Available online at www.sciencedirect.com

International Journal of Mass Spectrometry 253 (2006) 104–111

www.elsevier.com/locate/ijms

Structures and charge distributions of cationic and neutral Li_nX_m (X = Na and K)

Zhen-Yi Jiang[a,b], Kuo-Hsing Lee[c], Sheng-Tao Li[b], San-Yan Chu[c,*]

[a] Multi-disciplinary Materials Research Center, Xi'an Jiaotong University, Xi'an 710049, China
[b] State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China
[c] Department of Chemistry, National Tsing Hua University, Hsinchu, 30013, Taiwan

Received 16 March 2006; received in revised form 10 April 2006; accepted 10 April 2006
Available online 15 May 2006

Abstract

The structures, stability, and charge distributions in the Li_nX_m (X = Na and K, $n+m=1$–7, $m=1$–2) neutral and cationic clusters have been investigated using B3LYP method. Structural optimizations and frequency analyses were performed with the basis set of 6-311G(d). Our results reveal that all Li_nX_m clusters can be viewed as substitutions of peripheral Li atoms with Na or K atoms in the Li_{n+m}. Atomic charges depend on its position and ability to obtain/lose electron. In various mixed lithium species, Li_nX_m ($n+m=$ even number) and Li_nX_m^+ ($n+m=$ odd number) clusters are predicted to be more stable, which can be attributed to difficulty in removing an electron from the doubly occupied HOMO of a closed-shell system.

Keywords: Alkali metal cluster; Stability; Geometric configuration; Charge distributions; Evaporation experiments

1. Introduction

Study of small metal clusters has been a subject of intense interest from both experimental and theoretical points of view, mainly because of the strong dependence of their electronic structures and properties on their sizes and geometries as well as their elementary valence electron structure. In particular, alkali metal clusters have been considered to be one of the prototype systems for the study of size-dependent electronic properties, such as binding energy, ionization potential, electron affinity, etc. The pronounced abundances in the mass spectra of alkali metal clusters generally imply clusters of special stability at particular number of electrons viz. 2, 8, 18, 20, etc. Many theoretical calculations have been carried out for alkali metal clusters, however, most studies were focused on the pure alkali metal clusters [1–17], nevertheless much less is known for the mixed Li–Na or Li–K clusters [18–25].

In recent years a large number of binary clusters of lithium with some metallic or nonmetallic elements including sodium, aluminum, fluorine etc have been produced by laser vaporization of various lithium targets in high vacuum [18–22,26,27]. However the laboratory spectroscopy has not yet been well explained due to the lack of the reliable information of their geometrical and electronic structures. Despite the geometrical arrangements of Li_nNa_m ($n+m<5$) have been studied [18–25], their electronic charge distributions have not been reported. Deshpande et al. [28,29] studies Li_nNa and Na_nLi ($0<n<13$) clusters with ab initio molecular dynamic method, however, the reliable geometrical structures and charge distributions of these clusters have not been given due to the limitation of the molecular dynamic methods. Up to now no systematic study of geometries and charge distributions has been reported for Li_nX_m (X = Na and K) charged and neutral clusters. Hence it is of interest to carry on an investigation to reveal the geometrical and electronic charge distributions of doped lithium clusters in the Li_nNa_m and Li_nK_m ($n=1$–6, $m=1$–2) clusters.

2. Computational methods

Initial geometrical optimizations were performed at the B3LYP/6-31G(d) level without any symmetry constraints, except for those needed to maintain a particular geometry. These isomers were further optimized at B3LYP/6-311G(d) level. After optimizations, partial charges were obtained from natural pop-

---

* Corresponding author. Tel.: +886 35715131/33390.
E-mail addresses: jiang_chemphy@yahoo.com (Z.-Y. Jiang), sychu@mx.nthu.edu.tw (S.-Y. Chu).

1387-3806/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2006.04.002

ulation analysis (NPA) [30,31]. The NPA solves most of the problems of the Mulliken scheme by construction of a more appropriate set of atomic basis functions, and so the atomic charges from NPA are reliable and usually independent of the basis sets. The Mulliken atomic charge distributions were also reported for comparison in bracket at the same level despite its well-known shortcoming in overestimating the net atomic charge [30–33]. Frequency analyses were also performed at the final theoretical level to check whether the optimized structures are transition states or true minima on the potential energy surfaces of corresponding clusters. All of the obtained most stable charged and neutral Li_nX_m clusters were characterized as energy minima without imaginary frequencies. The first electron ionization potentials (IPs) of various clusters were calculated with adiabatic approximation. All calculations were carried out using the GAUSSIAN03 program [34].

In the geometry optimizations of $Li_nX_m (m = 1–2)$, we started with three structures; (1) the same structure as Li_{n+m} determined by Refs. [1–17] where one/two Li atoms were substituted by one/two X atoms, (2) the structure where one Li atom was added to a $Li_{n-1}X_m$ cluster, and (3) the structure where one/two X atoms were added to a Li_nX_{m-1}/Li_nX_{m-2} molecule.

3. Theoretical results

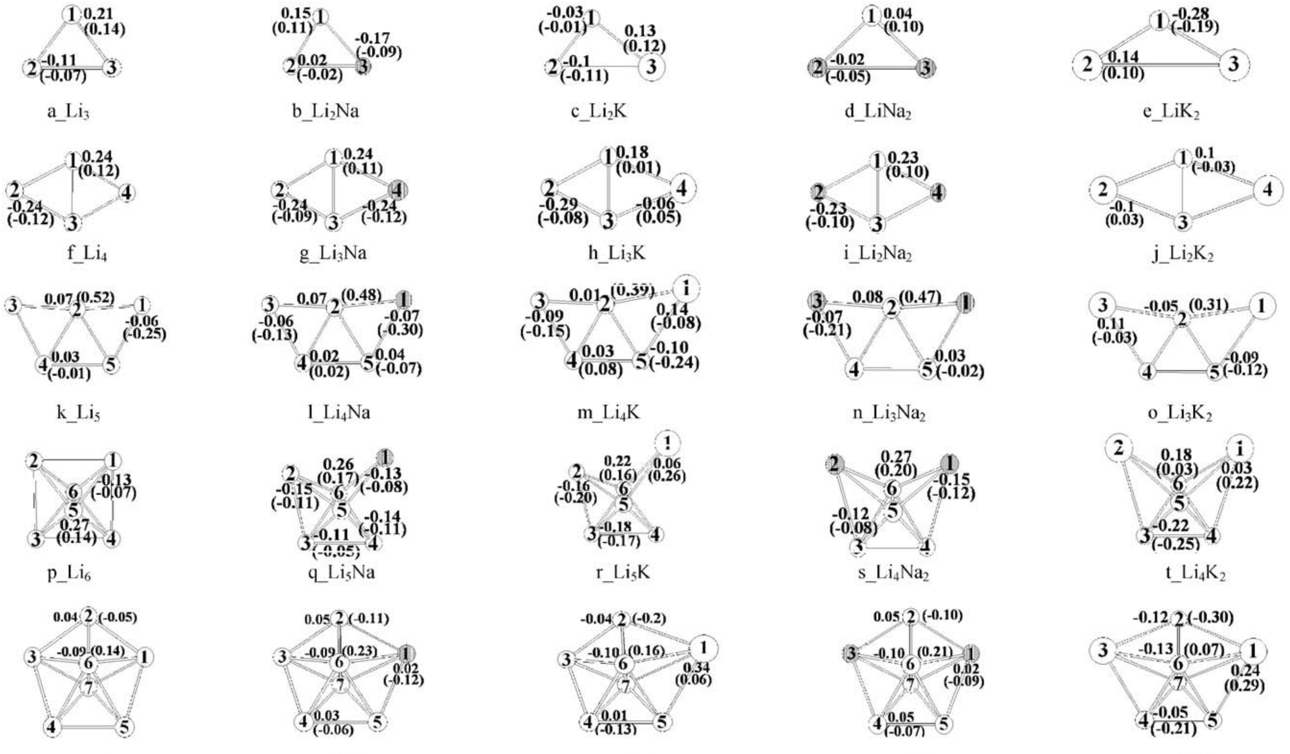
3.1. Geometry and charge distributions

The ground state geometric sketches of Li_nX_m and $Li_nX_m^+$ $(n + m = 3–7,\ m = 1–2)$ clusters were shown in Figs. 1 and 2, respectively. The “bonds” are shown for internuclear separations less than 3.6 Å (Li–Li), 3.7 Å (Li–Na), 4.3 Å (Na–Na), 4.5 Å (Li–K), and 5.9 Å (K–K), respectively. The internuclear separations of the geometrical structures of all ground states are given in Tables 1 and 2. The SCF energies and zero point energies (ZPE) of all clusters are reported in Tables 3 and 4.

The photoelectron spectra [35–37] of Li_n^- $(n = 2–5)$ clusters are similar to those of Na_n and K_n clusters in the relative peak positions and their envelopes, which suggest that the pure Li_n, Na_n and K_n clusters have analogical geometrical structures. Secondly, All theoretical studies of pure Li_n [1–17], Na_n [15,38–47] and K_n [1,44] $(n = 3–7)$ have also predicted their similarities in geometry. This is attributed to the fact that Li, Na and K atoms take a similar valence structure due to the same family in the periodic table. Thus the calculated geometrical and electronic structures of Li_nX_m (X = Li, Na, and K; $m = 1–2$) clusters should be analogous to those of pure Li_{n+m} clusters. Our calculations as follows agree with these initial guess, which suggest our theoretical methods and final structures to be reliable.

3.1.1. LiX

Li_2^+ $(^2\Sigma_g^+, D_{\infty h})$, $LiNa^+$ and LiK^+ $(^2\Sigma_g^+, C_{\infty v})$ have longer bond lengths relative to their neutral molecules $(^2\Sigma_g^+, C_{\infty v})$. Interestingly, the binding energies of Li_2^+ and $LiNa^+$ are 1.27 and 1.03 eV, respectively, which are higher than those of corresponding molecules (0.90 and 0.80 eV). Nevertheless the binding energy (0.56 eV) of LiK^+ is smaller than that of neutral LiK (0.66 eV). Our binding energies calculated agrees satisfactorily with experimental observations for Li_2 (1.057 eV) [48] and Li_2^+ (1.298 eV) [49]. The Li and Na atoms bear 0.46 and 0.54e charge



a_Li_3 b_Li_2Na c_Li_2K d_$LiNa_2$ e_LiK_2

f_Li_4 g_Li_3Na h_Li_3K i_Li_2Na_2 j_Li_2K_2

k_Li_5 l_Li_4Na m_Li_4K n_Li_3Na_2 o_Li_3K_2

p_Li_6 q_Li_5Na r_Li_5K s_Li_4Na_2 t_Li_4K_2

u_Li_7 v_Li_6Na w_Li_6K x_Li_5Na_2 y_Li_5K_2

Fig. 1. Neutral ground-state structures of Li_nX_m clusters. Li and K atoms are shown by the smaller and bigger white ball, respectively.

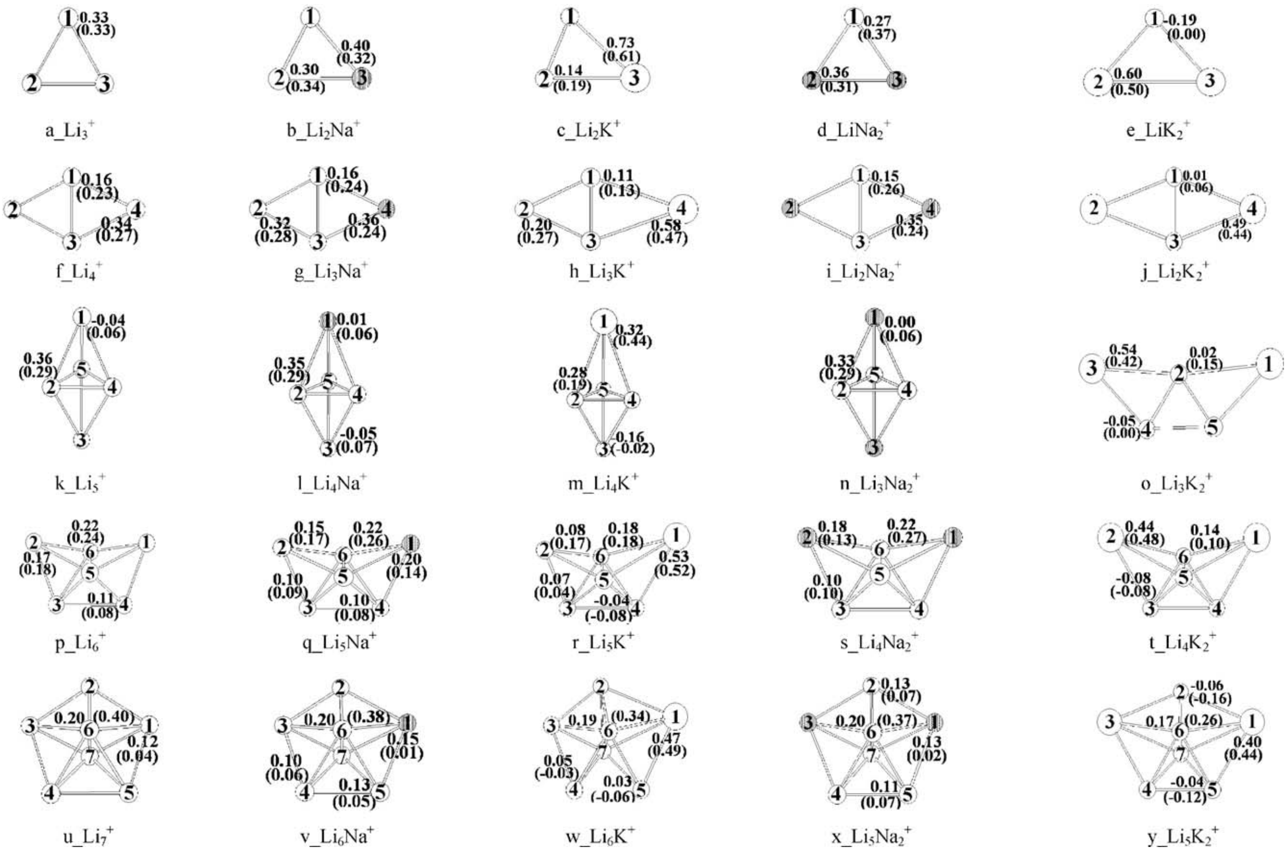


Fig. 2. Cationic ground-state structures of $Li_nX_m^+$ clusters. Li and K atoms are shown by the smaller and bigger white ball, respectively.

in the $LiNa^+$, respectively. The binding energy of Li_2^+ is greater than that of $LiNa^+$ cation, which suggests that Li_2^+ are more energetically favorable over the $LiNa^+$ cation.

The behaviors of Li_2 and LiNa upon ionization can be rationalized as follows [50]. As in the simple molecular orbital (MO) binding model, removal of a binding electron reduces the electron density between the nuclei, causing a bond length increase. The core/valence interactions in a molecule like Li_2 are actually quite large relative to the valence/valence interactions. In moving from a Li_2 diatom to Li_2^+ the core orbitals are stabilized by 0.24 hartree, which is more than the increase in energy for the loss of a bonding electron since alkali-metal dimers are weakly bonded. The presence of polarization in the ion and the core/valence electrons interactions [10] helps to stabilize the Li_2^+ and $LiNa^+$ bond and to enhance the attraction between the nuclei at long range. In LiK^+ system polarization effects are not marked and then finally cannot produce qualitative anomalies like the Li_2^+–Li_2 and $LiNa^+$–LiNa binding energy difference.

3.1.2. $Li_{3-m}X_m$

The global minima of Li_2Na and Li_2K are triangle ($^2A'$, C_s) configurations Fig. 1(b) and (c), which can be viewed as a substitution of the peripheral Li atom with the most negative charges by a Na/K atom in a triangle Li_3 ($^2B_2$, C_{2v}) molecule [2–7,11,12,14–16,21,23,51] Fig. 1(a). The electronic charges redistribute in the Li_2X after the X atom occupies the Li atomic position in the triangle Li_3 molecule. K and Na atoms bear positive and negative charges, respectively.

The structures of $LiNa_2$ and LiK_2 are determined as triangle ($^2B_2$, C_{2v}) configurations Fig. 1(d) and (e), which can be viewed as two substitutions of the peripheral Li atoms by two Na/K atoms in a triangle Li_3 ($^2B_2$, C_{2v}) cluster Fig. 1(a).

The symmetries of Li_3^+ ($^1A_1'$, D_{3h}), Li_2Na^+ and Li_2K^+ ($^1A_1$, C_{2v}) rise ($C_{2v} \rightarrow D_{3h}$, $C_s \rightarrow C_{2v}$) upon charging. The binding energies of Li_3^+, Li_2Na^+ and Li_2K^+ are 2.84, 2.52 and 1.80 eV, respectively, which are higher than those of corresponding molecules (1.43, 1.30 and 1.16 eV).

The binding energies of $LiNa_2^+$ and LiK_2^+ are 2.41 and 1.79 eV, respectively, which are also higher than those of corresponding molecules (1.16 and 0.93 eV). The higher binding energies of Li_3^+, Li_2Na^+, $LiNa_2^+$, Li_2K^+, and LiK_2^+cationic species can be attributed to filled-shell with two valence electrons.

3.1.3. $Li_{4-m}X_m$

Dahlseid et al. [19] and others [18,21] investigated several different neutral Li_3Na isomers with ab initio and DFT methods. We support their predictions that the energetically most favorable isomer is the planar rhombus ($^1A_1$, C_{2v}) Fig. 1(g). Both Li_3Na and Li_3K Fig. 1(h) can be described as a substitution of the peripheral Li atom with the most negative charges by a Na/K atom in a rhombus Li_4 (^1A_g, D_{2h}) molecule

Table 1
Distances between two atoms (L, Å) in Li_nX_m molecules

	Type	L		Type	L
Li_2		2.705	Li_6	1-2	3.527
LiNa		2.891		5-6	2.546
LiK		3.358	Li_5Na	1-2	4.304
Li_3	1-2	2.757		3-4	3.204
	2-3	3.299		2-3	3.276
Li_2Na	1-2	2.690		1-4	3.957
	2-3	3.546		1-5	3.065
	1-3	3.096		4-5	2.866
Li_2K	1-2	2.781		5-6	2.532
	2-3	4.478	Li_5K	1-5	3.550
	1-3	3.488		2-3	3.240
$LiNa_2$	1-2	3.001		2-5	2.871
	2-3	4.260		3-5	2.828
LiK_2	1-2	3.512		5-6	2.530
	2-3	5.898	Li_4Na_2	1-2	4.898
Li_4	1-2	3.010		3-4	3.082
	1-3	2.580		2-3	3.628
Li_3Na	1-2	3.005		1-5	3.120
	1-3	2.608		5-6	2.545
	1-4	3.216	Li_4K_2	1-2	5.436
Li_3K	1-2	3.022		3-4	3.178
	1-3	2.617		2-3	4.186
	1-4	3.748		1-5	3.607
Li_2Na_2	1-2	3.212		5-6	2.546
	1-3	2.636	Li_7	1-2	3.022
Li_2K_2	1-2	3.772		6-7	2.730
	1-3	2.646	Li_6Na	1-2	3.273
Li_5	1-2	2.974		1-6	3.217
	1-5	2.963		2-6	2.932
	2-5	2.859		6-7	2.758
	4-5	3.045		3-6	2.899
Li_4Na	1-2	3.203		3-4	3.041
	1-5	3.166	Li_6K	1-2	3.740
	2-5	2.888		1-6	3.761
	2-4	2.839		2-6	2.945
	4-5	3.035		6-7	2.754
	2-3	2.970		3-6	2.906
	3-4	2.972		3-4	2.994
Li_4K	1-2	3.706	Li_5Na_2	1-2	3.206
	1-5	3.710		2-6	2.963
	2-5	2.905		1-6	3.212
	2-4	2.806		6-7	2.784
	4-5	3.049		4-5	2.919
	2-3	2.971		4-6	2.914
	3-4	2.969	Li_5K_2	1-2	3.688
Li_3Na_2	1-2	3.199		2-6	2.971
	1-5	3.174		1-6	3.775
	2-5	2.869		6-7	2.782
	4-5	3.027		4-5	2.920
Li_3K_2	1-2	3.704		4-6	2.934
	1-5	3.704			
	2-5	2.865			
	4-5	3.049			

[2–8,10–12,14–16,21,51]. This substitution of the peripheral Li atom can lead to the slightest geometrical reconstruction because of the larger atomic radius of X atom. This replacement will keep the global minima of geometrical structures in the course of substitution from pure lithium to the mixed clusters. After substitution all charges will redistribute depending on the atomic positions and ability to obtain/lose electron. Different charges between Na and K atoms show the influence of IP on the charge distribution in Li_3Na and Li_3K molecules.

Calculations [18–20] on the Li_2Na_2 cluster indicates that the most stable neutral isomer is a rhombus (^1A_g, D_{2h}) configuration Fig. 1(i). The rhombus (^1A_g, D_{2h}) configurations Fig. 1(i) and (j) can be viewed as two substitutions of the peripheral Li atoms

Table 2
Distances between two atoms (L, Å) in $Li_nX_m^+$ cations

	Type	L		Type	L		Type	L
Li_2^+		3.088	$Li_3Na_2^+$	1-2	3.382	$Li_4K_2^+$	1-4	3.839
$LiNa^+$		3.357		2-4	2.740		1-5	3.903
LiK^+		3.854	$Li_3K_2^+$	1-2	4.112		3-4	3.285
Li_3^+	1-2	2.952		1-3	8.197		4-5	2.921
Li_2Na^+	1-2	2.957		1-5	3.574		5-6	2.548
	2-3	3.192		2-5	2.839	Li_7^+	1-2	3.183
Li_2K^+	1-2	2.841		4-5	3.654		6-7	2.438
	2-3	3.804	Li_6^+	1-4	3.074	Li_6Na^+	1-2	3.422
$LiNa_2^+$	1-2	3.196		1-5	3.058		1-6	3.265
	2-3	3.399		3-4	3.351		2-6	2.983
LiK_2^+	1-2	3.618		4-5	2.938		6-7	2.452
	2-3	4.702		5-6	2.530		3-6	2.966
Li_4^+	1-2	3.103	Li_5Na^+	1-4	3.307		3-4	3.221
	1-3	2.710		1-5	3.324	Li_6K^+	1-2	3.943
Li_3Na^+	1-2	3.065		4-5	2.961		1-6	3.895
	1-3	2.735		5-6	2.552		2-6	2.978
	1-4	3.380		2-3	3.079		6-7	2.452
Li_3K^+	1-2	3.015		2-5	3.061		3-6	2.968
	1-3	2.695		3-5	2.922		3-4	3.127
	1-4	4.032		3-4	3.315	$Li_5Na_2^+$	1-2	3.361
$Li_2Na_2^+$	1-2	3.335	Li_5K^+	1-4	3.913		2-6	2.997
	1-3	2.759		1-5	3.904		1-6	3.266
$Li_2K_2^+$	1-2	3.899		4-5	2.946		6-7	2.469
	1-3	2.690		5-6	2.534		4-5	3.077
Li_5^+	1-2	3.148		2-3	3.054		4-6	2.979
	2-4	2.692		2-5	3.050	$Li_5K_2^+$	1-2	3.885
Li_4Na^+	1-2	3.375		3-5	2.895		2-6	2.968
	2-3	3.155		3-4	3.313		1-6	3.908
	2-4	2.716	$Li_4Na_2^+$	1-4	3.312		6-7	2.472
Li_4K^+	1-2	3.969		1-5	3.328		4-5	3.070
	2-3	3.164		3-4	3.281		4-6	2.976
	2-4	2.700		4-5	2.946			
				5-6	2.575			

with the most negative charges by two Na/K atoms in a rhombus Li_4 cluster Fig. 1(f).

The Li_3X^+ and $Li_2X_2^+$ cationic species have analogical structures to their corresponding molecules. All atoms possess positive charges, and K atoms bear the most positive charges. The Li_3X^+ can be described as a substitution of the peripheral Li atom with the most positively charges by a Na/K atom in a rhombus Li_4^+ cations. The X atom apparently prefers to occupy the peripheral positions rather than those with the most negative/positive charge in the cluster when the electronic charges are taken into account in both neutral and cationic clusters.

3.1.4. $Li_{5-m}X_m$

Deshpande et al. [28] predicted the ground state of Li_4Na to be a bipyramid analogical to the Fig. 2(l) with MD method.

Table 3
B3LYP SCF energies and ZPEs values at 6-311G(d) level for Li_nX_m

Li_nNa_m				Li_nK_m		
n/m	Symmetry	Energy (a.u.)	ZPE (a.u.)	Symmetry	Energy (a.u.)	ZPE (a.u.)
1/1	$C_{\infty v}$	169.8074	0.0006	$C_{\infty v}$	607.4418	0.0005
2/1	C_s	177.3168	0.0013	C_s	614.9514	0.0011
3/1	C_{2v}	184.8489	0.0027	C_{2v}	622.4788	0.0025
4/1	C_s	192.3693	0.0037	C_s	630.0014	0.0035
5/1	C_s	199.9051	0.0056	C_{2v}	637.5368	0.0054
6/1	C_{2v}	207.4377	0.0069	C_{2v}	645.0693	0.0066
1/2	C_{2v}	332.1072	0.0010	C_{2v}	1207.3778	0.0008
2/2	D_{2h}	339.6393	0.0024	D_{2h}	1214.8998	0.0018
3/2	C_{2v}	347.1598	0.0033	C_{2v}	1222.4234	0.0029
4/2	C_{2v}	354.6939	0.0052	C_{2v}	1229.9559	0.0046
5/2	C_{2v}	362.2229	0.0063	C_{2v}	1237.4856	0.0057

Table 4
B3LYP SCF energies and ZPEs values at 6-311G(d) level for $Li_nX_m^+$

	Li_nNa_m			Li_nK_m		
n/*m*	Symmetry	Energy (a.u.)	ZPE (a.u.)	Symmetry	Energy (a.u.)	ZPE (a.u.)
1/1	$C_{\infty v}$	169.6168	0.0004	$C_{\infty v}$	607.2728	0.0003
2/1	C_{2v}	177.1626	0.0015	C_{2v}	614.8097	0.0013
3/1	C_{2v}	184.6830	0.0023	C_{2v}	622.3288	0.0022
4/1	C_{3v}	192.2184	0.0041	C_{3v}	629.8564	0.0038
5/1	C_s	199.7497	0.0053	C_{2v}	637.3901	0.0051
6/1	C_{2v}	207.2943	0.0069	C_{2v}	644.9321	0.0067
1/2	C_{2v}	331.9540	0.0011	C_{2v}	1207.2443	0.0009
2/2	D_{2h}	339.4746	0.0020	D_{2h}	1214.7619	0.0016
3/2	D_{3h}	349.0080	0.0037	C_2	1222.2865	0.0026
4/2	C_{2v}	354.5389	0.0049	C_{2v}	1229.8171	0.0044
5/2	C_{2v}	362.0818	0.0064	C_{2v}	1237.3558	0.0058

Present study concludes the different isomer Fig. 1(l). The Li_4Na and Li_4K molecules were found to be a planar trapezoid $({}^2A', C_s)$ Fig. 1(l) and (m), respectively. This can be described as a substitution of the peripheral Li atom by a Na/K atom in a planar trapezoid Li_5 $({}^2A_1, C_{2v})$ molecule [1–5,11,15,51] Fig. 1(k). We should note that our calculations found the $({}^2B_1, C_{2v})$ bipyramid similar to Fig. 2(k) as global minimum for the neutral lithium pentamer, which is in agreement with previous prediction [6]. It is more stable than that isomer Fig. 1(k) only by 0.04 eV, so they may coexist experimentally. For comparison the geometrical configuration Fig. 1(k) is reported here.

The planar trapezoid $({}^2A_1, C_{2v})$ Fig. 1(n) and Fig. 1(o) have been found as a global minimum for Li_3Na_2 and Li_3K_2, which can be viewed as two substitutions of the peripheral Li atoms by two Na/K atoms in a planar trapezoid $({}^2A_1, C_{2v})$ Li_5 cluster Fig. 1(k). The K atom bears positive charges due to its smaller IP value.

The bipyramid $({}^1A_1, C_{3v})$ configurations Fig. 2(l) and (m) have been found as a global minimum for Li_4Na^+ and Li_4K^+, which can be viewed as a substitution of the peripheral Li atom by a Na/K atom in the bipyramid $({}^1A_1', D_{3h})$ Li_5^+ cluster [3,11] Fig. 2(k). There exists a similar situation in $({}^1A_1', D_{3h})$ $Li_3Na_2^+$ cationic configuration Fig. 2(n). $Li_3K_2^+$ $({}^1A, C_2)$ Fig. 2(o) cationic configuration can be described a deviation from two substitutions of the peripheral Li atoms by two K atoms in the bipyramid $({}^1A_1', D_{3h})$ Li_5^+ cluster Fig. 2(k).

3.1.5. $Li_{6-m}X_m$

Deshpande et al. [28] studied the ground state of the Li_5Na. Present calculation supports their results. The Li_5Na and Li_5K molecules were found to be a three-dimensional $({}^1A', C_s)$ Fig. 1(q) and $({}^1A_1, C_{2v})$ Fig. 1(r), respectively. These can be described as a symmetry-lowing deviation after a substitution of the peripheral Li atom by a Na/K atom in an octahedron Li_6 $({}^1A_{1g}, D_{4h})$ molecule [5,11,17,28] Fig. 1(p).

The structures of Li_4Na_2 and Li_4K_2 have been concluded to be three-dimensional $({}^1A_g, D_{2h})$ configurations Fig. 1(s) and (t), which can be considered as a symmetry-lowing deviation after two substitutions of the peripheral Li atoms by two Na/K atoms in a octahedron Li_6 $({}^1A_{1g}, D_{4h})$ molecule Fig. 1(p).

Li_6^+ $({}^2A_1, C_{2v})$ [17] Fig. 2(p) can be viewed as a symmetry-lowing deviation from Li_6 $({}^1A_{1g}, D_{4h})$ molecule Fig. 1(p). The Li_5X^+ and $Li_4X_2^+$ cationic species are topologically analogical to their corresponding molecules. In fact, K atom always bears the most positive charges in $Li_{n-1}X^+$ and $Li_{n-2}X_2^+$ $(n = 5–7)$.

3.1.6. $Li_{7-m}X_m$

Deshpande et al. [28] investigated the global minimum of the Li_6Na molecule. Current calculations support their predictions. The Li_6Na and Li_6K molecules were found to be a pentagon $({}^2B_1, C_{2v})$ Fig. 1(v) and Fig. 1(w), respectively. This can be described as a substitution of the peripheral Li atom by a Na/K atom in a pentagonal ring Li_7 $({}^2A_2'', D_{5h})$ molecule [1,3,5,6,15,28,51] Fig. 1(u).

The geometrical rearrangement of Li_5Na_2 and Li_5K_2 were found as pentagonal $({}^2B_1, C_{2v})$ configurations Fig. 1(x) and (y), which can be depicted as two substitutions of the peripheral Li atoms by two Na/K atoms in a pentagonal ring Li_7 $({}^2A_2'', D_{5h})$ Fig. 1(u).

The Li_6X^+ and $Li_5X_2^+$ cationic species have the similar structures to their corresponding molecules. K atom always substitutes peripheral lithium atom with the most negative charges in $Li_{n-1}X^+$ and $Li_{n-2}X_2^+$ $(n = 5–7)$, however K atom bears the most positive charges after substitution due to their larger IP difference between Li and K atoms.

3.2. Relative stability

The experimental IPs [52–55] of Li_n $(n = 2–7)$ and adiabatic theoretical IPs of Li_nX and Li_nX_2 $(n = 0–7)$ are shown in Figs. 3 and 4. Li_n, Li_nX and Li_nX_2 $(n = 0–7)$ have a uniform magical-number character in the curves. The IP values exhibit the odd–even oscillations. Its tend to decrease with the increase in the size of these clusters, which suggests all clusters tend to be more and more unstable with increasing cluster size in this series. The oscillating behavior of the IPs reflects the change of spin multiplicity of the ground state of this series. Even-numbered

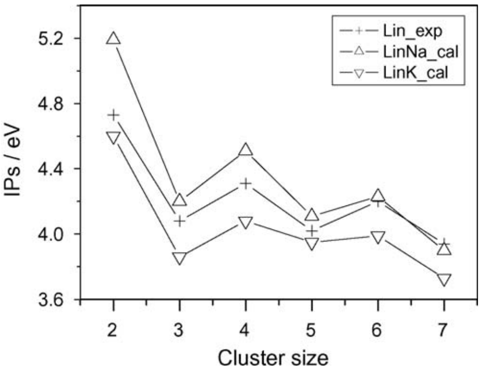


Fig. 3. IPs vs. the cluster size for Li_nX (X = Li, Na and K).

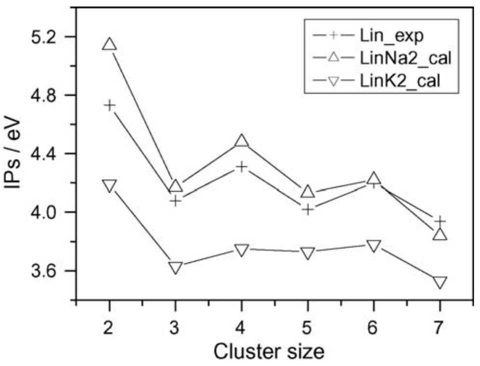


Fig. 4. IPs vs. the cluster size for Li_nX_2 (X = Li, Na and K).

clusters present the higher values of the IP with respect to their neighboring odd systems because it is more difficult to remove an electron from the doubly occupied HOMO of a closed-shell system than from a single occupied HOMO of an open-shell system.

To test the relative stabilities of cations further, the following energy variation of reactions is considered:

$$2(Li_n X_m{}^+) \rightarrow (Li_{n+1} X_m{}^+) + (Li_{n-1} X_m{}^+)$$

We define the energy variation in the formula as $D2(E_n) = E_{n+1} + E_{n-1} - 2E_n$, which is the second difference in energy for cationic series with invariable number of X atoms. Hence, we obtain the curves shown in Fig. 5 corresponding to the energy variations in the formula as $n + m$. It is evident that the $D2(E_n)$ is larger as odd $n + m$ and lower as even $n + m$ in Fig. 5, which suggests that those $Li_nX_m{}^+$ cationic species corresponding to odd $n + m$ are more statically stable. The second differences in energy for $Li_nX_2{}^+$ have analogical figure to Li_nX^+ cations, and not drawn due to page limitation. The oscillating behavior of the second difference in energy also reflects the change of spin multiplicity of the lowest energy state of this series. The inverse stability of cations also derives from the difficulty in removing an electron from the doubly occupied HOMO of a closed-shell system. In unimolecular dissociation of alkali clusters formed from an evaporative ensemble [56], those dissociation energies of the lowest dissociation channel for $X_n{}^+$ (X = Li, Na and K) show an odd–even alternation, which support our predictions of stability.

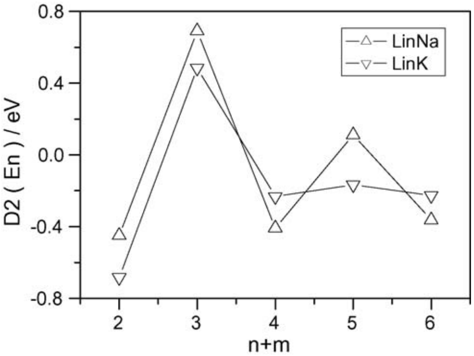


Fig. 5. Second difference in energy for cations vs. $n + m$.

Large peaks have been observed in the mass spectra of Li or Na clusters [57–59]. This peaks occurred for $N = 2$, 8, 20, 40, 58, and 92 where N is the number of electrons in the cluster. Knight et al. [59] explained the occurrence of these magic numbers in terms of an electronic shell model. Using a jellium model for clusters, they showed that the energy per atom in the cluster is lowered in comparison to its adjacent clusters when the electron shells are completely filled. This simple explanation and its remarkable ability to explain the experimental features imply that the abundance of clusters is governed by a very fundamental principle. The special stability of Li_2, LiX, Li_2X^+ and $LiX_2{}^+$ should be attributed to filled-shells with two valence electrons.

4. Summary

In this work, the charge distributions and stability of the Li_nX_m (X = Na and K, $n + m = 1$–7, $m = 1$–2) neutral and cationic clusters were studied with B3LYP at the basis set of 6-311G(d). Our results reveal that all $Li_{n-1}X$ or $Li_{n-2}X_2$ (X = Na and K) clusters can be derived from substitutions of the peripheral Li atoms with X atoms in the Li_n ($n = 2$–8). Atomic charges depend on its position and ability to obtain/lose electron. K atom bears the most positive charges in the cations. Larger heter-atoms favor to occupy outer positions in order to decrease geometrical reconstruction. The neutral bimetallic clusters remain more planar for the larger sizes ($n < 7$) than their corresponding cations ($n < 5$). In various Li_nX_m (X = Na and K, $n = 1$–6, $m = 1$–2) species, Li_nX_m ($n + m$ = even number) clusters are predicted to be of high stability, which can be explained by difficultly removing an electron from the doubly occupied HOMO of a closed-shell system. The special stability of Li_2, LiX, Li_2X^+ and $LiX_2{}^+$ should be attributed to filled-shells with two valence electrons. Their stability tends to decrease with the increase in the size of these clusters.

Acknowledgements

The authors acknowledge the support of Postdoctoral Science Foundation of China under Grant No.2004036454 and National Science Council and the Ministry of Education of Taiwan under Grant No. 89-FA-04-AA.

References

[1] P. Fantucci, J. Chem. Phys. 80 (1984) 325.

[2] B.K. Rao, P. Jena, Phys. Rev. B 32 (1985) 2058.

[3] I. Boustani, W. Pewestorf, P. Fantucci, V. Bonačić-Koutecký, J. Koutecký, Phys. Rev. B 35 (1987) 9437.

[4] I. Boustani, J. Koutecký, J. Chem. Phys. 88 (1988) 5657.

[5] G. Gardet, F. Rogemond, H. Chermette, J. Chem. Phys. 105 (1996) 9933.

[6] R.O. Jones, A.I. Lichtenstein, J. Hutter, J. Chem. Phys. 106 (1997) 4566.

[7] R. Rousseau, D. Marx, Phys. Rev. A 56 (1997) 617.

[8] R.O. Weht, J. Kohanoff, D.A. Estrin, C. Chakravarty, J. Chem. Phys. 108 (1998) 8848.

[9] S. Antonova, G. Lazarov, K. Urbanski, A.M. Lyyra, L. Li, G.H. Jeung, W.C. Stwalley, J. Chem. Phys. 112 (2000) 7080.

[10] M. Pecul, M. Jaszuński, P. Jørgensen, Mol. Phys. 98 (2000) 1455.

[11] R. Rousseau, D. Marx, Chem. Eur. J. 6 (2000) 2982.

[12] A.N. Alexandrova, A.I. Boldyrev, J. Phys. Chem. A 107 (2003) 554.

[13] R. Fournier, J.B.Y. Cheng, A. Wong, J. Chem. Phys. 119 (2003) 9444.

[14] S.E. Wheeler, K.W. Sattelmeyer, P.V.R. Schleyer, H.F. Schaefer III, J. Chem. Phys. 120 (2004) 4683.

[15] K.R.S. Chandrakumar, T.K. Ghanty, S.K. Ghosh, J. Phys. Chem. A 108 (2004) 6661.

[16] S.E. Wheeler, H.F. Schaefer III, J. Chem. Phys. 122 (2005) 204328.

[17] B. Temelso, C.D. Sherrill, J. Chem. Phys. 122 (2005) 064315.

[18] S. Pollack, C.R.C. Wang, T.A. Dahlseid, M.M. Kappes, J. Chem. Phys. 96 (1992) 4918.

[19] T.A. Dahlseid, M.M. Kappes, J.A. Pople, M.A. Ratner, J. Chem. Phys. 96 (1992) 4924.

[20] V. Bonačić-Koutecký, J. Gaus, M.F. Guest, J. Koutecký, J. Chem. Phys. 96 (1992) 4934.

[21] R. Antoine, D. Rayane, A.R. Allouche, M. Aubert-Frécon, E. Benichou, F.W. Dalby, P. Dugourd, M. Broyer, C. Guet, J. Chem. Phys. 110 (1999) 5568.

[22] J. Huennekens, I. Prodan, A. Marks, L. Sibbach, E. Galle, T. Morgus, L. Li, J. Chem. Phys. 113 (2000) 7384.

[23] D. Pavolini, F. Spiegeimann, J. Chem. Phys. 87 (1987) 2854.

[24] D.J. Searles, E.I. von Nagy-Felsobuki, J. Chem. Phys. 95 (1991) 1107.

[25] M. Urban, A.J. Sadlej, J. Chem. Phys. 103 (1995) 9692.

[26] B.K. Rao, P. Jena, J. Chem. Phys. 113 (2000) 1508.

[27] K. Yokoyama, N. Haketa, H. Tanaka, K. Furukawa, and H. Kudo, Chem. Phys. Lett. 330, 339.

[28] M.D. Deshpande, D.G. Kanhere, I. Vasiliev, R.M. Martin, Phys. Rev. A 65 (2002) 033202.

[29] M.D. Deshpande, D.G. Kanhere, P.V. Panat, I. Vasiliev, R.M. Martin, Phys. Rev. A 65 (2002) 053204.

[30] A.E. Reed, R.B. Weinstock, F. Weinhold, J. Chem. Phys. 83 (1985) 735.

[31] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.

[32] M. Orozco, F.J. Luque, J. Comput. Chem. 11 (1990) 909.

[33] F.J. Luque, M. Orozco, F. Illas, J. Rubio, J. Am. Chem. Soc. 113 (1991) 5203.

[34] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuta, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN 03, Revision A. 1, Gaussian Inc., Pittsburgh PA, 2003.

[35] A. Herrmann, E. Schumacher, L. Wöste, J. Chem. Phys. 68 (1978) 2327.

[36] K.M. McHugh, J.G. Eaton, G.H. Lee, H.W. Sarkas, L.H. Kidder, J.T. Snodgrass, M.R. Manaa, K.H. Bowen, J. Chem. Phys. 91 (1989) 3792.

[37] H.W. Sarkas, S.T. Arnold, J.H. Hendricks, K.H. Bowen, J. Chem. Phys. 102 (1995) 2653.

[38] J.L. Martins, J. Buttet, R. Car, Phys. Rev. B 31 (1985) 1804.

[39] V. Bonačić-Koutecký, P. Fantucci, J. Koutecký, Phys. Rev. B 37 (1988) 4369.

[40] P. Calaminici, K. Jug, A.M. Köster, J. Chem. Phys. 111 (1999) 4613.

[41] L. Kronik, I. Vasiliev, M. Jain, J.R. Chelikowsky, J. Chem. Phys. 115 (2001) 4322.

[42] S. Hotta, K. Doi, K. Nakamura, A. Tachibana, J. Chem. Phys. 117 (2002) 142.

[43] K.R.S. Chandrakumar, T.K. Ghanty, S.K. Ghosh, J. Chem. Phys. 120 (2004) 6487.

[44] F. Spiegelmann, D. Pavolini, J. Chem. Phys. 89 (1988) 4954.

[45] V. Bonačić-Koutecký, J. Pittner, C. Fuchs, P. Fantucci, M.F. Guest, J. Koutecký, J. Chem. Phys. 104 (1996) 1427.

[46] F. Calvo, S. Tran, S.A. Blundell, C. Guet, F. Spiegelmann, Phys. Rev. B 62 (2000) 10394.

[47] M. Sizun, F. Aguillon, V. Sidis, J. Chem. Phys. 119 (2003) 12805.

[48] K.K. Verma, M.E. Koch, W.C. Stwalley, J. Chem. Phys. 78 (1983) 3614.

[49] R.A. Bernheim, L.P. Gold, T. Tipton, J. Chem. Phys. 78 (1983) 3635.

[50] A.D. Buckingham, T.W. Rowlands, J. Chem. Edu. 68 (1991) 282.

[51] K.R.S. Chandrakumar, T.K. Ghanty, S.K. Ghosh, Int. J. Quant. Chem. 105 (2005) 166.

[52] C.E. Moore, Atomic Energy Levels as Derived from the Analysis of Optical Spectra, National Bureau of Standard, Washington, DC, 1949.

[53] D. Eisel, W. Demtröder, Chem. Phys. Lett. 88 (1982) 481.

[54] B. Vezin, P. Dugourd, D. Rayane, P. Labastie, J. Chevaleyre, M. Broyer, Chem. Phys. Lett. 206 (1993) 521.

[55] P. Dugourd, D. Rayane, P. Labastie, B. Vezin, J. Chevaleyre, M. Broyer, Chem. Phys. Lett. 197 (1992) 433.

[56] C. Bréchignac, H. Busch, Ph. Cahuzac, J. Leygnier, J. Chem. Phys. 101 (1994) 6992.

[57] K. Kimoto, I. Nishida, H. Takahashi, H. Kato, Jpn. J. Appl. Phys. 19 (1980) 1821.

[58] M.M. Kappes, R.W. Kunz, E. Schumacher, Chem. Phys. Lett. 91 (1982) 413.

[59] W.D. Knight, K. Clemenger, W.A.D. Heer, W.A. Saunders, M.Y. Chou, M.L. Cohen, Phys. Rev. Lett. 52 (1984) 2141.