization energies are around 4 eV [33, 34].

There are only few theoretical reports about  $\text{Li}_n\text{F}$  clusters, where  $n > 2$ . Allen’s group was the first theoretical predicted existence of  $\text{Li}_3\text{F}$  molecule with ten valence electrons [50]. Schleyer et al. were the theoretical predicted hypervalent structure both  $\text{Li}_3\text{F}$  and  $\text{Li}_4\text{F}$  clusters [29].

Ivanic et al. provide a slightly different explanation of the chemical bonding of the type  $\text{Li}_n\text{F}$ . Their theoretical calculations have shown that the  $\text{Li}_3\text{F}$  (10 valence electrons) and  $\text{Li}_5\text{F}$  (12 valence electrons) contains small clusters of Li atoms, such as  $\text{Li}_3$  or  $\text{Li}_5$ , which encapsulate halogen element. The  $\text{Li}_3\text{F}$  and  $\text{Li}_5\text{F}$  species contains extensively delocalized Li-Li bonding and there is a considerable ionic component to the F-Li. Unlike Schleyer’s group, Ivanic and colleagues believe that the Li atom (or atoms in the case of  $\text{Li}_5$  groups) which is farthest from the electronegative F carries a substantial negative charge, while the “inner” Li atoms have the positive net charges. The negative charges on these outer Li atoms are unusual in the clusters of the type  $\text{Li}_n\text{F}$ . The negative charges of Li atoms are possible in the cases where Li is bonded to other alkali metals [50].

Recent research has shown that the alkalide anions  $\text{Li}_2\text{F}^-$  and  $\text{Li}_6\text{F}^-$  with “excess” electrons can be used as building units to design new materials which have large first hyperpolarizabilities [51].

To date, the fluorine – doped lithium clusters mainly were examined via mass spectroscopy and ionization potential measurements. Studies of clusters by mass spectrometry represent a bridge between gas - phase chemistry and solid – state chemistry. The mass spectrometry plays an important role in the production the superalkali clusters, since the theoretical calculations indicate that their ions were thermodynamically stable with respect to the loss of lithium atoms, in the gas phase. Many mass spectrometric techniques have employed to detection of cluster ion  $\text{Li}_2\text{F}^+$ : Knudsen effusion cell [36, 37, 45], electron impact ionization [38], laser ablation [39], field desorption [40], spark source [41], secondary ion desorption [42], plasma desorption [43, 44], neutralization-reionization [30]. In our previous papers we have obtained  $\text{Li}_n\text{F}$  ( $n= 2-4$ ) clusters using the triple filament thermal ionization source for a mass spectrometry [52]. So far, no experimental data on  $\text{Li}_5\text{F}$  and  $\text{Li}_6\text{F}$  clusters.

The ionization potential is one of the fundamental properties of clusters which yield specific information on their size – dependent stability. The ionization potential is also an important thermochemical value for understanding the nature of bonding. However, experimental work concerning the ionization potentials of the  $\text{Li}_n\text{F}$  (where  $n \geq 2$ ) has been limited. The ionization potential (IP) of 3.78 eV for  $\text{Li}_2\text{F}$  was obtained by photoionization mass spectrometry [53]. In previous papers we have presented experimental and theoretical results of structure and the ionization potential of  $\text{Li}_n\text{F}$  ( $n= 2-4$ ) clusters. The ionization potentials determined by the thermal ionization mass spectrometry (TIMS) were  $3.8 \pm 0.2$  eV for  $\text{Li}_2\text{F}$ ,  $4.0 \pm 0.2$  eV for  $\text{Li}_3\text{F}$  and  $3.9 \pm 0.2$  eV for  $\text{Li}_4\text{F}$  [38, 52, 54, 55].

This paper is a continuation of our experimental studies of halogen – doped lithium clusters [56]. In this work we have focused attention on the investigation of the experimental setup for the applicability of Knudsen cell as a chemical reactor for generation of the superalkali  $\text{Li}_n\text{F}$  ( $n= 2 - 6$ ) clusters. We have also examined the conditions for determining of the ionization potential of these clusters in order to the influence of fluorine like impurity doping on the ionization potentials of the bare lithium clusters.

## 2. Experimental

The Knudsen-cell mass spectrometry (KCMS) is a powerful tool for generated new clusters and studying their stability. We used the Knudsen cell mass spectrometer in a nontraditional way for production and measurment of the ionization potentials of the fluorine – doped lithium clusters. The standard experimental setup of the KCMS implies that the cell is placed outside of ionization chamber. In this work the Knudsen cell was placed into ionization chamber of the mass spectrometere in order to obtain a better yield of the fluorine – doped lithium the cluster. The scheme for the ion source is presented in Fig. 1.

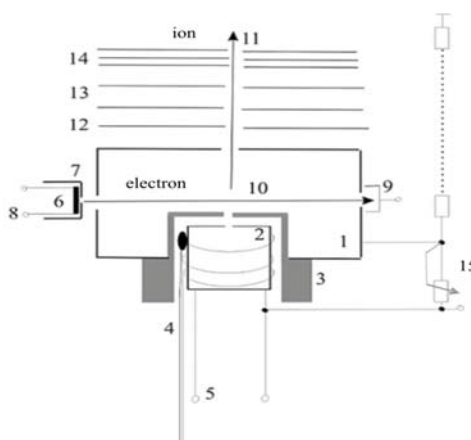


Figure 1. Schematic diagram of the ion source: 1. ionization chamber; 2. Knudsen cell; 3. ceramic shields; 4. thermocouple; 5. heater for chamber; 6. incandescent rhenium cathode; 7. Vehnelt cylinder; 8. heater for cathode; 9. electron trap; 10. electron beam; 11. ion beam; 12. Focusing electrode; 13. accelerating electrode; 14. deflectors electrode; 15. potential repeller.

The modified KCMS presented in Figure 1 allows detect both the ionic and neutral components. Neutral species were detected in the conventional way through electron impact ionization (EI mod). Electrons were obtained from a rhenium cathode inside a Vehnelt cylinder and extracted by a plate at a positive potential (+15V with respect to the cathode) positioned 2 mm away from cathode. The clusters, electron and ion beams were mutually perpendicular. In this case, the Knudsen cell held at equal voltage like the ionization chamber. In the case if the Knudsen cell is held at + 30V voltage with respect to the ionization chamber, the experimental setup permits direct identification of positive charge ionic components generated in the cell, thermal ionization mode (TI mode).

In this work we have used only TI mod for detection ion of clusters. The mass analyzer used in this research was a 12-inch radius, 90° magnetic sector instruments. Identification of the ions was achieved from their mass-to-charge ratios, ionization potential and isotopic abundance.

The height of the tungsten Knudsen cell was 7 mm, the outside diameter was 6mm and the orifice diameter was 0.1 mm. The Knudsen cell was heated with direct current through a tungsten wire. The heater was surrounded by one shields of ceramic material. The temperature measured by a Pt-Pt/Rh thermo-couple attached to the cell. A cell temperature stability of ±10K was achieved. Typical operating pressures in the ion sources region was  $5 \times 10^{-6}$  Torr.

The sample of the LiI/LiF mixture weighing 0,086g was placed into Knudsen cell at atmospheric pressure. In order to remove adsorbed moisture, the cell with the substance was dehydrated directly in the mass spectrometer at 150°C for several hours. Sample salt LiI was used as an additional source of Li ions, since the dissociation energy of LiI is lower than dissociation energy of LiF, and the vapor pressure of LiI is higher than vapor pressure LiF. Moreover, in the mass specter the peaks of iodine – doped lithium clusters appear at higher masses than the peaks of  $\text{Li}_n\text{F}$  clusters.

In order to determine the ionization potentials of above mention clusters the temperature dependence of the currents ( $I_i^+$ ) of the most abundant isotopes of  $\text{Li}_n\text{F}^+$  ( $n= 2 - 6$ ) were measured (Figure 3). Ion currents of the  $\text{Li}^+$  were measured as a function of temperature of the cell, too. The reference ion used in this work was the  $\text{Li}^+$  ion. To calculate ionization potentials of the clusters produced, we used the method of comparison. By calculating the logarithm of the ratio of  $\text{Li}^+$  to  $\text{Li}_n\text{F}^+$  ion intensities at a series of temperatures, the difference in ionization energies of the two species may be obtained using the Saha-Langmuir equation:

$$I_i^+ = A \exp[(\Phi - IP_i)/kT]$$

where  $I_i^+$  is the ion current ( $i$  are  $\text{Li}^+$  and  $\text{Li}_n\text{F}^+$ );  $A$  is the term containing reflection coefficients and statistical weighting factors (constant with temperature);  $IP$  is the ionization potential of the clusters;  $\Phi$  is the work function of the tungsten cell,  $k$  is Boltzman's constant,  $T$  is the temperature of the cell. The actual value of  $\Phi$  is difficult to determine and this uncertainty was avoided by simultaneous measurement of ion intensities of the species of known ionization energy, Li (5.39 eV), and of the investigated clusters.

### 3. Results and discussion

Experimental conditions for producing of the fluorine – doped lithium clusters were optimized by adjustments of the experimental setup, the composition of the sample and temperatures of the Knudsen cell.

The mass spectrum of the ionic beam  $\text{Li}_n\text{F}$  ( $n=2- 6$ ) clusters after evaporated from the Knudsen cell which was placed into ionization chamber is presented in Fig. 2. These clusters are formed by mixture LiF/LiI. The relative molar ratio of the LiF to the LiI salts was about 7:1 in all series of experiments.

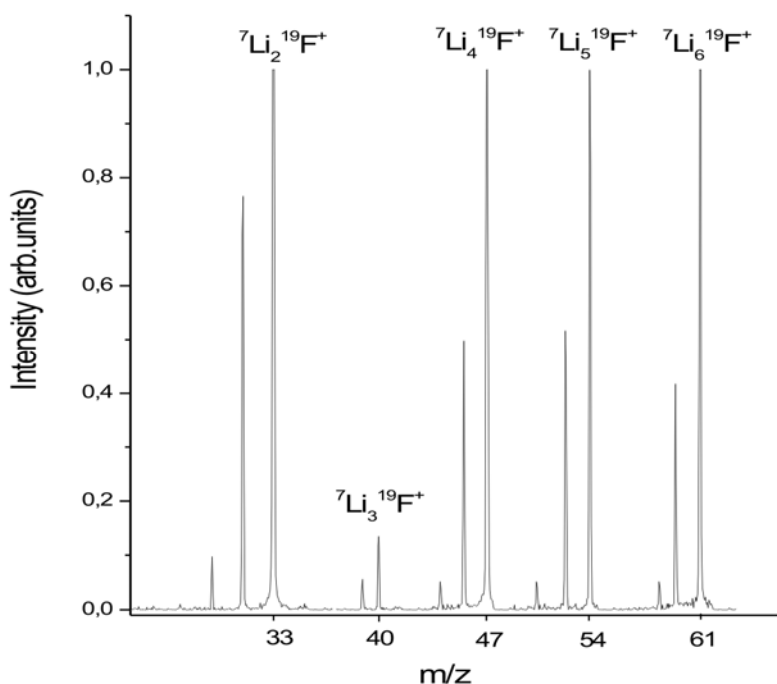


Fig. 2. The mass spectrum of the  $\text{Li}_n\text{F}$  ( $n=2-6$ ) clusters produced by 7:1 mixture of  $\text{LiF}/\text{LiI}$  after evaporated from the Knudsen cell in the thermal ionization mode (TI mode).

The signals for  $\text{Li}_2\text{F}^+$ ,  $\text{Li}_3\text{F}^+$ ,  $\text{Li}_4\text{F}^+$ ,  $\text{Li}_5\text{F}^+$  and  $\text{Li}_6\text{F}^+$  were detected. The mass peaks at  $m/z = 33, 40, 47, 54$  and  $61$  are assigned to  $\text{Li}_n\text{F}^+$  ( $n = 2, 3, 4, 5, 6$ ). Isotopic abundance of the  $\text{Li}_n\text{F}^+$  ( $n=2-6$ ) is in correlation with the isotopic contributions of the lithium and of the fluoride. Assignment of species was based on the pattern coefficients derived from the natural isotopic abundance of lithium (100% of  $^7\text{Li}$  and 8% of  $^6\text{Li}$ ) and of the corresponding halogen element (100% of  $^{19}\text{F}$ ). The signals at  $m/z = 51, 52, 53$  and  $54$  correspond to different isotopic combinations in  $\text{Li}_5\text{F}$ ;  $m/z=51$  (0.5% of  $^6\text{Li}_3\ ^7\text{Li}_2\ ^{19}\text{F}$ ),  $m/z=52$  (6.4% of  $^6\text{Li}_2\ ^7\text{Li}_3\ ^{19}\text{F}$ ),  $m/z=53$  (40.1% of  $^6\text{Li}_1\ ^7\text{Li}_4\ ^{19}\text{F}$ ),  $m/z=54$  (100% of  $^7\text{Li}_5\ ^{19}\text{F}$ ). The mass peaks at  $m/z 58, 59, 60$  and  $61$  seen in the mass spectrum indicated the presence of the  $\text{Li}_6\text{F}$  cluster with natural isotopic abundance;  $m/z=57$  (0.1% of  $^6\text{Li}_4\ ^7\text{Li}_2\ ^{19}\text{F}$ ),  $m/z=58$  (1% of  $^6\text{Li}_3\ ^7\text{Li}_3\ ^{19}\text{F}$ ),  $m/z=59$  (9.6% of  $^6\text{Li}_2\ ^7\text{Li}_4\ ^{19}\text{F}$ ),  $m/z=60$  (48.1% of  $^6\text{Li}_1\ ^7\text{Li}_5\ ^{19}\text{F}$ ),  $m/z=61$  (100% of  $^7\text{Li}_6\ ^{19}\text{F}$ ).

Earlier, the vaporization of lithium fluoride and the mixture  $\text{LiF}-\text{BeF}_2$  was studied using the standard KCMS, as the ion species,  $\text{Li}^+$ ,  $\text{LiF}^+$ ,  $\text{Li}_2\text{F}^+$  and  $\text{Li}_3\text{F}_2^+$  were identified [36, 37, 45]. The our experiment showed that the experimental setup where the Knudsen cell is placed into the ionization chamber of the mass spectrometer (Figure 1), permits obtaining positive ions of the  $\text{Li}_n\text{F}$  ( $n=2-6$ ) clusters. The  $\text{Li}_5\text{F}$  and  $\text{Li}_6\text{F}$  were detected for the first time. Additionally, the advantage the experimental setup presented in Figure 1 is that the ions  $\text{Li}_n\text{F}$  ( $n=2-6$ ) are produced simultaneously in one set of measurements to allows monitoring the stability of these ions. It was observed that the  $\text{Li}_2\text{F}^+$  peak had the most intensity. The peaks of  $\text{Li}_3\text{F}^+$  had the lowest intensities. The peaks corresponding to  $\text{Li}_6\text{F}^+$  and  $\text{Li}_4\text{F}^+$  are only slightly higher than intensity peaks of  $\text{Li}_5\text{F}^+$ . Also, we noticed that the above mention clusters have detected in temperature range 850–1080K. Based on these results, it can be concluded that the experimental setup presented in this paper provide an efficient way to obtaining the small fluorine – doped lithium clusters.

The ionization potentials of these clusters were determined from the slopes of the plots  $\ln$  (ion current of clusters) versus  $1/T$  and compared to the known ionization potential of reference ion.

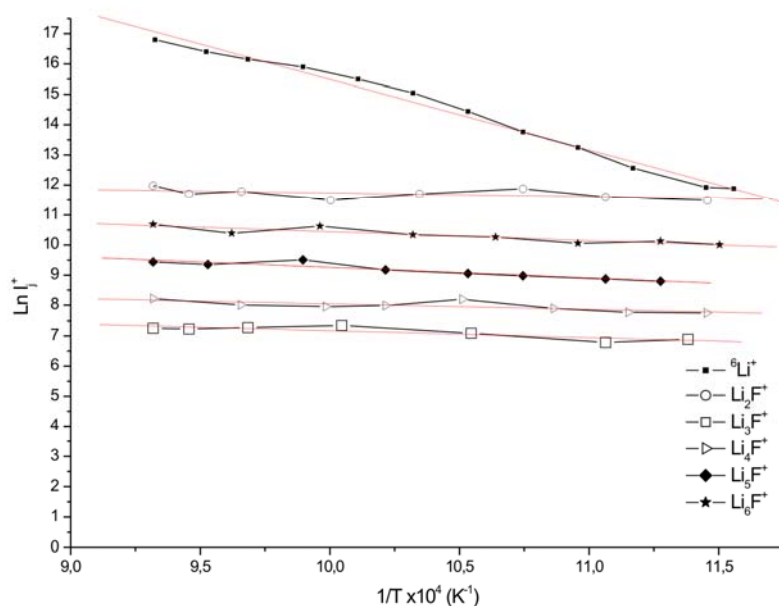


Fig 3. Plots of  $\ln$  (ion current of clusters) versus  $1/T$  for  $\text{Li}_n\text{F}$  ( $n=5, 6$ ) clusters.

The values of the ionization potentials of  $\text{Li}_n\text{F}$ , ( $n=2-6$ ) clusters obtained in the present experiment are summarized in Table 1 together with the IPs of  $\text{Li}_n$ , and  $\text{Li}_n\text{H}$  ( $n=2-6$ ) clusters obtained in the earlier paper.

Table 1. The experimental values of the ionization potentials for  $\text{Li}_n\text{F}$ ,  $\text{Li}_n$ , and  $\text{Li}_n\text{H}$  ( $n=2-6$ ) clusters.

Clusters	Ionization potentials of $\text{Li}_n$ (eV) [57]	Clusters	Ionization potentials of $\text{Li}_n\text{H}$ (eV) [58]	Clusters	Ionization potentials of $\text{Li}_n\text{F}$ (eV) This work
$\text{Li}_2$	$4.86 \pm 0.10$	$\text{Li}_2\text{H}$	$4.10 \pm 0.05$	$\text{Li}_2\text{F}$	$4.06 \pm 0.20$
$\text{Li}_3$	$4.35 \pm 0.10$	$\text{Li}_3\text{H}$	$4.67 \pm 0.06$	$\text{Li}_3\text{F}$	$4.15 \pm 0.20$
$\text{Li}_4$	$4.69 \pm 0.10$	$\text{Li}_4\text{H}$	$4.10 \pm 0.06$	$\text{Li}_4\text{F}$	$4.10 \pm 0.20$
$\text{Li}_5$	$4.02 \pm 0.10$	$\text{Li}_5\text{H}$	$4.12 \pm 0.06$	$\text{Li}_5\text{F}$	$4.29 \pm 0.20$
$\text{Li}_6$	$4.20 \pm 0.10$	$\text{Li}_6\text{H}$	$4.08 \pm 0.06$	$\text{Li}_6\text{F}$	$4.24 \pm 0.20$

The values of the ionization potentials for  $\text{Li}_n\text{F}$  ( $n=2, 3$ , and  $4$ ) presented in Table 1 agree with previous experimental data, which imply that IPs of these types of clusters can be measured by the experimental setup proposed in this work.

The results obtained showed that the ionization potentials of  $\text{Li}_n\text{F}$  ( $n=2-4$ ) are lower than that of the lithium atom ( $5.39$  eV), meaning that these clusters belong to the group of “superalkali” species. As listed in Table 1, the values of ionization potentials of  $\text{Li}_n\text{F}$  ( $n=2-6$ ) clusters are about  $4$  eV suggest that they belong to the group of F - centre clusters, too. Additionally, we observed that the IPs of  $\text{Li}_n\text{F}$  ( $n=5$  and  $6$ ) are slightly higher than the IPs of  $\text{Li}_n\text{F}$

( $n=2-4$ ). The ionization potentials of  $\text{Li}_n\text{F}$  ( $n=5$  and  $6$ ) are slightly different of the corresponding small metal clusters  $\text{Li}_n$  and hydrogen – doped lithium clusters.

Generally, the experimentally determined ionization potential trend  $\text{IP}(\text{Li}_2\text{F}) < \text{IP}(\text{Li}_4\text{F}) < \text{IP}(\text{Li}_3\text{F}) < \text{IP}(\text{Li}_6\text{F}) < \text{IP}(\text{Li}_5\text{F})$  does not follow the trend of the IPs of corresponding  $\text{Li}_n$  and  $\text{Li}_n\text{H}$  clusters.

#### 4. Conclusions

The apparatus based on magnetic sector instrument, where Knudsen cell was placed into ionization chamber is suitable method for the simultaneous production and measurement of the ionization potentials of the small lithium monofluoride clusters. The clusters of the type  $\text{Li}_n\text{F}$  ( $n=2-6$ ) were detected in a cluster beam which was generated using the 7:1 mixture of  $\text{LiF}$  and  $\text{LiI}$  as a sample for the Knudsen cell. All of these clusters are obtained simultaneously in one set of measurements and results obtained showed the order of the ion intensities was  $\text{Li}_2\text{F} > \text{Li}_4\text{F} > \text{Li}_6\text{F} > \text{Li}_5\text{F} > \text{Li}_3\text{F}$  in temperature range  $850-1080\text{K}$ . It is observed that the ions of clusters with an even numbered of lithium atoms ( $\text{Li}_2\text{F}^+$ ,  $\text{Li}_4\text{F}^+$ ,  $\text{Li}_6\text{F}^+$ ) are more stable than the ions of clusters with an odd numbered of lithium atoms ( $\text{Li}_3\text{F}^+$ ,  $\text{Li}_5\text{F}^+$ ). Ionization potentials determined by the thermal ionization mod were  $(4.29 \pm 0.25)$  eV for  $\text{Li}_5\text{F}$ , and  $(4.24 \pm 0.25)$  eV for  $\text{Li}_6\text{F}$ . The ionization potentials trend  $\text{IP}(\text{Li}_2\text{F}) < \text{IP}(\text{Li}_4\text{F}) < \text{IP}(\text{Li}_3\text{F}) < \text{IP}(\text{Li}_6\text{F}) < \text{IP}(\text{Li}_5\text{F})$  does not follow the trend of the IPs of corresponding  $\text{Li}_n$  and  $\text{Li}_n\text{H}$  clusters. These results represent experimental confirmation that clusters  $\text{Li}_n\text{F}$  ( $n=2-6$ ) belong in the class superalkali species.

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