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

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The Discovery of “Superalakalis”

- 1978. Kudo and Wu have experimentally detected the first “superalkali” cluster \( \text{Li}_3\text{O} \).

- \( \text{Li}_3\text{O} \) was obtained by the evaporation of \( \text{Li}_2\text{O} \) salt in the Knudsen cell mass spectrometry.
The Importance of Theory

- Many cluster properties, such as cluster geometries, cluster isomers, ionization energies, electron affinity, binding energies are not easily measured directly from experiment.

- Theoretical methods have been very useful in helping to interpret experimental data.
Why This Is an Unusual Cluster?

- The theoretical calculations by Schleyer et al. have shown that the clusters with “excess” electrons are thermodynamically more stable than octet molecules with eight valence electrons like Li\textsubscript{2}O.
- These clusters are named **hypervalent**.

Electronic structure of Li\textsubscript{3}O breaks the octet rule: this cluster has “excess” valence electron (has 9 valence electrons).
What Is the Origin of Their Thermodynamic Stability? Where Is Location of the “Excess” Electron?

The “excess” electron delocalizes over the all lithium atoms, and form a lithium “cage” or network of positive charge (Li$_3^+$).

Oxygen atom possess nearly maximum anionic charges (O$_2^-$).

The stability of the neutral Li$_3$O clusters is due to:
- the covalent interactions between the lithium atoms in the “cage”.
- the attractive electrostatic interactions between Li$_3^+$ cation and the anionic charges of oxygen.
The concept of “Superalkali” Clusters
Gutsev and Boldyrev

- In 1982, the theoretical calculations by Gutsev and Boldyrev have shown that the clusters with “excess” electron (Li₃O, Li₂F) **have the ionization energies lower than lithium atoms.**
- They had these clusters named “superalkali”.
- They introduced the concept of “superhalogen” clusters.
What Are “Superalkali” Clusters?

- “Superalkali” are clusters which possess ionization energies lower than those of alkali atoms (5.39–3.89 eV)
- “Superhalogens” clusters have electron affinities larger than those of halogen atoms.
- Gutsev and Boldyrev are still continuously researching the design of these clusters and concept expansion of them.
Why Study “Superalkali” Clusters?

In the past few decades, there are many theoretical publications about the applications of “superalkali” clusters.
Khana et al. have demonstrated that “superalkali” and “superhalogen” clusters **mimic the chemical behavior of elements** in the periodic table, and maintain their structural and electronic integrities when assembled with other species.
Generally, “superalkali” clusters have a strong tendency to give up an electron and to become a cationic species, while “superhalogens” tend to accept an electron and to become anionic species.
Potential Application

- “Superalkalis and Superhalogens” may be excellent candidates to combine with each other, so building “superatom”.

- Hence these clusters may be potential building blocks for the new cluster assembled materials with unique properties (large nonlinear optical response and an outstanding magnetic response).
Potential Application

- Because “superalkalis” have excellent capability to *reducing* (by electron transfer) hence it can be employed to reduce molecules, which have extremely high stability:
  - carbon dioxide (CO$_2$),
  - nitrogen oxides (NO$_x$, x = 1 and 2),
- This process can be utilized for the conversion of these molecules to useful products.

![Chemical reactions diagram]

“superalkali”
C$_{60}$ has external and internal surfaces that are chemically too inert, for this reason, it can be said, that C$_{60}$ is unable to store hydrogen to be useful in practical applications.

The general ways to improve the binding energy of the carbon sorbents with H$_2$ is the decorating C$_{60}$ sorbents with metal atoms.

C$_{60}$Y$_{12}$ complex can absorb up to 60 hydrogen molecules,

C$_{60}$Ca$_{32}$ can absorb up to 62 H$_2$ molecules
Wang et al. found that Li$_2$F can be strongly connected to C$_{60}$ through an ionic bonding, and form $C_{60}(Li_2F)_{12}$.

- the hydrogen storage capacities for solid sorbents C$_{60}$ can be greatly improved using “superalkali” Li$_2$F cluster, because Li$_2$F can enhance interactions between the hydrogen and C$_{60}$. 
Hydrogen Storage Materials

Considering the practical meanings

- Because Li$_2$F has been experimentally obtained, Wang have **predict** that the Li$_2$F-like materials with lower ionization energy might provide a new way to enhance the interaction between H$_2$ and sorbents, and eventually improve the capability of hydrogen storage in near future.
EXPERIMENTAL WORK
“Superhalogen” clusters

Superhalogen clusters were obtained using Accelerator Mass Spectrometry (AMS),

- A. E. Litherland et al. The anions of the Li, Be and B fluorides: The super-halogens and AMS, Observation of LiF$_3^{2-}$

Laser Ablation Mass Spectrometry

Xianglei Kong et al. have been published about 40 SCI papers in the past five years, concerning: the study of new embedded metal fullerenes, the structure and properties of new “superhalogens”.

- Superhalogen Species of Titanium Oxide Related Clusters Generated by Laser Ablation,
- Structures and Superhalogen Properties of Pt$_2$Cl$_n$ (2 ≤ n ≤ 10).
“Superalkali” clusters

Two methods were used to obtain lithium “superalkali” clusters

- Kudo, Thermochemical properties of gaseous Li$_2$F
- Wu, The stability of the molecules Li$_4$O and Li$_5$O; Li$_3$S and Li$_4$S
- Kudo, Observation of hypervalent CLi$_6$
- Kudo and Kira Zmbov, Observation of gaseous Li$_4$P: A hypervalent molecule by standard Knudsen cell mass spectrometry (1991)

- Lievens et al.
  Ionization potentials of Li$_n$O (2<n<70) clusters
  The influence of O and C doping on the ionization potentials of Li-clusters.
- Yokoyama, Tanaka, and Kudo,
  Structure of hyperlithiated Li$_3$O and evidence for electronomers.
  By laser ablation mass spectrometry
Production clusters

Mass spectrometry is a key method for producing clusters.

Three major components of mass spectrometers

- **Ion Source**
  - for producing cluster ions with a mix of size from the appropriate sample

- **Mass Analyzer**
  - for separate the cluster ions to their mass-to-charge ratio (their size)

- **Detector System**
  - for identification the cluster ions and
  - recording the relative stabilities of each of the detected ionic species
Production “superalkali” clusters in Vinca Institute

The magnetic sector mass spectrometer Constructed in the Department of Physical Chemistry by dr Miomir Veljkovic

The ion source has three ionization methods:
- the electron impact
- the surface ionization
- the Knudsen cell
The Ion Source

1 - electron source
2 - gas inlet
3 – standard the Knudsen cell
4 – the carrier for the surface ionization source or the Knudsen cell.
The Surface Ionization Source

The **triple filament source** of surface ionization (rhenium filaments of the same dimension 8mm × 1mm × 0.05mm) consists of the side (evaporation) filaments and central filament.

- Li$_2$Cl and Li$_3$Cl
- Li$_2$Br and Li$_3$Br
- Li$_2$I and Li$_3$I
- Li$_3$F$_2$, Li$_4$F$_3$
- Li$_6$F$_5$
- Na$_2$Cl, Rb$_2$Cl, Cs$_2$Cl
- K$_2$F, K$_2$Cl, K$_2$Br, K$_2$I

The samples were the solutions of sodium, rubidium, cesium chloride salt.

- The samples were the solutions of potassium salts with halogen elements.


The samples For $\text{Li}_nX$ clusters

- The samples were the solutions of $\text{LiX}/ \text{LiI}$ ($X = \text{F, Cl, Br}$) salt, (lithium salts with halogen elements), which were deposited on the side filaments.
- $\text{LiI}$ was used as an additional source of $\text{Li}$ ions, since the dissociation energy of $\text{LiI}$ is lower than dissociation energy of $\text{LiF}$, and the vapor pressure of $\text{LiI}$ is higher than vapor pressure $\text{LiF}$.
- The $C_{60}$/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 in the range of (200-2000 K).
It was observed that the presence of C$_{60}$ on the ionizing Re filament provides suitable conditions for the emission of Li$_3$X$^+$ ions (X= Cl, Br, I).

The presence of LiI and C$_{60}$ under high vacuum and at high temperatures leads to the formation of Li/C$_{60}^+$ ions by the surface ionization technique. (Djeric AJ, Veljkovic MV, Neskovic OM, Miletic MB, Zmbov KF. Fullerene Sci. Technol. 2000; 8: 461)

A possible explanation of the role of C$_{60}$ in that lithium halogenated systems, is the presence of an additional Li source from Li/C$_{60}$. 
The Knudsen 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 6 mm and the orifice diameter was 0.1 mm.
- The sample was placed into the Knudsen cell, at atmospheric pressure, then the Knudsen cell is put in the mass spectrometer, and heats up.
- The Knudsen cell is chemical reactor - the source of neutral clusters.
- The neutral clusters obtained from the cell were ionized used the electron impact method.

The standard experimental setup places Knudsen cell outside of the ion source.
Modification

- In the experimental research that was carried out at the Department of Physical Chemistry, the Knudsen cell was placed into the ion source.

- This enabled more efficient ionization of the neutral clusters formed in the cell, because the Knudsen cell orifice was closer to the electron beam than in the standard case.

Figure Schematic diagram of the ion source: 1. ionization chamber; 2. Knudsen cell; 3. ceramic shields; 4. thermocouple; 5. heater for chamber tungsten wire; 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.
Results

The sample was the LiI/LiF/fulerene mixture. Thanks to the changes and variation of the molar ratio of LiF and LiI, two series of clusters were obtained

Li\textsubscript{n}I and Li\textsubscript{n}F

(n = 2, 3, 4, 5, and 6).

Another modification was that the Knudsen cell can be held on at + 30V with respect to the ion source, it allowed direct identification of positive charge cluster ions generated in the cell.

Modification

Heating the Knudsen cell is an important question. In the standard case, the heater is tungsten wire which is uniformly wrapped around the Knudsen cell. In our experiments the heater is placed directly in the cell.

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 results showed that in this condition the Knudsen cell becomes a more efficient cluster source.
Results

The samples were lithium and potassium salts with halogen elements. The serial of lithium and potassium mononuclear “superalkali” clusters such as, $\text{Li}_n\text{Br}$, $\text{Li}_n\text{Cl}$, $\text{K}_n\text{X}$ ($n = 2 - 6$) were obtained.

- The “superalkali” 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.

Our results have shown that the combination of the Knudsen cell and surface ionization is a simple, inexpensive, and efficient method for obtaining “superalkali” clusters.

Generally, 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.
THANK YOU FOR YOUR ATTENTION!