

# “SUPERALKALNI“ KLASTERI, PROIZVODNJA, POTENCIJALNA PRIMENA KAO MATERIJAL ZA SKLADIŠTENJE ENERGIJE

## “SUPERALKALI” CLUSTERS, PRODUCTION, POTENTIAL APPLICATION LIKE ENERGY STORAGE MATERIALS

Suzana VELIČKOVIĆ<sup>1</sup> and Xianglei KONG<sup>2</sup>

<sup>1</sup>Department of Physical Chemistry, VINČA Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, Belgrade, Serbia

<sup>2</sup>The State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, China

<https://doi.org/10.24094/mkoiee.020.8.1.15>

*Jedan od glavnih događaja prošlog veka bilo je prepoznavanje klastera kao gradivnih blokova novih materijala. „Superalkalni“ klasteri zbog svoje energije ionizacije koja je niža od alkalnih atoma, predstavljaju odlična redukciona sredstva; stoga su prepoznati kao dobri kandidati za sintezu neobično jedinjenja. „Superalkali“, igra važnu ulogu u nauci o hemiji i materijalima zbog svog potencijala da služe kao strukturne jedinice za sastavljanje novih nanostrukturisanih funkcionalnih materijala, kao što su nelinearni optički materijali, materijali za skladištenje vodonika, kao i odličan redukциони reagens za smanjenje emisije ugljen-dioksida, azot-oksida i molekularnog azota. Jedan od načina za dobijanje klastera je korišćenje nekonvencionalnih metoda. Do danas, masena spektrometrija se pokazala ključnom metodom koja nema alternativu u oblasti proizvodnje „superalkalijskih“ klastera. Međutim, da bi se dobili ovi klasteri, potrebno je izvršiti modifikacije masenih spektrometra dostupnih na tržištu. U ovom radu će biti predstavljene mogućnosti dobijanja „superalkalnih“ klastera kombinacijom dve klasične metode masene spektrometrije, poput Knudsenove ćelije i površinske ionizacije u magnetnom masenom spektrometru. Modifikovana klasična površinska jonizacija masena spektrometrija potvrdila se kao efikasna i jeftina metoda za dobijanje ovih klastera.*

**Ključne reči:** „Superalkalni“ klasteri; masena spektrometrija; Knudsenova ćelija

*One of the major developments of the past century was the recognition of clusters as building blocks of new materials. “Superalkali” clusters because of their ionization energies which lower than alkaline atoms, present the excellent reducing agents; hence, they are recognized as good candidates for the synthesis of unusually compounds. “Superalkalis”, plays an important role in the chemistry and material science because of their potential to serve as structural units for the assembly of novel nanostructured functional materials, such as nonlinear optical materials, hydrogen storage materials, as well as an excellent reduction reagent for decreasing emissions of carbon dioxide, nitrogen oxides, and molecular nitrogen. One way to get a cluster is to use unconventional methods. To date, the mass spectrometry has proven itself a crucial method, which has no alternative, in the field of the production “superalkali” clusters. However, in order to obtain these clusters, it is necessary to make modifications of the mass spectrometers available on the market. Within this paper, the possibilities of obtaining “superalkali” clusters by combining two classical methods of mass spectrometry such as, Knudsen cell and the surface ionization within a magnetic mass spectrometer will be presented. The modified classic surface ionization mass spectrometry has confirmed to be an efficient and inexpensive method for obtaining these clusters.*

**Key words:** “Superalkali” clusters; mass spectrometry; Knudsen cell

<sup>1</sup> Corresponding author, email: vsuzana@vin.bg.ac.rs

## 1 Introduction

The direct translation of the word cluster means group, however, in different disciplines clusters have different meanings. In physics and chemistry, a cluster means a group of atoms or molecules formed by interactions ranging from very weak van der Waals to strong ionic bonds with regular and arbitrarily scalable repetition of a basic unit. Clusters can be composed of a few to a few thousand basic units, and their size is intermediate between atoms and balks. The most important feature of clusters is that their characteristics can be changed by adding a single atom or electron. Clusters possess a large number of energetically close isomers, and the number of isomers grows huge with increasing cluster size, this is different from molecules that have a well-defined composition and structure (organic compound have only a small number of isomers). The fact that clusters can be produced from almost any element in the periodic table leads to a wide-ranging interest of researchers in the studies of clusters of various compositions. In the cluster area, another great discovery was the fact that clusters could be the basic structural unit of new materials, which are relatively easy and cheap to produce in laboratory conditions [1, 2].

“Superalkalis” are a class of heterogeneously clusters that are characterized by lower ionization energies than that of an alkali metals atom (Li, Na, K, Rb, Cs). Here, it should be highlighted, that “superhalogen” clusters that possess higher electron affinities than those of electronegative elements (such as, F, Cl, O, and so on) exist as well. The concept of “superalkal” and “superhalogen” were defined by Gutsev and Boldyrev, who are still continuously researching the design of these clusters and concept expansion of them. They described mononuclear “superalkals” like a series of molecules  $ML_{k+1}$ , where M is an electronegative atom with the maximal formal valence k, while L is an alkali metal atom (for example,  $OLi_4$ ,  $CLi_6$ ,  $FLi_2$ ,  $FNa_2$  or  $Li_2F$ ,  $Na_2F$ ,  $Li_4O$ ,  $Li_6C$ ); while the general formula for “superhalogen” is  $MX_{k+1}$  where M can be an element of metals, k represents the valence and the number of center atom M, X represents highly electronegative ligands, for example  $NaF_2$ ,  $LiF_2$ ,  $Pt_2Cl_3$ , (unfortunately, they used the mark M in both cases which can lead to confusion) [3-15].

The mononuclear  $Li_nF$  ( $n = 2$  and  $3$ ) clusters violate stoichiometry based on the octet rule since they have nine or more valence electrons. However, theoretical calculations by Schleyer et al. indicate that stability of this cluster originates from their chemical bonding which consists of the attractive electrostatic interaction between the positively charged metal “network” ( $Li_n^+$ ) and negatively charged electronegative atom ( $F^-$ ) [16].

The theoretical work of several research groups has shown that in addition to mononuclear, there are other types of “superalkalis” such as, binuclear (M is two different electronegative atom, for example,  $CNLi_2$  or  $Li_2CN$  cluster), polynuclear (M is  $CO_3$ ,  $SO_3$ ,  $PO_4$ ,  $AsO_4$ ), bimetallic (L are “mixed” alkali atoms, for example,  $LiNaCl$  cluster), and non-metallic species [17]. These clusters, their chemical bonds, which are more complex than previously described, as well as their isomers, go beyond the scope and goal of this paper and therefore are not described in detail.

The aim of this paper is to briefly present theoretical research of potential applications and to describe ways to obtain “superalkali” clusters.

## 2 Potential application

Castelman and Khana have recently demonstrated that “superalkali”/“superhalogen” clusters mimic the chemical behavior of elements in the periodic table, and maintain their structural and electronic integrities when assembled with other species. Hence “superalkalis/superhalogens” may be excellent candidates to combine with other atoms or clusters. For example, together “superalkali” and “superhalogen”, can form new kinds of clusters, called “superatoms”. Those “superatoms” may serve as potential building blocks for the new cluster assembled materials with unique properties [18, 19].

Li et al. have predicted a series of “superatom” clusters which exhibit extraordinarily large non-linear optical response [20]. Paduani et al. have shown that mononuclear “superalkali”  $Li_3O$ ,  $Li_4O$ , and  $Na_8$  clusters can be combined with Gd or V and form compounds with an outstanding magnetic response [21, 22].

Generally, “superalkali” clusters have a strong tendency to give up an electron and to become a cationic species, while “superhalogens” have a tendency to accept an electron and to become anionic species. For these reasons, “superalkali” and “superhalogen” clusters are recognized as strong reduction and oxidation reagents, respectively. Because “superalkalis” possess excellent reducibility they can be employed to reduce carbon dioxide (CO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>, x = 1 and 2), and nitrogen (N<sub>2</sub>) molecules, which have extremely high stability [23, 24, 25].

It is well known that carbon dioxide emission, due to ever so quick industrialization, is a problem everywhere on our planet. Materials for capturing CO<sub>2</sub> need to have a high and selective absorption. There are many proposed materials for this purpose, such as monoethanolamine, porous organic polymers, carbon materials, zeolites, metal-organic frameworks [26, 27, 28, 29]. However, these materials have many weaknesses, such as low selectivity and high cost. Hence a different strategy for decreasing the concentration of CO<sub>2</sub> in the atmosphere is proposed. This new strategy requires suitable compounds for the complete oxidation or reduction of the thermally stable CO<sub>2</sub> molecule. Czapla and Skurski have calculated that the “superhalogen” series Sb<sub>n</sub>F<sub>5n+1</sub> (n = 1–3), especially the largest cluster Sb<sub>3</sub>F<sub>16</sub>, can ionize CO<sub>2</sub> by accepting an electron from it [30]. However, Park and Meloni have shown that the chemical bond formed between Li<sub>3</sub>F<sub>2</sub> and CO<sub>2</sub> is stronger than that of a “superhalogen” cluster and CO<sub>2</sub>. Due to the easy electron transfer from the “superalkali” Li<sub>3</sub>F<sub>2</sub> clusters to the CO<sub>2</sub>, it is formed CO<sub>2</sub><sup>-</sup>, despite the fact that CO<sub>2</sub> possesses no positive electron affinity. This process can be utilized for the conversion of CO<sub>2</sub> to useful products (methanol fuel and carboxylic acid) [23].

Nitrogen oxides (NO<sub>n</sub>, n = 1, 2) are known to be major air pollutants because NO and NO<sub>2</sub> gases react with certain organic compounds forming smog and destroying ozone, which has a significant impact on human health (damage to lung tissue and reduction in lung function) [31, 32]. To date, urea or ammonia with or without the use of a catalyst are used for the reduction of NO<sub>n</sub>. In this case, NO<sub>n</sub> are converted into nitrogen molecule, water and carbon dioxide. Srivastava has found that “superalkali” FLi<sub>2</sub> represents the effective mean in the single-electron reduction of NO<sub>n</sub> into NO<sub>n</sub><sup>-</sup> [24].

Nitrogen (N<sub>2</sub>) is the most abundant gas molecule on Earth, and very useful for biological systems, but not in the form of molecules. Nitrogen is an inertness gas due to its negative electron affinity of 1.8 eV, and high ionization energy (15.0 eV), which is why it is so difficult for reduction and oxidation [33]. The process of converting N<sub>2</sub> into a useful form is called fixation or activation. To date industrial way to activate N<sub>2</sub> (nitrogen fixation) is converting N<sub>2</sub> to ammonia (NH<sub>3</sub>) using Haber–Bosch hydrogenation. This reaction occurs under extreme conditions - temperature range from 600 to 800 K, and pressures as high as 500 atm. Biological fixation performed by the nitrogenase enzyme, the iron (Fe) and the molybdenum iron (MoFe) proteins, is the reaction that occurs under much less extreme conditions (ca. 290 K and 0.8 atm) than the Haber–Bosch hydrogenation [34].

Many studies have been done in both practical and theoretical areas to discover more effective ways to activate N<sub>2</sub>, which is based on the greatest possible distancing of the nitrogen atom. Computational analysis has confirmed that in the metal complexes, such as aluminum clusters with nitrogen, Al<sub>44</sub>N<sub>2</sub><sup>+</sup>, can successfully stretch the N-N bond length up to the average value of 1.65 Å [35]. Schleyer and co-workers investigated the complexes of N<sub>2</sub> with various lithium “superalkali” clusters (Li<sub>2</sub>, Li<sub>4</sub>, Li<sub>6</sub>, and Li<sub>8</sub>). They have shown that in the complex Li<sub>n</sub>-N<sub>2</sub> occurs to stepwise cleavage of the N-N bond and elongated the bond length up to 3.023 Å [36]. Park and Meloni have calculated bond length between N<sub>2</sub> in (Li<sub>3</sub>F<sub>2</sub>)<sub>6</sub>N<sub>2</sub> is 5.501 Å, such that it can be concluded that N<sub>2</sub> is completely separated. The activation of diatomic nitrogen can be explained in terms of the addition of electrons, from “superalkali” Li<sub>3</sub>F<sub>2</sub> clusters, into the N<sub>2</sub> empty MOs, as a result, increases the distance between the atoms of the nitrogen [25].

“Superalkali” clusters have the potential to become effective hydrogen storage materials because their positively charged metal “network” can bond with molecular hydrogen through electrostatic interactions. Wang et al. found an improved electron transfer between H<sub>2</sub> and “superalkali” (Li<sub>2</sub>F)-coated C<sub>60</sub>. They have shown that 68H<sub>2</sub> molecules can be stably stored by the C<sub>60</sub>(Li<sub>2</sub>F)<sub>12</sub>

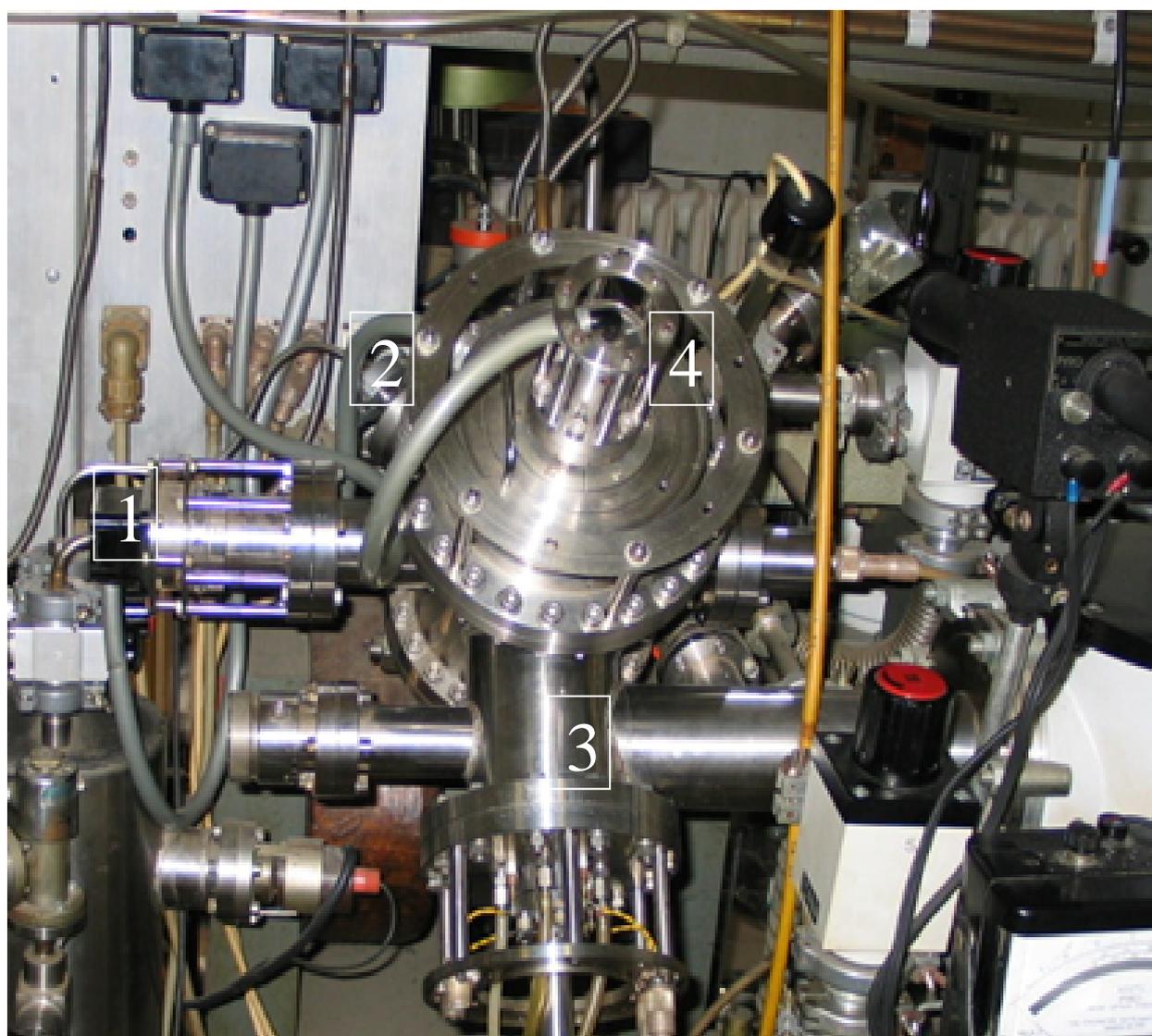
cluster. This result suggests that the hydrogen storage capacities for solid sorbents can be greatly improved using “superalkalis”, which can enhance interactions between the hydrogen and host [37].

In the past few decades, there are many theoretical publications about the applications of “superalkali” clusters, but the experimental research is rare.

### 3 Production “superalkali” clusters

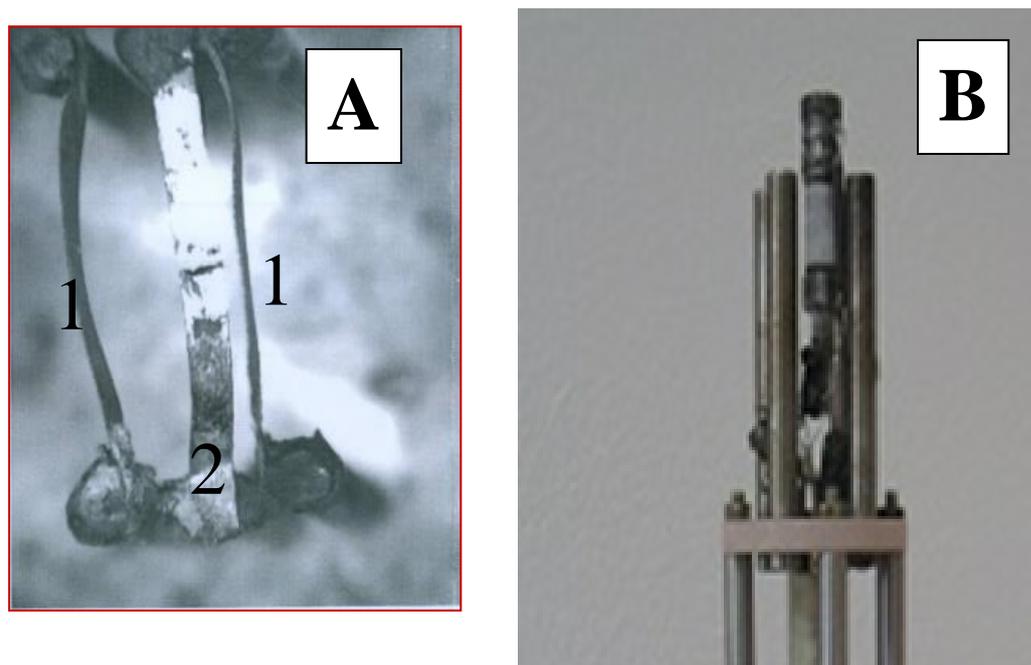
Mass spectrometry is a key method for producing clusters. It can be briefly described that three major components of mass spectrometers have following roles: ion source, for producing cluster ions with a mix of size from the appropriate sample; a mass analyzer, for separate the cluster ions to their mass-to-charge ratio; and detector system, for identification the cluster ions and recording the relative stabilities of each of the detected ionic species. To date, many ion sources have been used for obtaining mononuclear “superalkali” clusters; among them, the most significant are Knudsen cell-electron impact and laser ablation [9-12, 39]. It should be noted that the production of clusters requires significant modifications of commercial mass spectrometers.

The magnetic sector mass spectrometer, with the ionization chamber which is equipped with three classical ionization methods ( the electron impact, the surface ionization, and the Knudsen cell) was constructed in the Department of Physical Chemistry (Figure 1).



**Figure 1.** The ionization chamber of the magnetic sector mass spectrometer, 1 - electron source, 2 - gas inlet, 3 - standard Knudsen cell, 4 – the carrier for the surface ionization source or the Knudsen cell.

The triple filament source of surface ionization which consists of the side (evaporation) filament and central filaments and the Knudsen cell are presented in Figure 2.



**Figure 2.** A) The triple filament source of surface ionization, 1 – the side filament, 2 – the central filament. B) The Knudsen cell.

There are several ways to use this mass spectrometer as the source of “superalkali” clusters.

Generally, the surface ionization is a method for generating ions at the hot metal filaments, but it has been shown that this method can be used to obtain these kinds of clusters. The triple filament source of surface ionization was used for that purpose (Figure 2A). The ion source is made of three rhenium filaments of the same dimension ( $8\text{mm} \times 1\text{mm} \times 0.05\text{mm}$ ). The samples were the solutions of  $\text{LiX/LiI/C}_2\text{H}_5\text{OH}$ , ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ), which were deposited on the side filaments, while the  $\text{C}_{60}$ /toluene solution was deposited on the central filament. The temperature of the side evaporation filaments was in the range of (200 - 1000 K), while the temperature range of central filament was (200-2000 K). The resulting mononuclear clusters were of the type  $\text{Li}_n\text{X}$ ,  $n=2$  and 3, ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) [39].

It is known that the small size “superalkali” clusters of type  $\text{Li}_n\text{X}$ , ( $\text{Li}_3\text{O}$ ,  $\text{Li}_2\text{F}$ ,  $\text{Li}_6\text{C}$ ,  $\text{Li}_4\text{O}$ ,  $\text{Li}_4\text{S}$ ,  $\text{Li}_4\text{P}$ ,  $\text{Li}_2\text{CN}$ ) were obtained by the standard Knudsen cell mass spectrometry combined with the electron impact ionization [9-12].

The standard experimental setup places Knudsen cell outside of the ionization chamber. Neutral clusters are obtained from an appropriate mixture of inorganic salts, which heats up in the Knudsen's cell. The neutral clusters obtained from the cell were ionized used the electron impact method. However, in the experimental research that was carried out at the Department of Physical Chemistry, the Knudsen cell was placed into the ionization chamber so that the Knudsen cell orifice was closer to the electron beam than in the standard case. This enabled more efficient ionization of the neutral clusters formed in the cell. Another modification was that the Knudsen cell can be held on at + 30V with respect to the ionization chamber, it allowed direct identification of positive charge cluster ions generated in the cell. The Knudsen's cell was cylindrical in shape, was made of tantalum or nickel. The height of the cylinder was 7 mm, the outside diameter was 6mm and the orifice diameter was 0.1 mm (Figure 2B). The sample was the  $\text{LiI/LiF/C}_{70}$  mixture. Thanks to the mentioned changes and variation of the molar ratio of  $\text{LiF}$  and  $\text{LiI}$ , two series of clusters were obtained  $\text{Li}_n\text{I}$  and  $\text{Li}_n\text{F}$  ( $n = 2, 3, 4, 5$ , and 6), for the first time [40].

Heating the Knudsen cell is an important issue. In the standard case, the heater is tungsten wire which is uniformly wrapped around the Knudsen cell. The results showed that the Knudsen cell becomes a more efficient cluster source if the heater is placed directly in the cell. The filament of the surface ionization source can be used as a heater. This filament of rhenium is placed in the centre of the bottom of Knudsen cell. In this experimental setup, the temperature of the cell is not uniform throughout the inner cavity. The heater temperature was between 500 - 2700 K. The sample was inorganic salt such as, MX, M - Li or K, X - F, Cl, Br, I, which were loaded in this Knudsen cell. The serial of lithium and potassium mononuclear clusters such as  $\text{Li}_n\text{Br}$ ,  $\text{Li}_n\text{Cl}^+$ ,  $\text{K}_n\text{X}$  ( $n = 2 - 6$ ) were obtained. The binuclear clusters like as  $\text{K}_n\text{Br}_{n-1}^+$  ( $n = 3 - 5$ ),  $\text{Li}_n\text{Cl}_2^+$  ( $n = 4 - 7$ ), and  $\text{Li}_n\text{Cl}_{n-1}^+$  ( $n = 3 - 5$ ) were detected, too [41-47].

## 4 Conclusion

“Superalkalis”, are excellent reducing substances, and thus, are attracting more and more attention in recent years. Theoretically, the potential for discovering new “superalkalis” is limitless, so hence their practical application remains still a challenge.

It has been shown that the combination of the Knudsen cell and surface ionization is a simple, inexpensive, and efficient method for obtaining mononuclear and binuclear “superalkali” clusters. However, the experimental works on “superalkalis” are still limited to the detection of cluster ions in the gas phase; hence more efforts should be paid to produce “superalkalis” in large quantities.

## Acknowledgment

The research was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia, Contract number: 451-03-68/2020-14/200017

## References

- [1] **Reinhard, P.G., Suraud, E.**, *Introduction to Clusters Dynamics*, WILEY-VCH Verlag GmbH, Weinheim, 2004.
- [2] **Castleman, A. W., S. N. Khanna, S. N.**, Clusters, Superatoms, and Building Blocks of New Materials, *J. Phys. Chem. C*, 113 (2009), pp. 2664–2675.
- [3] **Gutsev G. L., Boldyrev A. I.**, DVM-X $\alpha$  calculations on the ionization potentials of  $\text{MX}_{k+1}^-$  complex anions and the electron affinities of  $\text{MX}_{k+1}$  “superhalogens”, *Chem. Phys.*, 56 (1981), pp. 277-283.
- [4] **Gutsev G. L., Boldyrev A. I.**, DVM X $\alpha$  calculations on the electronic structure of “superalkali” cations, *Chemical Physics Letters.*, 92, (1982), pp. 262-266.
- [5] **Rehm E., Boldyrev A. I., Schleyer P. v. R.**, Ab initio study of superalkalis. First ionization potentials and thermodynamic stability, *Inorg. Chem.*, 31 (1992), pp. 4834-4842.
- [6] **Boldyrev A. I., Wang L.-S.**, Beyond Classical Stoichiometry: Experiment and Theory, *J. Phys. Chem. A*, 105 (2001), pp. 10759-10775.
- [7] **Wang X. B., Ding C. F., Wang L. S., Boldyrev A. I., Simons J.**, First experimental photoelectron spectra of superhalogens and their theoretical interpretations, *J. Chem. Phys.*, 110, (1999), pp. 4763-4771.
- [8] **Alexandrova A. N., Boldyrev A. I., Fu Y. J., Yang X., Wang X. B., Wang L. S.**, Structure of the  $\text{Na}_x\text{Cl}_{x+1}^-$  ( $x = 1-4$ ) clusters via *ab initio* genetic algorithm and photoelectron spectroscopy, *J. Chem. Phys.*, 121, (2004), pp. 5709-5719.
- [9] **Kudo H.**, Observation of Hypervalent  $\text{ClLi}_6$  by Knudsen-effusion Mass Spectrometry, *Nature.*, 355, (1992), pp. 432-434.
- [10] **Kudo H., Wu C. H., Ihle H. R.** Mass-spectrometric study of the vaporization of  $\text{Li}_2\text{O}(s)$  and thermochemistry of gaseous  $\text{LiO}$ ,  $\text{Li}_2\text{O}$ ,  $\text{Li}_3\text{O}$ , and  $\text{Li}_2\text{O}_2$ , *J. Nucl. Mater.*, 78, (1978), pp. 380-389.
- [11] **Wu C. H.**, The stability of the molecules  $\text{Li}_4\text{O}$  and  $\text{Li}_5\text{O}$ , *Chem. Phys. Lett.*, 139 (1987), pp. 357-359.

- [12] **Kudo H., Zmbov K. F.**, Observation of gaseous  $\text{Li}_4\text{P}$ : A hypervalent molecule, *Chem. Phys. Lett.* 187 (1991), pp. 77-80.
- [13] **Kudo H., Yokoyama K., Wu C. H.**, The stability and structure of the hyperlithiated molecules  $\text{Li}_3\text{S}$  and  $\text{Li}_4\text{S}$ : An experimental and ab initio study, *J. Chem. Phys.*, 101, (1994), pp. 4190-4197.
- [14] **Kudo H., Yokoyama K.**, The Structures and Bonding of Hyperlithiated Molecules, *Bull. Chem. Soc. Jpn.*, 69 (1996), pp. 1459-1469.
- [15] **Shi Y., Bian S., Ma Y., Wang Y., Ren J., Kong X.**, Structures and Superhalogen Properties of  $\text{Pt}_2\text{Cl}_n$  ( $2 \leq n \leq 10$ ) Clusters, *J. Phys. Chem. A*, 123, (2019), pp. 187-193.
- [16] **Schleyer P. V. R.**, *New Horizons in Quantum Chemistry Lowdin P-O, Pullman B (eds). Reidel Dordrecht.* 1983.
- [17] **Sun W.-M., Wu D.**, Recent Progress on the Design, Characterization, and Application of Superalkalis, *Chem. Eur. J.*, 25, (2019), pp. 9568 – 9579.
- [18] **Reber A. C., Khanna S. N., Castleman A. W. J.**, Superatom Compounds, Clusters, and Assemblies: Ultra Alkali Motifs and Architectures, *J. Am. Chem. Soc.*, 129, (2007), pp. 10189-10194.
- [19] **Claridge S. A., Castleman A.W., Khanna S. N., Murray C. B., Sen A., Weiss P. S.**, Cluster-Assembled Materials. *ACS Nano.*,3, (2009), pp. 244-255.
- [20] **Li Y., Wu D., Li Z. R.**, Compounds of superatom clusters: Preferred structures and significant nonlinear optical properties of the  $\text{BLi}_6\text{-X}$  ( $\text{X} = \text{F}, \text{LiF}_2, \text{BeF}_3, \text{BF}_4$ ) motifs, *Inorg. Chem.*, 47 (2008), pp. 9773-9778.
- [21] **Paduani C.**, Magnetic Hyperalkali Species of Gd-Based Clusters, *J. Phys. Chem. A*, 122 (2018), pp. 5037–5042.
- [22] **Zhang X., Wang Y., Wang H., Lim A., Gantefoer G., K. Bowen H., Reveles J. U., Khanna S. N.**, On the Existence of Designer Magnetic Superatoms, *J. Am. Chem. Soc.*, 135, (2013), pp. 4856–4861.
- [23] **Park H., Meloni G.**, Reduction of carbon dioxide with a superalkali, *Dalton Trans.*,46, (2017), pp.11942–11949.
- [24] **Srivastava A. K.**, Reduction of Nitrogen Oxides ( $\text{NO}_x$ ) by Superalkalis, *Chemical Physics Letters*, 695 (2018) pp. 205-210.
- [25] **Park H., Meloni G.**, Activation of Dinitrogen with a Superalkali Species,  $\text{Li}_3\text{F}_2$ , *Chem-PhysChem.*, 19, (2018), pp. 256 – 260.
- [26] **Hansen J., Johnson D., Lacin A., Lebedeff S., Lee P., Russell G.**, Climate Impact of Increasing Atmospheric Carbon Dioxide, *Science*, 213, (1981) pp. 957–966.
- [27] **Mirzaei S., Shamiri A., Aroua M. K.**, Simulation of Aqueous Blend of Monoethanolamine and Glycerol for Carbon Dioxide Capture from Flue Gas, *Energy Fuels*, 30, (2016), pp. 9540–9553.
- [28] **McDonald T. M., Lee W. R., Mason J. A., Wiers B. M., Hong C. S., Long J. R.**, Capture of Carbon Dioxide from Air and Flue Gas in the Alkylamine-Appended Metal–Organic Framework  $\text{mmen-Mg}_2(\text{dobpdc})$ , *J. Am. Chem. Soc.*,134, (2012), pp. 7056–7065.
- [29] **Plaza M. G., Garcia S., Rubiera F., Pis J. J., Pevida C.**, Post-combustion  $\text{CO}_2$  capture with a commercial activated carbon: Comparison of different regeneration strategies, *Chem. Eng. J.*,163, (2010), pp. 41–47.
- [30] **Czapla M., Skurski P.**, Oxidizing  $\text{CO}_2$  with superhalogens, *Phys. Chem. Chem. Phys.*, 19, (2017), pp. 5435–5440.
- [31] **Omidvarborna H., Kumar A., Kim D. S.**,  $\text{NO}_x$  emissions from low-temperature combustion of biodiesel made of various feedstocks and blends, *Fuel Process. Technol.*, 140, (2015) pp. 113-118.
- [32]  $\text{NO}_x$  How Nitrogen Oxides Affect The Way We Live And Breathe, Available online at: <https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P10006ZO.txt> (Retrieved 20-12-2017).

- [33] **Shaver M. P., Fryzuk M. D.**, Activation of Molecular Nitrogen: Coordination, Cleavage and Functionalization of N<sub>2</sub> Mediated By Metal Complexes , *Adv. Synth. Catal.*, 345, (2003), pp. 1061–1076.
- [34] **Howard J. B., Rees D. C.**, Structural Basis of Biological Nitrogen Fixation, *Chem. Rev.*, 96, (1996), pp. 2965–2982.
- [35] **. Cao B., A. Starace K., Judd O. H., Bhattacharyya I., Jarrold M. F., Lopez J. M., Aguiado A.**, Activation of Dinitrogen by Solid and Liquid Aluminum Nanoclusters: A Combined Experimental and Theoretical Study, *J. Am. Chem. Soc.*, 132, (2010), pp. 12906–12918.
- [36] **Roy D., Vazquez A. N., Schleyer P.v. R.**, Modeling Dinitrogen Activation by Lithium: A Mechanistic Investigation of the Cleavage of N<sub>2</sub> by Stepwise Insertion into Small Lithium Clusters, *J. Am. Chem. Soc.*, 131, (2009), pp. 13045–13053.
- [37] **Wang K., Liu Z., Wang X., Cui X.**, Enhancement of hydrogen binding affinity with low ionization energy Li<sub>2</sub>F coating on C<sub>60</sub> to improve hydrogen storage capacity, *Int. J. Hydrogen Energy*, 39, (2014), pp. 15639–15645.
- [38] **Yokoyama K., Haketa N., Hasimoto M., Furukawa K., Tanaka H., Kudo H.**, Production of hyperlithiated Li<sub>2</sub>F by a laser ablation of LiF–Li<sub>3</sub>N mixture, *Chem.Phys.Lett.*, 320, (2000), pp. 645-650.
- [39] **Veličković S., Đorđević V., Cvetičanin J., Đustebek J., Veljković., Nešković O.**, Ionization energies of Li<sub>n</sub>X (n = 2,3; X = Cl, Br, I) molecules, *Rapid Commun. Mass Spectrom.*, 20, (2006), pp. 3151-3153.
- [40] **Djustebek J., Veličković S., Jerosimić S., Veljković.**, Mass spectrometric study of the structures and ionization potential of Li<sub>n</sub>I (n=2, 4, 6) clusters, *J. Anal. Atom. Spectrom.*, 26, (2011), pp. 1641-1647.
- [41] **Veličković S., Djustebek J., Veljković F., Radak B., Veljković M.**, Formation and ionization energies of small chlorine-doped lithium clusters by thermal ionization mass spectrometry, *Rapid Commun. Mass Spectrom.*, 26, (2012), pp. 443-448.
- [42] **Veličković S., Djustebek J., Veljković., Veljković M.**, Formation of positive cluster ions Li<sub>n</sub>Br (n = 2 – 7) and ionization energies studied by thermal ionization mass spectrometry, *J. Mass Spectrom.*, 47, (2012), pp. 627-631.
- [43] **Veljković F., Djustebek J., Veljković M., Veličković S., Perić-Grujić A.**, Production and ionization energies of K<sub>n</sub>F (n=2–6) clusters by thermal ionization mass spectrometry, *Rapid Commun. Mass Spectrom.*, 26, (2012), pp. 1-6.
- [44] **Veljković F., Djustebek., Veljković M., Perić-Grujić A., Veličković S.**, Study of small chlorine-doped potassium clusters by thermal ionization mass spectrometry, *J. Mass Spectrom.*, 47, (2012), pp. 1495-1499.
- [45] **Milivanović M., Veličković S., Veljković F., Jerosimić S.**, Structure and stability of small lithium-chloride Li<sub>n</sub>Cl<sub>m</sub><sup>(0,1+)</sup> (n < m, n = 1 –6, m = 1 – 3) clusters, *Physical Chemistry Chemical Physics*, 19, (2017), pp. 30481-30497.
- [46] **Milovanović B., Milovanović M., Veličković S., Veljković F., Perić-Grujić A., Jerosimić S.**, Theoretical and experimental investigation of geometry and stability of small potassium-iodide KnI (n = 2 – 6) clusters, *Int. J. Quantum Chem.*, 119, (2019), pp. 26009-26026.
- [47] **Mitić M., Milovanović M., Veljković F., Perić-Grujić A., Veličković S., Jerosimić S.**, Theoretical and experimental study of small potassium-bromide KnB<sup>r(0,1+)</sup> (n =2-6) and K<sub>n</sub>B<sub>m-1</sub><sup>(0,1+)</sup> (n = 3 - 5) clusters, *Journal of Alloys and Compounds*, 835, (2020), pp. 155301- 155301.