Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary information (ESI)

Germanium-based superatom clusters as excess electron compounds with significant static and dynamic NLO response; A DFT Study

Atazaz Ahsin, Ahmed Bilal Shah, Khurshid Ayub*

Department of Chemistry, COMSATS University Islamabad, Abbottabad Campus, Abbottabad, KPK, 22060, Pakistan

Correspondence:

khurshid@cuiatd.edu.pk (K. A.)

1. Optimized geometric analysis

The obtained geometric parameters of these clusters are given in Table 1 (ESI). The obtained point group symmetry of Ge_5AM_3, Ge_9AM_5 and $Ge_{10}AM_3$ (where AM = Li, Na, K) are C_S, C_{4V}, and C_2 respectively. The calculated equilibrium bond length ($X_{Ge\text{-}Ge}$) in the Ge_5AM_3 series are lie in the range of 2.53 to 2.54 Å. Similarly, the obtained values of $X_{Ge\text{-}Ge}$ bond length in the Ge_9AM_5 series are slightly enhanced and lie in the range of 2.57 to 2.68 Å. However, the calculated average values of $X_{Ge\text{-}Ge}$ bond lengths between germanium atoms in $Ge_{10}AM_3$ clusters are further increased. Thus the observed trend average computed bond length (Ge-Ge) within the clusters series is $Ge_5AM_3 < Ge_9AM_5 < Ge_{10}AM_3$. One can also conclude that, with the increased cluster size, there is a gradual enhancement in bond distance between the germanium atom from Ge_5 to Ge_9 and then to Ge_{10}.

Furthermore, the computed average bond lengths ($X_{Ge\text{-}AM}$) for Ge_5AM_3 clusters lie in the range of 2.51 to 3.34 Å. In the series (Ge_5AM_3), the observed bond length increases monotonically with increased metal sized. Thus highest computed bond length $X_{Ge\text{-}AM}$ (where AM = Li, Na, K) value of 3.34 Å is observed for the Ge_5K_3 cluster while the lowest of 2.51 Å is indicated for the Ge_5Li_3 cluster. Similarly, the calculated value of ($X_{Ge\text{-}AM}$) bond lengths for the of zintl Ge_9AM_5 lie in the rage of 2.57 to 3.33 Å. The highest obtained value of 3.33 Å for Ge_9K_5 is attributed to large sized alkali metal.

Table S1: Point group symmetry, average computed $X_{Ge\text{-}Ge}$ bond length (in Å), average computed $X_{Ge\text{-}AM}$ bond lengths (in Å where AM=Li, Na, K), binding energy per atom (E_B in kcal mol^{-1}), and total energy (E_{tot} in hartree) of studied superalkali clusters.

Ge_5AM_3				
Superalkalis	**Symmetry**	**$X_{Ge\text{-}Ge}$**	**$X_{Ge\text{-}AM}$**	**E_{tot}**
Ge_5Li_3 (A)	C_S	2.56	2.51	10408.09
Ge_5Na_3 (B)	C_S	2.53	2.84	10872.40
Ge_5K_3 (C)	C_S	2.52	3.34	12185.41
Ge_9AM_5				
Ge_9Li_5 (D)	C_{4V}	2.57	2.57	18731.62
Ge_9Na_5 (E)	C_{4V}	2.66	3.01	19505.47
Ge_9K_5 (F)	C_{4V}	2.68	3.33	21693.84

$Ge_{10}AM_3$				
$Ge_{10}Li_3$ (G)	C_2	2.84	2.56	20793.65
$Ge_{10}Na_3$ (H)	C_2	2.65	2.94	21257.97
$Ge_{10}K_3$ (I)	C_2	2.73	3.24	22571.01

2. **Optimized geometric coordinates at CAM-B3LYP/6-311+G(d,p)**
   The optimized geometries and their cartesian coordinates at above functional are given in Table 2.

Table S2: Optimized geometric coordinates of Ge_5AM_3, Ge_9AM_5, $Ge_{10}AM_3$ clusters

Ge_5AM_3 (where AM=Li, Na K)

A

1	**32**	**0**	**-1.884226**	**0.850537**	**0.000000**
2	**32**	**0**	**-0.389141**	**-0.677590**	**1.349466**
3	**32**	**0**	**-0.389141**	**-0.677590**	**-1.349466**
4	**32**	**0**	**0.840445**	**1.340237**	**0.000000**
5	**32**	**0**	**1.891553**	**-0.894711**	**0.000000**
6	**3**	**0**	**0.037077**	**-2.981132**	**0.000000**
7	**3**	**0**	**-0.389141**	**1.805857**	**2.325246**
8	**3**	**0**	**-0.389141**	**1.805857**	**-2.325246**

B

1	**32**	**0**	**-2.124191**	**0.843194**	**0.000000**
2	**32**	**0**	**-0.274994**	**-0.225238**	**1.380866**
3	**32**	**0**	**-0.274994**	**-0.225238**	**-1.380866**
4	**32**	**0**	**1.554371**	**0.977147**	**0.000000**
5	**32**	**0**	**1.317566**	**-1.618584**	**0.000000**
6	**11**	**0**	**-0.274994**	**2.394316**	**1.429215**
7	**11**	**0**	**-1.559439**	**-1.904018**	**0.000000**
8	**11**	**0**	**-0.274994**	**2.394316**	**-1.429215**

C

1	**32**	**0**	**-2.053163**	**0.690772**	**0.000000**
2	**32**	**0**	**-0.176512**	**-0.343358**	**1.363159**
3	**32**	**0**	**-0.176512**	**-0.343358**	**-1.363159**
4	**32**	**0**	**1.676226**	**0.862787**	**0.000000**
5	**32**	**0**	**1.428969**	**-1.735165**	**0.000000**
6	**19**	**0**	**-1.680455**	**-2.387954**	**0.000000**
7	**19**	**0**	**-0.176512**	**2.456993**	**1.732894**

8	19	0	-0.176512	2.456993	-1.732894

Ge_9AM_5

D

1	32	0	1.877671	0.000000	-1.399972
2	32	0	-1.410469	1.410469	0.807043
3	32	0	-1.877671	0.000000	-1.399972
4	32	0	0.000000	-1.877671	-1.399972
5	32	0	0.000000	1.877671	-1.399972
6	32	0	0.000000	0.000000	2.533846
7	32	0	1.410469	-1.410469	0.807043
8	32	0	-1.410469	-1.410469	0.807043
9	32	0	1.410469	1.410469	0.807043
10	3	0	0.000000	3.762213	0.394238
11	3	0	0.000000	0.000000	-3.306325
12	3	0	3.762213	0.000000	0.394238
13	3	0	-3.762213	0.000000	0.394238
14	3	0	0.000000	-3.762213	0.394238

E

1	32	0	-0.000044	-1.296794	1.891368
2	32	0	1.594194	0.819133	-1.285309
3	32	0	-0.000037	-1.299661	-1.889546
4	32	0	-1.801465	-1.497280	0.000983
5	32	0	1.801365	-1.497385	0.000990
6	32	0	0.000070	2.439021	-0.001499
7	32	0	-1.594464	0.821109	1.284116
8	32	0	-1.594127	0.819221	-1.285318
9	32	0	1.594512	0.821022	1.284119
10	11	0	3.874235	0.104991	0.000071
11	11	0	0.000040	0.873018	-3.285682
12	11	0	0.000022	0.877962	3.284110
13	11	0	-3.874220	0.105245	0.000031
14	11	0	-0.000097	-3.204240	0.002418

F

1	32	0	-0.000023	1.797508	1.341929
2	32	0	1.428077	-1.390586	-0.836325
3	32	0	-0.000090	-1.798469	1.338650
4	32	0	-1.904868	-0.001538	1.363939
5	32	0	1.904707	-0.001564	1.364082
6	32	0	0.000090	0.002559	-2.523112
7	32	0	-1.427761	1.391643	-0.832651
8	32	0	-1.428051	-1.390481	-0.836404

9	32	0	1.427892	1.391549	-0.832578
10	19	0	4.466674	0.001246	-0.919075
11	19	0	0.000220	4.436661	-0.733006
12	19	0	-4.466471	0.001591	-0.919423
13	19	0	-0.000152	-4.437295	-0.735491
14	19	0	-0.000225	-0.003250	4.069048

Ge_0AM_3

G

1	32	0	2.142890	0.133790	-0.775192
2	32	0	-0.881017	-1.887825	0.770452
3	32	0	-2.142890	-0.133790	-0.775192
4	32	0	0.000000	1.288547	-1.861020
5	32	0	0.000000	-1.288547	-1.861020
6	32	0	-1.256068	0.453309	1.817801
7	32	0	0.881017	1.887825	0.770452
8	32	0	-1.613176	2.366289	-0.009281
9	32	0	1.256068	-0.453309	1.817801
10	32	0	1.613176	-2.366289	-0.009281
11	3	0	0.000000	0.000000	4.104612
12	3	0	-2.267041	-2.716739	-1.441740
13	3	0	2.267041	2.716739	-1.441740

H

1	32	0	2.216692	0.563433	-0.580820
2	32	0	-0.430143	-1.998719	0.767084
3	32	0	-2.216692	-0.563433	-0.580820
4	32	0	0.000000	1.261030	-1.856468
5	32	0	0.000000	-1.261030	-1.856468
6	32	0	-1.312450	0.272097	1.758832
7	32	0	0.430143	1.998719	0.767084
8	32	0	-1.980202	1.965648	-0.333863
9	32	0	1.312450	-0.272097	1.758832
10	32	0	1.980202	-1.965648	-0.333863
11	11	0	-1.858055	-3.072946	-1.242730
12	11	0	0.000000	0.000000	3.912281
13	11	0	1.858055	3.072946	-1.242730

I

1	32	0	2.142890	0.133790	-0.775192
2	32	0	-0.881017	-1.887825	0.770452
3	32	0	-2.142890	-0.133790	-0.775192
4	32	0	0.000000	1.288547	-1.861020
5	32	0	0.000000	-1.288547	-1.861020
6	32	0	-1.256068	0.453309	1.817801

7	32	0	0.881017	1.887825	0.770452
8	32	0	-1.613176	2.366289	-0.009281
9	32	0	1.256068	-0.453309	1.817801
10	32	0	1.613176	-2.366289	-0.009281
11	19	0	-2.267041	-2.716739	-1.441740
12	19	0	2.267041	2.716739	-1.441740
13	19	0	0.000000	0.000000	4.104612
