ENDOHEDRAL $(X@Zn_nS_n)^q$ CLUSTERS, X=Li, Na, K, F, Cl, Br, n=4-16, q=0, 1, -1

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INTRODUCTION

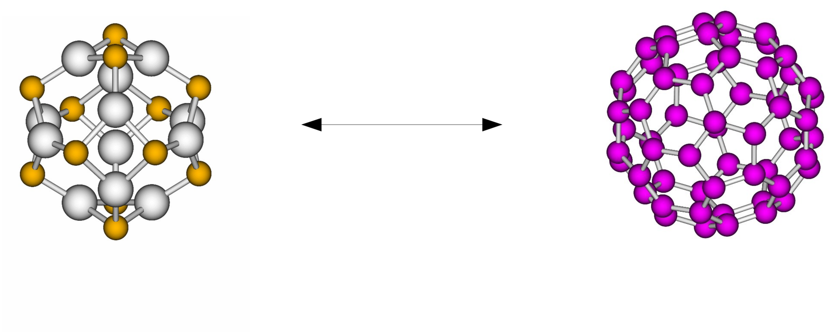
There has been an increased interest in theorical studies on II-VI clusters. Isolated neutral Zn_nS_n clusters, n= 4 - 47 have been theorically [1,2] studied in previous studies. The most stable structure were seen to be spheroid-like bubble structures, resembling carbon fullerenes. These structures have recently been synthesized experimentally, but in the cationic form [3].

Structural Pattern:

N_4 =6+N_8

N_6 =i-4-2N_8

$Zn_{12}S_{12}$ C_{60}



Structural Pattern:

N_5 =12 +N_7

N_6 =i-4-N_7

On the present work we have introduced alkali metals and halogens to characterized the endohedral compounds of these cationic, anionic and neutral clusters. They continue being bubbles built by squares and hexagons. Zn atoms are more inside than S atoms.

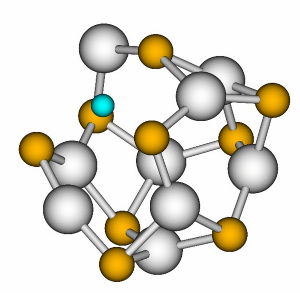
METHOD

Endohedral $(X@Zn_nS_n)^q$ clusters were described using the density functional theory (DFT). The relativistic compact effective core potentials and shared-exponent basis set [4] of Stevens, Krauss, Basch and Jasien [SKBJ(d))] was used for Zn and S atoms at the B3LYP level of theory [5]. There, the Zn d electrons are treated as valence electrons, giving 20 valence electrons per Zn. For X atoms, 6-311+G* basis set was used. All calculations were run using Gaussian 03.

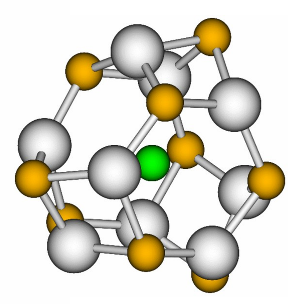
RESULTS AND DISCUSSION

First of all we have analized isolated neutral, cationic and anionic clusters.

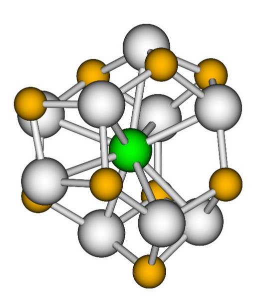
	Neutral	Cationic		Anionic	
i	r_{Zn}(Å)	r_{Zn}(Å)	IP(eV)	r_{Zn}(Å)	EA(eV)
4	1,72	1,78	8,63	1,77	2,00
6	2,22	2,25	7,97	2,29	1,97
8	2,66	2,72	8,47	2,72	1,95
9	2,81	2,82	8,18	2,87	1,96
10	3,00	3,00	8,00	3,05	2,07
11	3,16	3,59	7,87	3,21	2,03
12	3,28	3,30	8,28	3,33	1,97
13	3,48	3,47	7,94	3,53	2,10
14	3,60	3,59	7,87	3,65	2,10
15	3,72	3,73	8,05	3,77	2,07
16	3,88	3,85	8,05	3,89	2,10



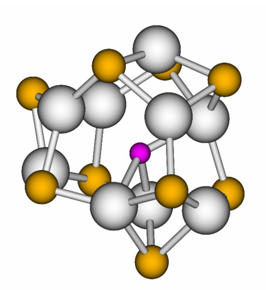
$Li@Zn_9S_9$



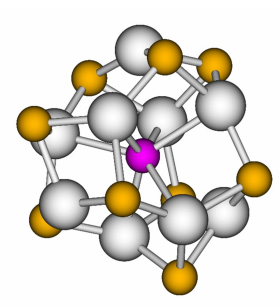
$Na@Zn_9S_9$



$K@Zn_9S_9$



$F@Zn_9S_9$



$Cl@Zn_9S_9$

Alkali metals (Li, Na, K) and halogens (F, Cl, Br) are introduced in the previously described spheroids. The data represent here is only for the endohedral clusters where the alkali metal or halogen atom put inside is kept in the middle.

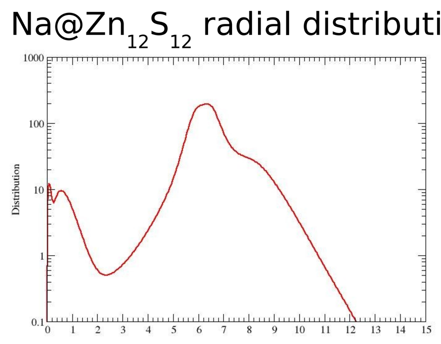
	r_{Zn}(Å)	q_X		r_{Zn}(Å)	q_X
$Li@Zn_4S_4$	2,13	0,32	$K@Zn_9S_9$	3,07	0,69
$(Li@Zn_4S_4)^+$	2,08	0,27	$K@Zn_{12}S_{12}$	3,45	0,64
$Na@Zn_9S_9$	3,03	0,60	$K@Zn_{15}S_{15}$	3,86	0,66
$Na@Zn_{12}S_{12}$	3,28	-0,22	$K@Zn_{16}S_{16}$	3,84	-0,07
$Na@Zn_{13}S_{13}$	3,64	0,65	$(K@Zn_9S_9)^+$	2,99	0,56
$Na@Zn_{15}S_{15}$	3,73	-0,16	$(K@Zn_{12}S_{12})^+$	3,41	0,61
$Na@Zn_{16}S_{16}$	3,83	-0,22	$(K@Zn_{16}S_{16})^+$	3,92	0,70
$(Na@Zn_9S_9)^+$	2,99	0,57			
$(Na@Zn_{13}S_{13})^+$	3,60	0,66			

q_X = natural charge

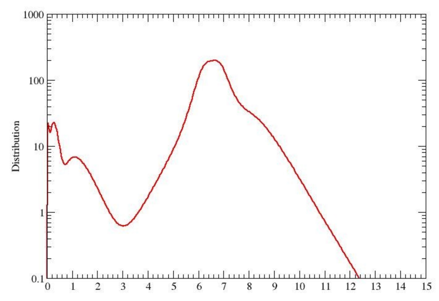
	r_{Zn}(Å)	q_X		r_{Zn}(Å)	q_X
$Cl@Zn_9S_9$	2,78	-0,93			
$Cl@Zn_{12}S_{12}$	3,21	-0,95	$Br@Zn_{12}S_{12}$	3,23	-0,93
$(Cl@Zn_9S_9)^-$	2,80	-0,93	$(Br@Zn_9S_9)^-$	2,84	-0,91
$(Cl@Zn_{12}S_{12})^-$	3,20	-0,96	$(Br@Zn_{12}S_{12})^-$	3,22	-0,95

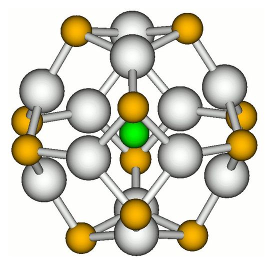
We can notice the electronic structure of the alkali metals and halogens at the radial distribution figures.

$Na@Zn_{12}S_{12}$ radial distribution



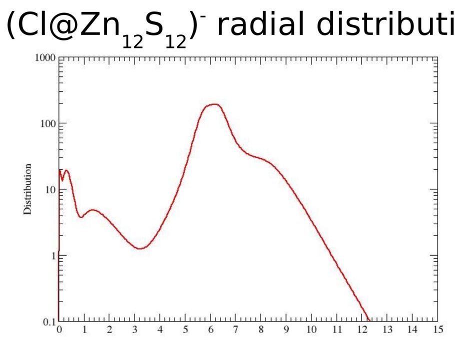
$K@Zn_{12}S_{12}$ radial distribution



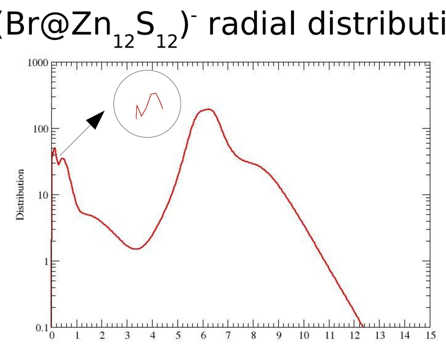


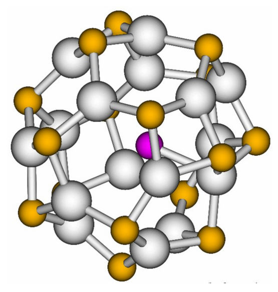
$Na@Zn_{12}S_{12}$

$(Cl@Zn_{12}S_{12})^-$ radial distribution



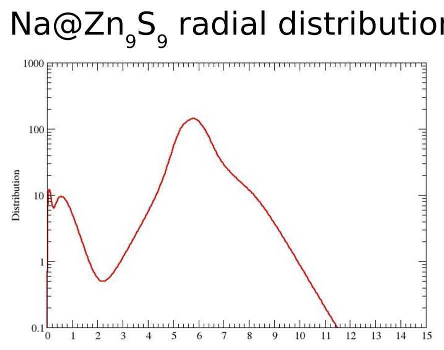
$(Br@Zn_{12}S_{12})^-$ radial distribution



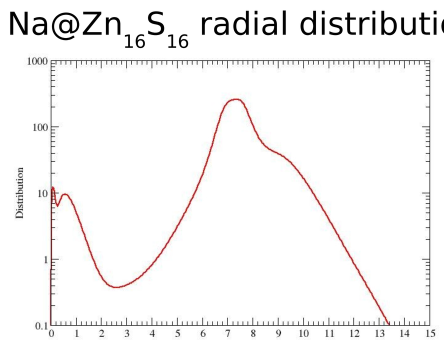


$Cl@Zn_{16}S_{16}$

$Na@Zn_9S_9$ radial distribution



$Na@Zn_{16}S_{16}$ radial distribution



* There are lots of properties involved:
  - Atoms's size and charge
  - Clusters's size and shape
* Alkali metals are easier to be trapped in the center of the cluster than halogens. The last ones, move very easy to one side of the cluster or make bonds with Zn atoms.
* These structures are stable. They may be synthesized experimentally.

ACKNOWLEDGMENTS

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BIBLIOGRAPHY

[1] J.M. Matxain et al., Phys. Rev. A, 2000, 61, 512
[2] S. Hamad et al., J. Phys. Chem. B, 2005, 109, 2703
[3] A. Burnin et al., J. Phys. Chem. A, 2005, 109, 5026
[4] W. J. Stevens et al., Can. J. Chem., 1992, 70, 612
[5] A. D. Becke, J. Chem. Phys. 1993, 98, 5648