

Geometric structure of the magic number clusters $\text{Li}_n\text{Na}_{8-n}$, $\text{Na}_n\text{K}_{8-n}$, and $\text{K}_n\text{Li}_{8-n}$

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Abstract. The mixed alkali clusters $\text{Li}_n\text{Na}_{8-n}$, $\text{Li}_n\text{K}_{8-n}$, and $\text{Na}_n\text{K}_{8-n}$ were studied by Kohn-Sham theory with a gradient corrected (PBE) exchange-correlation functional. Geometry optimization was done with a Tabu Search algorithm to find possible global minima, followed by local optimization with a quasi-Newton method. For the pure clusters and all Na_nK_m mixed clusters, the predicted global minimum is a dodecahedron having D_{2d} symmetry in its ideal form. There are various structures among the predicted global minima of Li_nNa_m and Li_nK_m : they all have in common that the Li_n subunit achieves maximal coordination and forms a compact core at, or near, the center of the cluster. The clusters Li_nNa_m and Li_nK_m all have near zero asphericity, in line with the prediction of the ellipsoidal jellium model for 8 electrons, and the asphericity is nonzero but small in all other clusters. The clusters Li_4Na_4 , Na_4K_4 , and K_4Na_4 each have the four atoms of the lighter element near the center of mass and these clusters are more stable than those of other compositions. Calculated ionization potentials and static dipole polarizabilities agree rather well with experimental values but do not allow a structure assignment to be made.

Keywords: Clusters, structure, global optimization, density functional theory

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1. Introduction

The jellium model for metal clusters replaces nuclear charges by a uniform positive charge density background contained within a sphere or ellipsoid and treats the electrons in the usual way [1]. The resulting object, a “jellium”, is simpler than the usual molecular model of point charges at fixed nuclear positions. Instead of N atomic coordinates and charges, it takes only 4 or 5 variables to specify entirely a jellium: the net charge, the number of electrons N , the electron density ρ (or, equivalently, the volume), and at most two variables to describe the shape of a simple bounding surface (usually a ellipsoid). The ellipsoidal jellium model (EJM) [1] is appropriate for metal clusters because they lack strong directional bonds and may even be fluxional. Thus one can build a general understanding of the electronic structure of alkali and coinage metal clusters with a relatively small number of EJM calculations. In particular, the EJM can explain the special stability associated with certain number of electrons as revealed by abundances in mass spectra, ionization energies, and chemical reactivities. The EJM also leads to qualitative predictions about the preferred geometric shape (spherical, oblate, or prolate) of clusters as a function of number of electrons. In particular, when that number corresponds to an electronic shell closing ($N = 8, 20, 40, 58, \dots$ electrons) the cluster is predicted to have a quasi-spherical shape as well

as enhanced stability. But by definition, the EJM ignores nuclear positions and can not make detailed predictions about geometric structure. In previous theoretical studies of clusters of Ag, Li, and Be [2–4], we used Kohn-Sham Density Functional Theory (KS-DFT) to predict the global minima structures of clusters with up to 20 atoms and noted that the EJM predicts reasonably well the overall shape of low energy structures and the cluster sizes having special stability. But the EJM is clearly insufficient for detailed predictions of structure because many distinct isomers of A_n can have similar shapes, and there can be many homotops of $A_qB_{(n-q)}$ corresponding to every A_n “parent structure”. Here I report the results of calculations based on KS-DFT and a global optimization method to predict the lowest energy structures of 8-atom pure and mixed alkali clusters. These clusters are all roughly equivalent in the EJM, and are predicted to be stable (“magic”) by EJM, since they all have eight delocalized electrons. Measured ionization potentials (IP) of Li_nNa_m confirm the magic character of these clusters when $n + m = 8$ [5]. By looking at the different 8-atom mixed alkali clusters with KS-DFT one can study aspects of cluster physics that are beyond the EJM. As it turns out, there is a lot of variety among the KS-DFT optimized structures at different compositions, and there is a clear energetic preference for evenly mixed A_4B_4 clusters.

2. Computational details

All KS-DFT calculations were done with the Gaussian03 software [6]. The nonempirical gradient corrected exchange-correlation functional of Perdew, Burke, and Ernzerhof (PBEPBE Gaussian keyword) [7] and 6-311++G(d) basis sets were used. Global optimization was performed on the KS-DFT energy surface by the Tabu Search in Descriptor Space (TSDS) method [8]. In a TSDS run, a large number of topologically distinct structures are generated and their energy is evaluated. For each A_nB_m structure, interatomic distances between nearest neighbours are set equal to values d_{AA} , d_{BB} , d_{AB} that are typical of local minima. Descriptors such as moments of inertia (I_a, I_b, I_c) and mean atomic coordinations “ c ” for atoms of the two types (c_A, c_B) are used as auxiliary variables to guide the search for the global minimum. The TSDS strategy involves a bias that favors exploration of very diverse (in terms of descriptors) structures at the beginning of the search, and favors intensification the search in regions of descriptor space where low energy structures were found at the end of the search. Details of the TSDS method can be found in Ref. [8].

Here, every search involved an initial set of 30 random structures and their KS-DFT energy, followed by 320 TSDS cycles, i.e., 320 additional structures were generated and their KS-DFT energy calculated. Local optimization was performed for the 15 best structures out of those 350. The “best structures” are those that have the lowest energy with the constraint that they must be sufficiently different from each other as indicated by their descriptors. We used four basic descriptors for A_nB_m clusters

$$c_A = (1/n) \sum_{i=1}^n c_i \quad (1)$$

$$r_A = \left((1/n) \sum_{i=1}^n (c_i - c_A)^2 \right)^{1/2} \quad (2)$$

$$\zeta = \frac{(I_a - I_b)^2 + (I_b - I_c)^2 + (I_c - I_a)^2}{I_a^2 + I_b^2 + I_c^2} \quad (3)$$

$$\eta = (2I_b - I_a - I_c)/I_a \quad (4)$$

where the sums run over atoms of type A, c_i is the coordination of atom i obtained from a simple interatomic distance criterion, and $I_a \geq I_b \geq I_c$ are the three moments of inertia calculated after assigning a fictitious mass of 1 to every atom. Descriptors c_B and r_B are calculated when $m \neq 0$ with formulas analogous to above. The descriptors c_A, r_A, c_B, r_B are essential to express whether clusters are compact or open, which type of atom (A or B) is more highly coordinated (and closer to the center of mass), and to distinguish between structures where coordinations are all nearly equal (cage-like structures) and those where they differ a lot. Descriptors c and r are defined in analogy to c_A, r_A but with the sums in Eqs (1) and (2) running over all atoms. The descriptor ζ is the asphericity, and η expresses the shape (prolate or oblate). One more descriptor is important to distinguish between homotops of a same basic structure,

$$M = \frac{N_{AB}}{N_{AA} + N_{BB} + N_{AB}} \quad , \quad (5)$$

where N_{AB} is the number of A–B neighbour pairs, etc., so that M expresses the degree of mixing. One more descriptor used in the current version of our TSDS code expresses the mean electronegativity difference between neighbouring atoms and is redundant with M in the case of binary clusters. So, in effect, the search was guided by $(2 \times 2 + 2 + 1) = 7$ descriptors.

Second energy derivatives were *not* calculated for the structures produced by the local optimization routine, so there is no guarantee that the structures shown here are minima: they could be higher order critical points. However, metal clusters lack directional bonding and the high energy barrier associated with it, and as a result quasi-Newton algorithms almost always end up at or near local minima of metal clusters. For example, in a recent study of neutral and charged aluminum clusters [9], we found only one case out of 36 where the lowest energy structure found by the combination of TSDS and quasi-Newton optimization gave a higher order critical point, and the local minimum in that instance was lower in energy by only 0.01 eV. Since we are interested in the trends in low energy structures as a function of composition, and not in the properties of any specific cluster, calculation of energy second derivatives and vibrational frequencies is not essential.

3. Results

3.1. Structure of the global minima

First I will discuss the structure and energies of the putative global minima (GM) only. Table 1 shows the structure type found in each case while Figs 1 through 4 show the actual structures. The meaning of acronyms in Table 1 are as follows. DD is a dodecahedron with D_{2d} symmetry in its ideal form. It can be viewed as the result of capping two triangular faces of an octahedron, or, as two 4-atom trapeze rings linked and perpendicular to each other. PBP is a pentagonal bipyramid (7 atoms) and 1-PBP has a capping atom on one of its triangular faces. TT is a tetracapped tetrahedron having T_d symmetry in its ideal form. CTP is a 7-atom centered trigonal prism, and the extra atom in 1-CTP caps a square face of the prism. CPBP stands for centered pentagonal bipyramid: it is an unusual structure made possible by the large size mismatch between Li and K.

Homotops are cluster isomers A_nB_m of a same type that differ by how the various sites are occupied (by A or B) [10]. Let us introduce a notation for homotops of a given structure type. A number equal to the coordination is assigned to each *site* of a structure. For example, the four inner sites of the TT have coordination 6 in the ideal form, so they are assigned the index “6”; the four outer sites are assigned the

Table 1

Abbreviated description of the lowest energy structure found for each 8-atom alkali cluster; see text for the meaning of the acronyms

	n,m							
	8,0	7,1	6,2	5,3	4,4	3,5	2,6	1,7
Li_nNa_m	1-PBP	1-PBP	TT	TT	TT	1-CTP	1-CTP	1-CTP
Na_nK_m	DD	DD	DD	DD	DD	DD	DD	DD
K_nLi_m	DD	1-CTP	1-CTP	CPBP	TT	1-CTP	1-PBP	CPBP

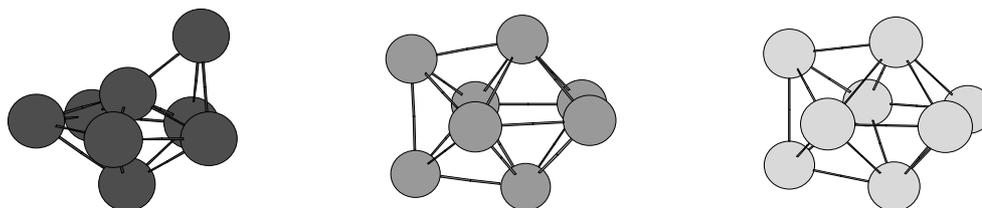
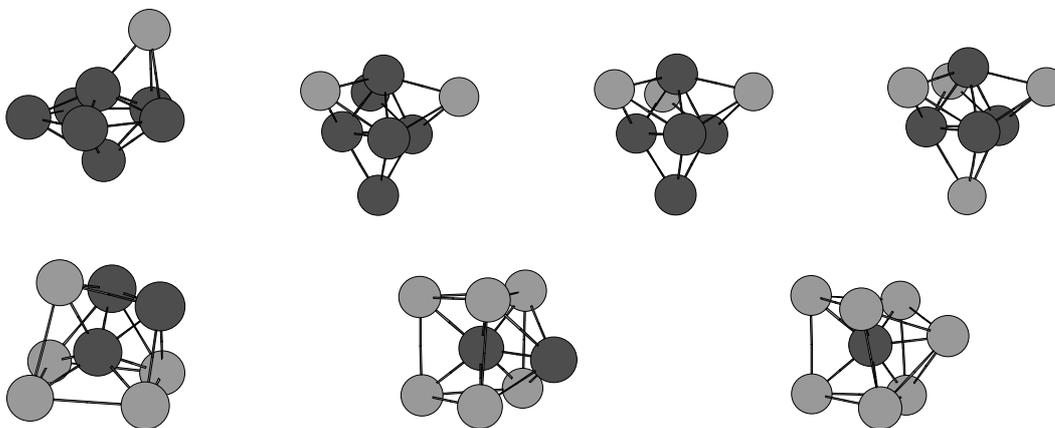
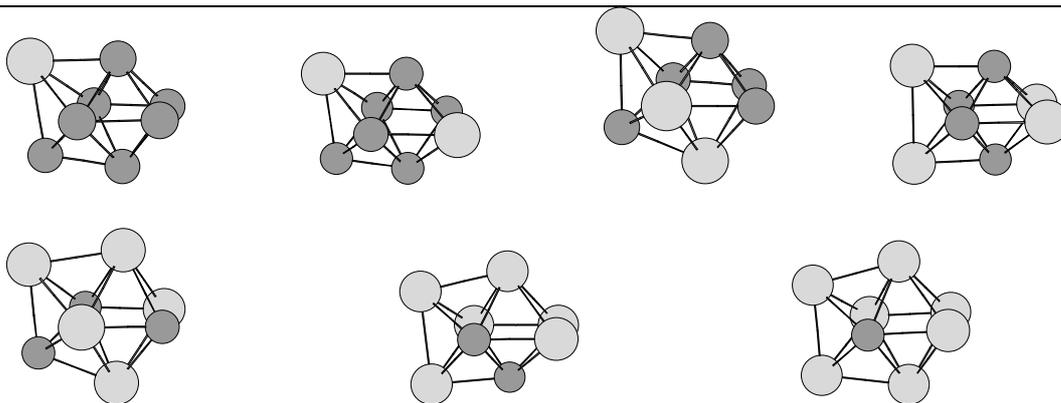
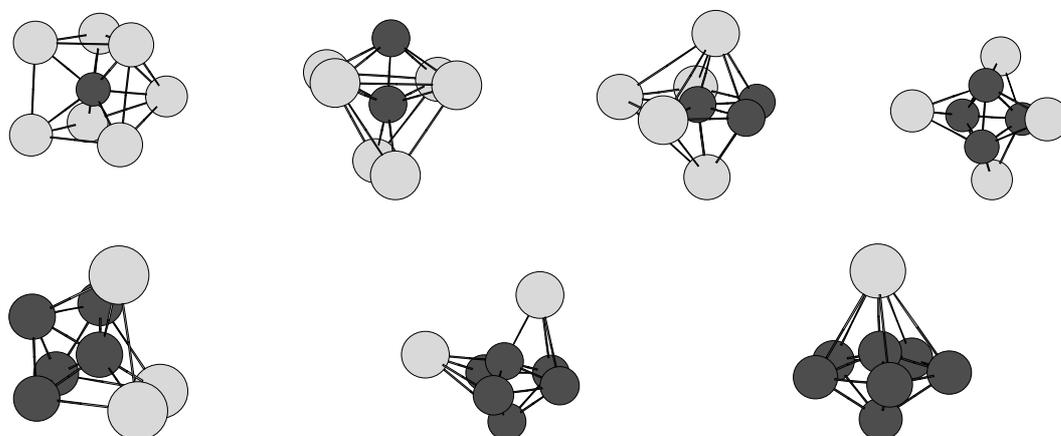


Fig. 1. Lowest energy isomers of the pure clusters.

Fig. 2. Lowest energy isomers of Li_nNa_m clusters.

index “3”. Likewise, sites of other structure types are: 5 and 4 for DD; 7, 6, 5, 4, and 3 for 1-PBP (“3” is the capping atom, “7” is the axial atom next to it, “6” is the other axial atom of the PBP, etc.); 7, 6, and 5 for the CPBP; and 7, 5c, 5p, and 4 for the 1-CTP. In 1-CTP there are two sites that are 5-coordinated, the capping position (5c) and four of the six positions in the prism that are bonded to the capping atom (5p). Then, homotops will be named by enumerating the sites occupied by the minority element or, in the case of A_4B_4 clusters, by the heavier element. Sometimes this is not sufficient for distinguishing between all possible homotops, one more piece of information is needed. The number of *neighbour pairs* of the minority (or heavier) element can serve that purpose in most cases. Then, almost every homotop can be given a unique name. For example, I will name the GM of Li_nNa_m as follows: Li_7Na 1-PBP/3/0, Li_6Na_2 TT/33/0, Li_5Na_3 TT/333/0, Li_4Na_4 TT/3333/0, Li_3Na_5 1-CTP/75c5p/3, Li_2Na_6 1-CTP/75c/1, $LiNa_7$ 1-CTP/7/0. In these examples, the number of bonds in the name is redundant but useful, and it is required in some of the other cases for generating unique names.

The mean coordination $((nc_A + mc_B)/8)$ is roughly the same for all clusters, it varies between 4.50 and 4.75. The rms deviation of atomic coordinations from the average, r , is small (0.63 to 0.75) for

Fig. 3. Lowest energy isomers of Na_nK_m clusters.Fig. 4. Lowest energy isomers of K_nLi_m clusters.

the DD structure. Values of r for the other structures are $r = 1.50$ (TT), $r \approx 1.1$ (1-PBP), $r \approx 0.95$ (1-CTP) and $r \approx 0.9$ (CPBP). The clusters Na_8 , K_8 , and Na_nK_m prefer the DD structure, which has the lowest r . In previous studies [2,3] we also found that, among metal cluster structures with same c , those with a low r are often preferred and in some cases this gives rise to cage-like structures (some Be_n clusters). The favored geometry for Li_8 is 1-PBP, but the DD isomer is only 0.026 eV higher in energy. Previous KS-DFT calculations using the local density approximation (LDA) found the GM of Li_8 to be a 1-CTP [11,4], but according to the present PBE functional calculations, the 1-CTP does not appear to be the GM nor a low-lying energy isomer. Deshpande et al. performed simulated annealing with LDA followed by local optimization with a generalized-gradient approximation (GGA) functional [14]. They describe the GM of Li_8 that they found as a C_{3v} symmetry “centered trigonal prism with an atom capping one of the rectangular faces”, i.e., a 1-CTP. But their accompanying figure shows a structure that looks very different from the (C_{2v} symmetry) 1-CTP of Fig. 2, it looks rather like a CPBP. On the other hand, the predicted DD structure of Na_8 agrees with earlier LDA calculations [12].

In binary clusters where two elements have sufficiently different cohesive energies or electronegativities, it may be favorable to maximize the coordination of one of the element, leading to larger r values. That is what we see here for Li_nNa_m and Li_nK_m clusters, but not Na_nK_m . The asphericity descriptor,

Table 2

Total PBE/PBE energies (hartree) of the clusters. The energy of atoms are: Li: -7.4600573 ; Na: -162.1560945 ; K: -599.6920022

n, m	Li_nNa_m	Na_nK_m	K_nLi_m
8, 0	-59.96168	-1297.45423	-4797.69652
7, 1	-214.65300	-1734.98536	-4205.48781
6, 2	-369.34148	-2172.51645	-3613.27122
5, 3	-524.03178	-2610.04611	-3021.05510
4, 4	-678.72198	-3047.57775	-2428.83926
3, 5	-833.40432	-3485.10659	-1836.62178
2, 6	-988.09097	-3922.63704	-1244.40366
1, 7	-1142.77758	-4360.16657	-652.18554

ζ , is close to 0.06 for all the DD structures, it is 0.07 for Li_8 (1-PBP), and it is essentially zero for all others. Asphericity typically varies between 0.00 and 0.25 in clusters of Ag, Li, and Be with 6 or more atoms. So the ζ of the mixed alkali clusters are all very small, in line with the EJM: a spherical closed electronic shell (8 electrons) drives the nuclei into a (nearly) spherical configuration. The DD can be seen as a compromise structure that is not quite spherical but has a low r . Another noteworthy feature is that many Li_nNa_m and Li_nK_m clusters have a interior Li atom that is “solvated” by the other atoms, and that is analogous to pure Li clusters [11]. This was also seen by Desphande et al. in their *ab initio* molecular dynamics optimization study of $LiNa_n$ clusters ($n = 1-12$) [13]. In elemental metal clusters the first interior atom is normally seen only at $n \geq 13$, but Li_n clusters are unusual. They have interior atoms at very small size, and two or three interior atoms at moderate ($n \approx 14-20$) size [11,4,3]. The formal (Mulliken) charge on those interior atoms is large which has led Sung et al. to describe these atoms as being “solvated”. The Mulliken populations in the present work confirm that centrally located, highly coordinated, Li atoms have large formal charges, and this indicates a type of interaction that is peculiar to Li (as opposed to Na or K).

The average nearest-neighbor distances in the pure clusters are: Li-Li: 2.99 Å ; Na-Na: 3.56 Å ; K-K: 4.52 Å . In the A_4B_4 clusters, average distances are: Li-Li: 2.95 Å ; Na-Na: 3.56 Å in Li_4Na_4 and 3.75 Å in Li_4K_4 ; K-K: 4.73 Å (in Li_4K_4); Li-Na: 3.20 Å ; Li-K: 3.66 Å ; Na-K: 3.92 Å . So, A-B bonds are 2-3% shorter than the average of A-A and B-B bonds. This is indicative of a small ionic contribution to bonding. The shortest mixed bonds are found in LiK_7 (Li-K: 3.59 Å), $LiNa_7$ (Li-Na: 2.94 Å), and Na_4K_4 (Na-K: 3.92 Å).

Deshpande et al. did a systematic search for the GM of Li_nNa_m , $n + m = 8$, [14] using a method that differs from this work in two ways. Firstly, they searched for the GM by molecular dynamics simulated annealing on the LDA energy surface, whereas here TSDS was used to search the PBE GGA energy surface. Secondly, for the local optimization, they used the Perdew-Wang GGA functional instead of the PBE GGA functional used here. Also, they reported putative GM but no low-lying energy isomers. The structures I find for Li_nNa_m differ somewhat from theirs. Judging from Fig. 1 of Deshpande et al., they found GM that are CPBP ($n = 8$), 1-PBP/4 ($n = 7$), and 1-PBP/43/0 ($n = 6$), and those differ from Fig. 2. On the other hand, there seems to be perfect agreement between Fig. 2 and the figure in Ref. [14] for the cases $n = 5-0$. Deshpande et al. describe the Li_2Na_6 and Li_1Na_7 structures as dodecahedra (DD) but their figure shows structures that are 1-CTP, so it is unclear if there actually is agreement between the present study and theirs. To my knowledge the structures of Na_nK_m and K_nLi_m clusters have not been investigated, but a ESR matrix experiment showed that Na_2K_5 adopts the PBP/66/1 structure [15].

Table 3

Atomization energies (AE, in eV) of the mixed clusters. The numbers immediately below are *differences* between the AE of the mixed cluster and the corresponding weighted average of AEs of pure clusters

n, m	Li_nNa_m	Na_nK_m	K_nLi_m
8, 0	7.652	5.591	4.367
7, 1	7.524	5.461	5.000
	-0.109	-0.023	-0.226
6, 2	7.318	5.330	5.417
	-0.201	-0.045	-0.235
5, 3	7.162	5.160	5.848
	-0.299	-0.028	-0.259
4, 4	7.003	5.044	6.286
	-0.395	-0.065	-0.290
3, 5	6.631	4.852	6.680
	-0.277	-0.026	-0.276
2, 6	6.376	4.703	7.056
	-0.276	-0.030	-0.245
1, 7	6.119	4.530	7.432
	-0.274	-0.010	-0.213

3.2. Energies of global minima

Table 2 gives the total energies in atomic units of each cluster and Table 3 shows the atomization energies (AE). Dividing the pure clusters AEs by eight times the experimental cohesive energy gives 0.58 (Li), 0.63 (Na), and 0.58 (K). Those values are typical for metal clusters of that size. Based on the calculated size dependent energies of various pure metal clusters, we believe the stabilization associated with having a closed electronic shell (8 electrons) is on the order of a few tenths of an eV. To a first approximation the AEs of mixed clusters are the weighted average of the AEs of the corresponding pure clusters. The small deviations from those weighted averages,

$$\Delta(\text{AE}) = (n/8)\text{AE}(A_8) + (m/8)\text{AE}(B_8) - \text{AE}(A_nB_m) \quad , \quad (6)$$

are instructive (see the negative numbers in Table 3). First, the $\Delta(\text{AE})$ are all negative. Second, $|\Delta(\text{AE})|$ is largest when $n = m = 4$. In the case of Li_4Na_4 and Li_4K_4 this corresponds to a high symmetry (T_d) structure which may partly explain the extra stability. The variations of $|\Delta(\text{AE})|$ among Na_nK_m clusters, which all have the same structure type (DD), are quite small, but they tend to be largest when $(n - m)$ is small.¹ These trends are consistent with small ionic contributions to bonding. Third, the $\Delta(\text{AE})$ values are much bigger for Li containing clusters. This can not be explained from the elements' electronegativities. There is clearly an energetic preference for Li atoms to maximize coordination in the mixed clusters, at the expense of Na or K atoms. This was also observed in smaller ($n + m \leq 6$) Li_nNa_m clusters [5]. There is an analogy also with pure Li_n clusters ($n > 6$) whose energetically favored structures are very different from those of other metal clusters in that they have more interior atoms than is possible in even the most compact structure one might get by packing slightly compressible spheres. The Li_n clusters are characterized by a mix of long (3.0 Å) Li-Li bonds and short (2.5 Å) Li-Li* bonds where Li* is a centrally located "solvated" atom. Sung et al. explained those unusual bonding

¹Also, on average, $|\Delta(\text{AE})|$ is larger when n and m are even.

Table 4
HOMO-LUMO gap of the global minima

n, m	Li_nNa_m	Na_nK_m	K_nLi_m
8, 0	0.75	1.09	0.72
7, 1	0.87	1.00	0.79
6, 2	1.15	0.93	0.79
5, 3	1.14	0.91	0.77
4, 4	1.14	0.82	0.75
3, 5	1.26	0.80	1.00
2, 6	1.33	0.75	0.95
1, 7	1.44	0.72	1.01

Table 5
Ionization potentials (IPs) from experiment, and the calculated vertical (VIPs) and adiabatic (AIPs) values for $\text{Li}_n\text{Na}_{8-n}$.

n	8	7	6	5	4	3	2	1	0
Expt [5]	4.16	–	–	–	–	4.04	4.08	4.00	4.00
Theory VIP	4.49	4.31	4.64	4.61	4.54	4.42	4.40	4.42	4.42
Theory AIP	4.28	4.23	4.42	4.40	4.40	4.20	4.19	4.18	4.29

characteristics of Li clusters on the basis of the easier *sp* hybridization in Li compared to Na or K [11]. The present results suggest that the energetic preference for geometries with solvated interior Li atoms carries over to mixed Li_nB_m clusters.

3.3. Electronic properties

The HOMO-LUMO gaps (in eV) of the pure and mixed clusters are given in Table 4. If one compares the gaps of mixed clusters to weighted average of the pure clusters, one finds that Li_nNa_m (for all n) and K_nLi_m (for $n=1, 2$, and 3) have relatively large gaps. Other mixed clusters have gaps roughly in line with those of pure clusters. Interestingly, the high symmetry TT clusters, even those with A_4B_4 composition, do not have particularly large gaps. The largest gaps are found for the “solvated Li^+ ion” clusters Li_nNa_m ($n = 1, 2, 3$).

Dipole moments calculated with a modest basis set like here (6–311++G(d)) are probably not accurate for this kind of clusters, but they should be qualitatively correct. Likewise, Mulliken atomic charges are unreliable except, maybe, for a qualitative description of the electronic structure. With these limitations in mind, I will now discuss dipole moments and atomic charges. The dipole moments in Li_nNa_m are all smaller than 0.3 D except Li_3Na_5 where it is 0.5 D. In the other two series the dipole moments vary a lot and are sometimes quite large. For Na_nK_m they are, in order from $n = 7$ to $n = 1$: 2.7, 2.2, 2.3, 0.0, 1.0, 0.6, and 0.1 Debye. For K_nLi_m they are, in order from $n = 7$ to $n = 1$: 0.1, 1.3, 2.9, 0.0, 4.1, 3.5, and 2.4 Debye. The atomic charges in mixed clusters are almost always positive on Li in Li_nNa_m , and on K in the other two series. Interior Li atoms have very large Mulliken charges (1 or larger in absolute value) in these clusters: Li_7Na , Li_3Na_5 , Li_1Na_6 , and LiNa_7 ; and Li_7K , Li_5K_3 , Li_3K_5 , Li_2K_6 , and LiK_7 .

The IPs have been measured for several mixed Li-Na clusters by Benichou et al. [5]. They are listed in Table 5 along with calculated vertical ionization potentials (VIP) and adiabatic IPs (AIP). The AIPs are in good agreement with experiment, they overestimate the experimental IPs by a near constant value of 0.17 eV. However, the variations across the $\text{Li}_n\text{Na}_{8-n}$ series are very small. Unfortunately, the biggest variations occur in cases where experimental data is not available. The calculations predict IPs that are significantly larger for $n = 6, 5, 4$ which are the three cases where the structure is TT.

Table 6
Static dipole polarizability per atom for $\text{Li}_n\text{Na}_{8-n}$, in \AA^3

n	8	7	6	5	4	3	2	1	0
Expt [16]	10.4	8.2	14.6	14.3	16.5	17.4	19.2	–	16.8
Theory	10.6	11.1	12.0	12.4	12.8	12.6	13.2	13.7	14.1

The static dipole polarizability has been measured for the $\text{Li}_n\text{Na}_{8-n}$ series and a few other mixed Li-Na clusters [16]. I calculated polarizabilities, and this is compared to the experimental results in Table 6. It should be pointed out, however, that two factors can strongly affect the calculated polarizabilities. *First*, polarizabilities are sensitive to the choice of basis sets, and though the basis used here is probably adequate for structures and relative energy differences, it may not be good enough for accurate predictions of polarizability. *Second*, polarizabilities are calculated at 0 K but they are measured near room temperature. An increase in temperature can lead to increased metal-metal bond lengths and a corresponding increase in polarizability. The effect of temperature should be larger in sodium rich clusters because they are more weakly bound than lithium rich cluster. Antoine et al. [16] observed that, *in general*, there is a smooth decrease in the polarizability as the proportion of Li atom increases in Li_nNa_m clusters ($n + m = 2, 3, 4, 8$), and this is exactly what is seen in the calculations. However, the experimental polarizability in the 8-atom series of $\text{Li}_n\text{Na}_{8-n}$ clusters does *not* change smoothly with n (Table 6, and Table 3 in Ref. [16]). In particular the large experimental polarizabilities for Li_3Na_5 and Li_2Na_6 are puzzling. It may be that those clusters are fluxional and undergo large amplitude vibrations at room temperature, or that the room temperature structures are different from those of Fig. 2. The small isomer energies calculated here (see next section and Table 7) do suggest that one would need to calculate polarizabilities for several isomers in order to account for the measured room temperature polarizabilities of mixed Li-Na clusters, in addition to using a better basis set and modeling the effect of temperature on polarizability. This is beyond the scope of this study.

3.4. Higher energy isomers.

Table 7 gives the name and energy, relative to that of the GM, of other structures found by TSDS optimization. The GM themselves are included to facilitate comparisons. For simplicity I refer to these structures as “isomers” but one should keep in mind that they may not all be local minima. Many structures differ only by small distortions from each other suggesting that some of them are *not* local minima. It would be very tedious and costly in computer resources to fully characterize each structure of each species, and it would not be very useful in the absence of detailed spectroscopic data. In the present context, low energy “isomers” can point to the existence of either true isomers or fluxional structures. The following discussion of “isomers” and their REs can also be useful for insight into what structural features are favorable energetically, and how this changes with composition.

Let us look at the pure clusters first. Relative energies (RE) are in the range 0.01 to 0.10 eV. Such small energy differences (less than 0.1 eV) are quite difficult to calculate accurately by theory, and they are surely not reliable in an absolute sense with the present level of theory. But they do suggest that the spectra and properties of Li_8 and K_8 (and maybe even Na_8) will change significantly in going from, say, 4 K to 77 K and to 300 K and above. This shows the necessity of very high levels of theory if one wishes to do quantitative assignment of spectra for the purpose of structure determination of a specific cluster species.

At this point it may be worth pointing out that there are typically several repeats among the 15 structures found by TSDS. A glance at Table 7 shows that the number of *distinct* structures found were only 3

Table 7

Descriptive name and relative energy (eV) of isomers

n, m	Li_nNa_m	Na_nK_m	K_nLi_m
8, 0	1-PBP	DD	DD
	DD: 0.026 DD: 0.057	SAP: 0.076 TT: 0.090	DD: 0.37 TT: 0.096
7, 1	1-PBP/3	DD/4	1-CTP/7
	TT/3: 0.052 DD/4: 0.102 TT/6: 0.325	SAP*/4: 0.076 TT/6: 0.099	DD/4: 0.328
	TT/33	DD/44/0	1-CTP/75c/1
6, 2	1-PBP/43/0: 0.016 1-CTP/5p4/0: 0.072 DD/44/0: 0.094 CPBP/66/0: 0.112 DD/54/0: 0.232	DD/54/1: 0.028 TT/63/0: 0.106	CPBP/75/1: 0.020 DD*/55/1: 0.177 TT*/66/1: 0.271
	TT/333/0	DD/554/2	CPBP/755/3
	1-PBP/443/1: 0.060 1-PBP/443/0: 0.099 1-PBP/444/2: 0.152 DD/544/3: 0.222 TT/633/2: 0.232 TT/633/1: 0.264	DD/544/3: 0.012 TT/333/0: 0.052 TT/666/3: 0.072 TT/663/2: 0.086 TT/663/3: 0.098	1-CTP/75c5p/3: 0.061 TT/666/3: 0.092 1-PBP/655/3: 0.331
	TT/3333/0	DD/4444/2	TT/4444/6
	1-PBP/4443/2: 0.124 TT/6333/3: 0.211 TT/6333/2: 0.243	DD/5544/3: 0.023 DD/5544/4: 0.035 DD/5544/5: 0.045 TT/3333/0: 0.063 TT/6333/2: 0.107 TT/6333/3: 0.122 TT/6663/6: 0.133	
3, 5	1-CTP/75c5p/3	DD/555/2	1-CTP/5p44/2
	TT/666/3: 0.010 1-PBP*/765/3: 0.054 TT*/666/3: 0.099 DD/554/3: 0.199 DD/554/3: 0.263	DD/544/1: 0.015 DD/544/3: 0.032 DD*/544/1: 0.055 TT/666/3: 0.066 TT/633/1: 0.103	1-PBP/443/1: 0.013 1-CTP/5c44/1: 0.248 TT/633/1: 0.292
	1-CTP/75c/1	DD/55/1	1-PBP/43/0
	1-CTP/75p/1: 0.065 CPBP/76/1: 0.111 DD/55/1: 0.127 DD/55/1: 0.202 SAP*/55/1: 0.253	DD/44/0: 0.014 DD/44/1: 0.024 1-CTP/75c: 0.067 TT/63/0: 0.095 TT/63/1: 0.108	TT/33/0: 0.074 DD/44/1: 0.125 TT/63/0: 0.357
	1-CTP/7	DD/5	CPBP/6
CPBP*/7: 0.028 TT/6: 0.246 TT/3: 0.509	TT/6: 0.085 TT/3: 0.097	1-CTP/4: 0.082 TT/3: 0.123 12-O/4: 0.152	

for Li_8 , 3 for Na_8 , 4 for K_8 , 4 for Li_7Na , etc. This is because, during the search, TSDS generates many variations of the low energy structures already found in its attempt to discover even lower energy structures. These variants may appear sufficiently different from each other, on the basis of descriptors, but upon local optimization they often converge to the same local minimum. With certain choices of optimization parameters, one can increase the likelihood that TSDS discovers the GM; with other choices one can increase the number of distinct structures that TSDS finds. These are different, and to some extent contradictory, optimization goals. The choice of optimization parameters made in this study aimed at a high likelihood of finding the GM.

Now, let us look at the mixed clusters. There are lots of details in Table 7, not all of them important, but some general observations should be made. *First*, TSDS discovered one or more isomers within 0.1 eV for all clusters except LiK_7 , Li_4Na_4 , and Li_4K_4 ; it found two or more isomers within 0.1 eV of the GM in 10 out of 21 cases. The number of low energy isomers is relatively smaller for K_nLi_m , probably because these two elements have very different sizes and cohesive energies. *Second*, most isomers are well described by one of the structure types DD, TT, 1-PBP, 1-CTP, CPBP, or SAP. In some cases (names marked by an asterisk in Table 7) the structure is distorted and could be better described in other ways. The last isomer of Li_7K is a Li_6 octahedron with one Li atom and one K atom capping neighbouring triangular faces. *Third*, Na_nK_m isomers are almost all of type DD and TT. There is a lot more variety in structures in Li_nNa_m and Li_nK_m , probably as a result of bigger differences (size, cohesive energy, electronegativity) in the elements themselves. *Finally*, one can see a number of trends by looking within groups of homotops. Take for example the 1st and 3rd isomers of Li_7Na , TT/3 and TT/6. The energy difference (0.27 eV) shows a large energetic preference for putting Li atoms near the center so as to maximize their coordination. This is expected from the cohesive energies of Li and Na, 1.63 and 1.113 eV respectively. The TT homotops of Na_4K_4 also show that having more atoms of the element with higher cohesive energy (Na) near the cluster's center lowers the cluster's energy, and this effect can also be seen elsewhere in Table 7. The DD homotops of Na_4K_4 show a different kind of trend: among isomers having same type and same coordinations, the ones with fewer K–K neighbouring pairs are more stable. In other words, it is energetically favorable for Na and K to mix. It is just the opposite in Li_nNa_m , for example, Li_4Na_4 TT/6333/3 (3 Na–Na neighbour pairs) is more stable than TT/6333/2 (2 Na–Na neighbour pairs) by 0.032 eV. Also, comparing the two sets of isomers, one generally finds more Li–Li pairs in Li_3Na_5 than Na–Na pairs in Na_3K_5 . In short, Li and Na do not mix easily. At this point it is useful to make some generalizations about the relative stability of homotops.

- (1) High coordination sites are occupied in priority by Li, then by Na or K with a slight preference for Na, in the lowest energy homotops;
- (2) in Na_nK_m clusters, the number of Na–K neighbouring pairs is maximum or nearly so in low energy homotops;
- (3) if we denote by " A_c " an atom of element A at a site of coordination c , then homotops with the largest number of neighbouring A_c – A_c pairs have a lower energy;
- (4) when $c' \neq c$, the homotops with lowest energy are those with the *largest* number of $A_{c'}$ – A_c pairs for TT, and *smallest* number of $A_{c'}$ – A_c pairs for 1-PBP.

These rules should be applied in the given order (1) to (4). They are not followed strictly, but they account for the energy order in homotops with few exceptions.

4. Conclusion

The KS-DFT calculations and global optimization of 21 mixed alkali clusters A_nB_{8-n} ($A, B = Li, Na, K$) revealed a rich variety of geometric structures and clear energetic trends that can not be accounted for by the jellium model for such a series of isovalent clusters. Generally, the most stable A_nB_{8-n} clusters are those with a composition equal to, or near, $n = 4$. This can be rationalized as resulting from a combination of higher symmetry in these clusters, larger ionic contributions to bonding, and larger mean coordination of the lightest element (the one with higher cohesive energy). The calculated ionization potentials and polarizabilities of Li_nNa_{8-n} clusters agree fairly well with experiment, but this is not enough to assign structure. Higher levels of theory as well as better models of the effect of

temperature would be needed especially for calculations of polarizabilities. Curiously, in the $\text{Li}_n\text{Na}_{8-n}$ series, clusters with $n = 6, 5, 4$ have the largest IPs, whereas clusters with $n = 1, 2, 3$ have the largest HOMO-LUMO gaps. The large HOMO-LUMO gaps of $\text{Li}_n\text{Na}_{8-n}$ ($n = 1, 2, 3$) indicate special stability associated with the 1-CTP structure where a central Li atom is solvated by surrounding atoms. A glance at the structure names and relative isomer energies in Table 7 gives an idea of the complexity of mixed alkali clusters and how challenging it is to make meaningful comparisons of calculated cluster properties to experimental measurements considering that those are normally done near room temperature and will typically represent averages over several isomers.

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