

σ -Aromaticity and σ -Antiaromaticity in Alkali Metal and Alkaline Earth Metal Small Clusters

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We extended the aromaticity concept to small σ -aromatic alkali metal and alkaline earth metal clusters. We performed ab initio calculations (B3LYP/6-311+G* and CCSD(T)/6-311+G*) on a selected group of triatomic and tetraatomic metal clusters. We have shown that the introduction of aromaticity and antiaromaticity in Li_3^+ and Li_3^- ions, respectively, can be used to explain their relative stability and their structure. For the tetraatomic 6σ -electron Li_2Mg_2 species we predicted that the cyclic σ -aromatic structures of Li_2Mg_2 are more stable than the classical linear Li-Mg-Mg-Li structure, thus showing the importance of the aromaticity in metal clusters. We believe that the further advancing of the aromaticity concept into metal clusters will be a useful tool in understanding chemical bonding in these species.

1. Introduction

In chemistry many chemical languages are used to describe chemical bonding. In organic chemistry, which has the largest number of chemical compounds, for most cases chemical bonding can be adequately represented by a single Lewis structure, involving a simple two-center two-electron ($2c-2e$) bond model. If the chemical bonding cannot be represented by a single Lewis structure, we use the concept of resonance of classical structures with $2c-2e$ bonds in each structure. An important class of such species is that of aromatic molecules, of which the resonance of Kekule structures in benzene is a good example. In solid metals we use the electron-sea model, which pictures metal as an array of metal cations in a “sea” of valence electrons. In organometallic chemistry the chemical bonding of the central metal cluster is described on the basis of Wade’s rules, and the organic moieties are represented in the same way, as conventional organic molecules. There is, of course, a universal molecular orbital language, which is applicable to all molecules. However, molecular orbitals are delocalized, which makes their use in organic chemistry inconvenient. Moreover, every type of molecule will have its own set of occupied molecular orbitals. This causes the molecular orbital language to be very complicated. The question is: can we extend the classical $2c-2e$ language, which is so simple and successful for millions of organic compounds, to metal systems? The major problem with this idea is the deficit of electrons in metals. As a result we have only a few molecules where the electronic structure can be represented by the $2c-2e$ model. However, we believe that the use of the aromaticity concept may help to advance the classical view of chemical bonding into metal clusters and eventually into solid metals.

In this work, we present our interpretation of chemical bonding in some main group metal clusters on the basis of the concept of σ -aromaticity. The concept of aromaticity was recently advanced into organometallic^{1–5} and all-metal systems.^{6–15} Robinson’s aromatic metal clusters^{1–5} are only π -aromatic, while the all-metal clusters^{6–15} are both π - and

σ -aromatic. The question is: what kind of advantage we can gain by using the aromaticity concept for metal clusters? With the help of aromaticity we were able to explain the geometric structure of two mixed metal clusters MAl_4^- and MAl_6^- ($\text{M} = \text{Li, Na, K, and Cu}$).^{6,9,10,12} Also, the presence of the multifold aromaticity in MAl_4^- ^{6,9,10} and MAl_6^- ¹² can easily explain why these species are particularly stable, when other theoretical models such as the “jelly model” and Wade’s rules have failed to predict the structure of these species as well as their extra stability.¹² Another example of the usefulness of aromaticity is the appearance of the cyclic isomer in the series of molecules XAl_3^- ($\text{X} = \text{Si, Ge, Sn, and Pb}$),⁷ MAl_3 ($\text{M} = \text{P and As}$),^{16,17} and MGa_3 ($\text{M} = \text{P and As}$).¹⁸ One would assume that a pyramidal structure with M being the central atom having one lone pair and three $2c-2e$ bonds with three Al(I) or Ga(I) ligands should be the global minimum. Indeed, such classical structure was found to be a stable isomer for all above species. However, in our calculations of XAl_3^- ($\text{X} = \text{Si, Ge, Sn, and Pb}$),⁷ and in calculations of Archibong and co-workers^{16–18} it was found that the cyclic structure is the most stable isomer for species where the electronegativity of the atom M is close to the electronegativity of the Al or Ga atoms. The recognition of the presence of the cyclic aromatic isomers helped in the interpretation of photoelectron spectra of the corresponding anionic species recently observed by Wang and co-workers⁷ and Neumark and co-workers.^{19,20} These examples have already shown the usefulness of the aromaticity concept and we believe that the advances of the aromaticity concept further into metal and nonmetal clusters will help us better understand chemical bonding, structure, and stability of these species as well as serve as a better interpretation of spectroscopic data.

In this article we will consider metal clusters with σ -aromaticity only. In such clusters only valence s-AOs are involved in chemical bonding.

2. Theoretical Methods

We performed ab initio calculations on a wide variety of structures for series of cations, anions, and neutral species, which we believe possess σ -aromaticity, to search for the global minimum. We initially optimized geometries and calculated

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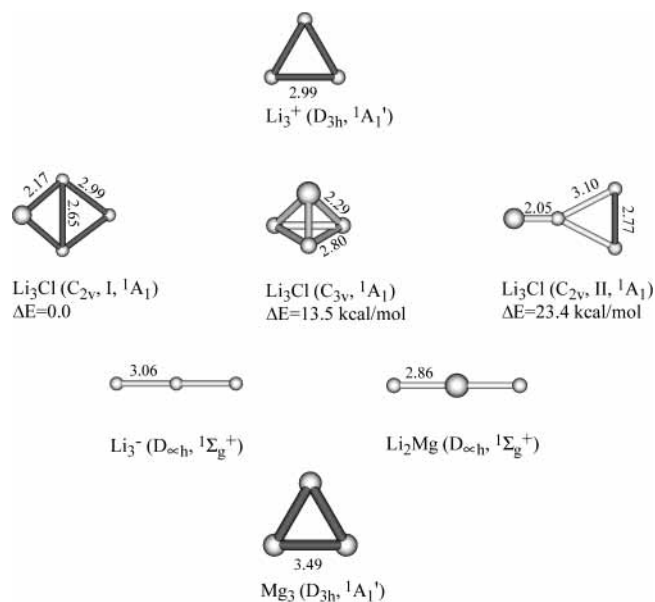


Figure 1. Optimized geometric structures of the selected triatomic σ -aromatic and σ -antiaromatic clusters (geometry at CCSD(T)/6-311+G* and the relative energies at CCSD(T)/6-311+G(2df)//CCSD(T)/6-311+G*). Bond lengths are in angstroms.

frequencies using analytical gradients with polarized split-valence basis sets (6-311+G*)^{21–23} and a hybrid method known in the literature as B3LYP.^{24–26} The most stable structures for all species were further optimized using the coupled-cluster method [CCSD(T)]^{27–29} with the 6-311+G* basis sets. Then the energies of the most stable structures were refined using the CCSD(T) method and the more extended 6-311+G(2df)

basis sets. All calculations were performed using the Gaussian 98 program.³⁰ Molecular orbitals (MOs) were calculated at the RHF/6-311+G* level of theory. All MO pictures were made using the MOLDEN 3.4 program.³¹

3. Theoretical Results

3.1. σ -Aromatic and σ -Antiaromatic Triatomic Systems.

The simplest metal cluster is Li_3^+ , which is known to have a triangular structure as its global minimum.³² Our optimized geometry, shown in Figure 1, agrees well with the previous calculations. The Li_3^+ cluster has only one completely delocalized bonding σ -molecular orbital shown in Figure 2. The delocalized MO can be used to interpret chemical bonding in Li_3^+ . However, our goal is to use the language of the σ -aromaticity. This can be done through the resonance of three classical structures (Figure 3) for Li_3^+ with one $2c-2e$ Li–Li bond. The $1a_1'$ -MO is a sum of the $2s$ -AOs of three lithium atoms and is very similar to the completely delocalized π -MO in the C_3H_3^+ cation.¹¹ The only difference is that the π -MO is a sum of $2p_z$ -AOs of carbons. The delocalized π -MO in C_3H_3^+ renders its π -aromaticity according to the famous $4n+2$ Huckel rule. On the basis of the analogy between the π -delocalized MO in C_3H_3^+ and the σ -delocalized MO in Li_3^+ we would like the latter cation to be called σ -aromatic. σ -Aromaticity is not new in chemistry, since it was formerly introduced for hydrocarbons.^{33–35}

If the Li_3^+ cation is σ -aromatic we should expect a special stability relative to nonaromatic reference molecules, as a result of its cyclic delocalization of the σ -electrons. The special stability is expressed as resonance energy. It is however inconvenient to work with a cation. We therefore optimized geometry for the Li_3Cl neutral molecule, containing the Li_3^+

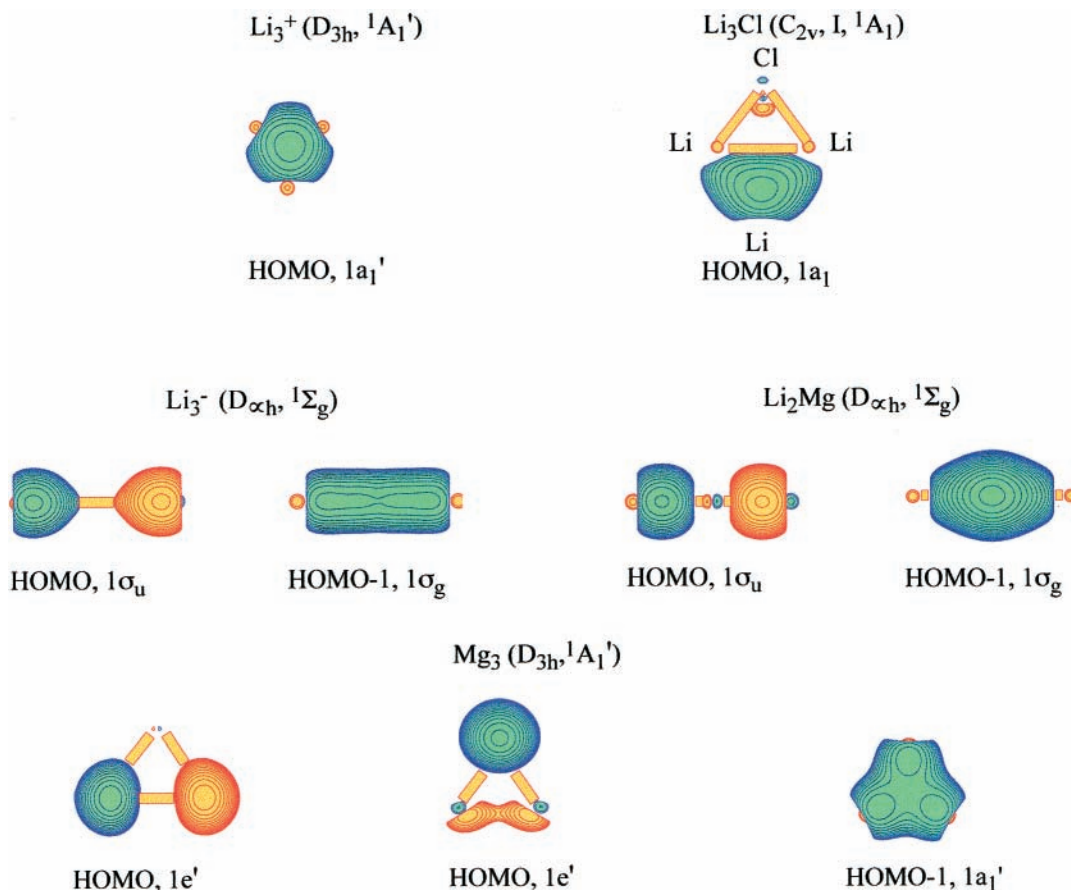


Figure 2. Molecular orbitals of the selected triatomic σ -aromatic and σ -antiaromatic clusters.

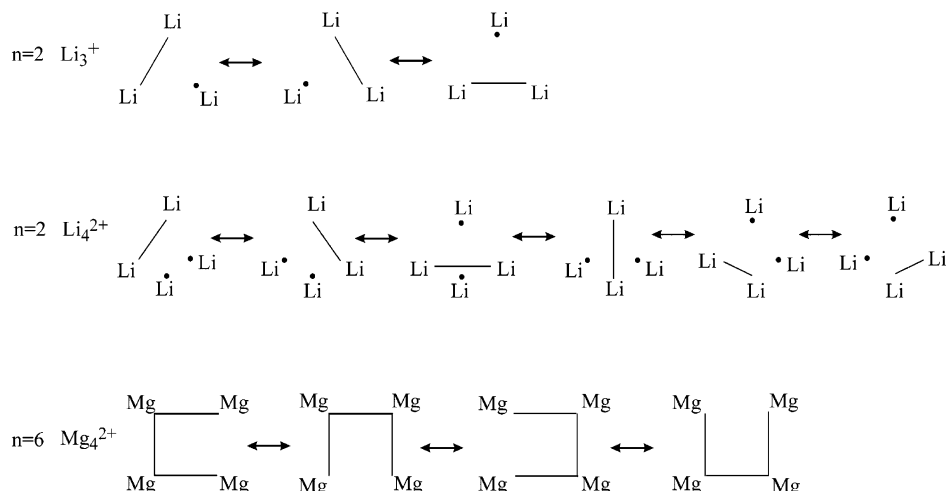


Figure 3. Resonance structures of Li_3^+ , Li_4^{2+} , and Mg_4^{2+} .

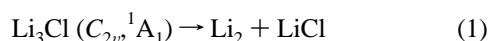
TABLE 1: Calculated Molecular Properties of the Structure C_{2v}, I (Figure 1) of Li_3Cl^a

$\text{Li}_3\text{Cl}, C_{2v}, I (^1A_1)^b$	B3LYP/6-311+G*	CCSD(T)/6-311+G*
$E_{\text{tot}}, \text{au}$	-482.90413	-482.16473
$R(\text{Cl}-\text{Li}_t), \text{\AA}$	4.455	4.405
$R(\text{Cl}-\text{Li}_b), \text{\AA}$	2.188	2.173
$R(\text{Li}_t-\text{Li}_b), \text{\AA}$	2.582	2.650
$\omega_1(a_1), \text{cm}^{-1}$	502 (71)	527
$\omega_2(a_1), \text{cm}^{-1}$	322 (63)	317
$\omega_3(a_1), \text{cm}^{-1}$	225 (23)	219
$\omega_4(b_1), \text{cm}^{-1}$	126 (3)	131
$\omega_5(b_2), \text{cm}^{-1}$	413 (3)	443
$\omega_6(b_2), \text{cm}^{-1}$	193 (41)	195

^a The infrared intensities (in km/mol) are given in parentheses.

^b Subscripts "t" and "b" means terminal and bridged.

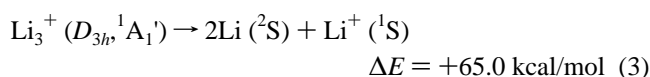
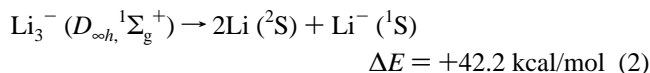
cation and the Cl^- anion. According to our calculations, the bidentate structure ($C_{2v}, I (^1A_1)$, Figure 1) with Cl^- coordinated to the edge of the Li_3^+ triangular is a global minimum in agreement with previous calculations.³⁶ The Cl^- anion only slightly perturbs the σ -aromatic HOMO in Li_3Cl when compared to the isolated Li_3^+ cation as can be seen in Figure 2. The σ -resonance energy in the Li_3^+ cation can be calculated as the energy of the reaction 1



where Li_2 and LiCl are reference classical molecules. At our highest level of theory (CCSD(T)/6-311+G(2df)//CCSD(T)/6-311+G*+ZPE/CCSD(T)/6-311+G* here and elsewhere) the energy of the reaction 1 was found to be 35.7 kcal/mol. The calculated resonance energy is certainly very high compared to the Li_2 dissociation energy (23.1 kcal/mol). Thus, we believe that the introduction of the σ -aromaticity in the Li_3^+ cation is justified. Because of the aromatic nature of the Li_3^+ cation, its neutral counterpart the Li_3 radical should have a rather low ionization potential. That is indeed a case. The best IP of Li_3 was measured to be $4.08 \pm 0.05 \text{ eV}$ ³⁷ and calculated to be $\text{IP}_v = 4.14 \text{ eV}$ and $\text{IP}_a = 4.06 \text{ eV}$.³⁸ This value is appreciably lower than the $\text{IP} = 5.390 \text{ eV}$ ³⁹ of the Li atom and therefore the Li_3 radical can be considered as a superalkali.^{40,41} According to our calculation, the Li_3Cl molecule containing the superalkali Li_3^+ cation is very stable and can be observed in the gas phase or in matrix isolation. Calculated harmonic frequencies (Table 1) can be used for its identification. It would be difficult if even possible to make a solid Li_3Cl . However, it may be possible to make a solid Li_3X salt with some X other a Cl^- counteranion.

The very unusual solid salt $\text{Li}_3\text{O}^+\text{NO}_2^-$ containing the Li_3O^+ superalkali cation has been known for more than 60 years.⁴²

The counting rule for σ -electrons is $4n+2$ if only the s-AOs are responsible for bonding. Then, for σ -antiaromatic species the counting rule is $4n$. The Li_3^- anion is a good example of σ -antiaromatic system with 4σ -electrons. The electronic configuration for the singlet state of Li_3^- at the D_{3h} symmetry is $1a_1'^2 1e'^2$, and the triangular structure with the singlet electronic state must undergo the Jahn–Teller distortion. Indeed, it is known that Li_3^- is linear.³² Two σ -delocalized MOs (Figure 2) can be approximately localized into two $2c-2e$ bonds and the linear structure of Li_3^- can be formally considered as a classical structure. This situation is similar to the antiaromatic cyclobutadiene structure, which can be considered as having two double and two single carbon–carbon bonds, and thus, is formally a classical structure. The $\text{Li}-\text{Mg}-\text{Li}$ triatomic molecule is linear (Figure 1) and it is isoelectronic to Li_3^- and certainly can be considered as having two $2c-2e$ $\text{Mg}-\text{Li}$ bonds. The antiaromaticity should manifest itself in a reduction of the stability of the molecule. Below, we present two reactions showing that the atomization energy of Li_3^- (reaction 2) is indeed substantially lower than the atomization energy of Li_3^+ (reaction 3).



When two more electrons are added, the number of σ -electrons again satisfies the $4n+2$ rule, and the corresponding cluster is expected to be aromatic again. However, the Mg_3 cluster is a weakly bound van der Waals complex (the atomization energy was found to be just 5.2 kcal/mol). We believe that this does not contradict the aromaticity concept. As one can see in Figure 2, in Mg_3 all bonding, nonbonding, and antibonding MOs, composed of the 3s atomic orbitals, are occupied, and in such a case the net bonding effect is expected to be close to zero. The same holds for the reference hydrocarbon aromatic molecules. If we were able to make a $\text{C}_6\text{H}_6^{6-}$ hexaanion of benzene in some external stabilizing field, we would have 6 $2p_z$ -lone pairs with zero contribution to bonding. Even the number of π -electrons satisfies the $4n+2$ rule. This is because of the fact that all bonding, nonbonding and antibonding MOs composed of $2p_z$ -AOs are occupied.

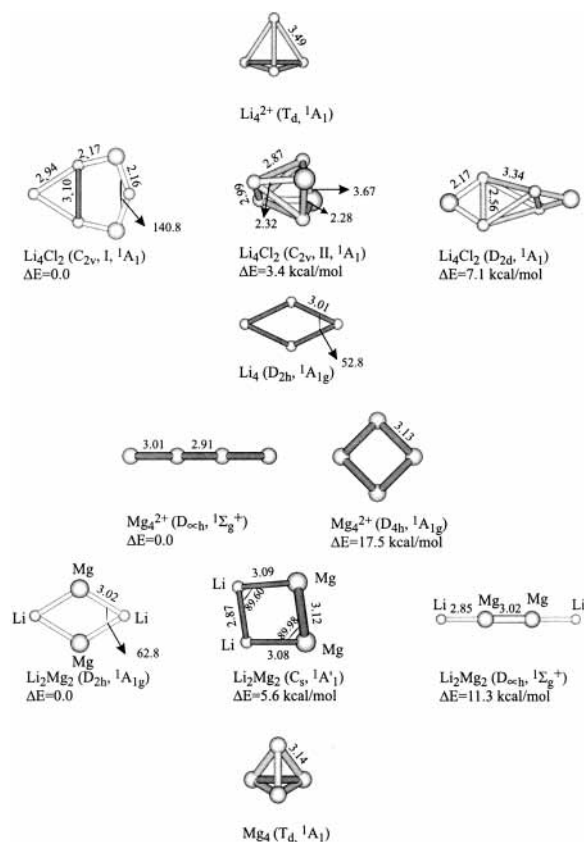
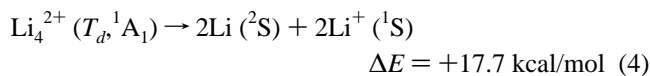


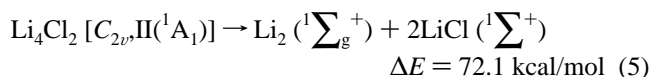
Figure 4. Optimized geometric structures of the selected tetraatomic σ -aromatic and σ -antiaromatic clusters (geometry at CCSD(T)/6-311+G* and the relative energies at CCSD(T)/6-311+G(2df)//CCSD(T)/6-311+G*). Bond lengths are in angstroms.

3.2. σ -Aromatic and σ -Antiaromatic Tetraatomic Systems.

A similar approach can be used to explain aromaticity and antiaromaticity in tetraatomic clusters. The Li_4^{2+} dication is the simplest tetraatomic metal cluster, with just two σ -electrons. It adopts a tetrahedral structure (Figure 4), and its electronic structure can be represented by six classical resonance structures (Figure 3). While the Li_4^{2+} dication is not expected to be stable because of the Coulomb repulsion, it does have a local minimum at the tetrahedral structure. The calculated dissociation energy for the reaction (4) was found to be slightly positive:



To evaluate the resonance energy we need to subtract the destabilizing effect of the Coulomb repulsion from two extra positive charges. One way to do this is to assume that the Coulomb repulsion of two extra charges in Li_4^{2+} can be approximately evaluated by placing one point charge of +0.5 e on each of the four Li nuclei. If we subtract the repulsion energy thus calculated (142.6 kcal/mol) from the atomization energy in the reaction 4 we get the resulting value of 160.3 kcal/mol. From this value, and from the dissociation energy of Li_2 , the resonance energy is 137.2 kcal/mol. We can also evaluate the σ -resonance energy another way. Surrounding the dication with two counteranions, such as Cl^- , and forming Li_4Cl_2 neutral molecule, can stabilize the doubly charged Li_4^{2+} cation. We performed geometry optimizations and frequency calculations for a variety of alternative structures with the stoichiometry Li_4Cl_2 . We found that the planar structure $C_{2v}, \text{I} ({}^1A_1)$ is the global minimum for this stoichiometry. This structure is actually a complex between the Li_3^+ cation and $\text{Cl}-\text{Li}-\text{Cl}^-$ anion and does not contain the Li_4^{2+} cation. It is not a surprise that the Li_4Cl_2 molecule prefer a structure with the triangular σ -aromatic Li_3^+ cation, rather than a structure with the tetrahedral σ -aromatic Li_4^{2+} cation. This is because of the high Coulomb repulsion in the latter. However, according to our calculation, the structure $C_{2v}, \text{II} ({}^1A_1)$ containing the Li_4^{2+} tetrahedral cluster is a local minimum being just 3.4 kcal/mol higher than the global minimum structure. The calculated harmonic frequencies for these two structures are summarized in Table 2. Molecular orbitals presented in Figure 5 clearly show the presence of the Li_3^+ and Li_4^{2+} clusters in the $C_{2v}, \text{I} ({}^1A_1)$ and $C_{2v}, \text{II} ({}^1A_1)$ structures, respectively. These results show that the enormous repulsion energy can almost be overcome by the large resonance energy in the Li_4^{2+} cation. We now can evaluate the resonance energy in the Li_4^{2+} cation from reaction 5



The resonance energy evaluated in this way is lower than the energy evaluated above, but still the quantity is quite high.

TABLE 2: Calculated Molecular Properties of the Structure C_{2v}, I and C_{2v}, II (Figure 1) of Li_4Cl_2^a

$\text{Li}_4\text{Cl}_2, C_{2v}, \text{I} ({}^1A_1)^b$	B3LYP/6-311+G*	CCSD(T)/6-311+G*	$\text{Li}_4\text{Cl}_2, C_{2v}, \text{II} ({}^1A_1)^b$	B3LYP/6-311+G*	CCSD(T)/6-311+G*
$E_{\text{tot}}, \text{ au}$	-950.79969	-949.43826	$E_{\text{tot}}, \text{ au}$	-950.79086	-949.43020
$R(\text{Cl}-\text{Li}_b), \text{ \AA}$	2.182	2.160	$R(\text{Cl}-\text{Li}_b), \text{ \AA}$	2.301	2.280
$R(\text{Cl}-\text{Li}_i), \text{ \AA}$	2.190	2.172	$R(\text{Cl}-\text{Li}_i), \text{ \AA}$	2.350	2.318
$R(\text{Li}_b-\text{Li}_{b'}), \text{ \AA}$	3.236	3.237	$R(\text{Li}_b-\text{Li}_{b'}), \text{ \AA}$	2.634	2.663
$R(\text{Li}_b-\text{Li}_i), \text{ \AA}$	3.000	3.101	$R(\text{Li}_b-\text{Li}_i), \text{ \AA}$	2.858	2.866
$R(\text{Li}_i-\text{Li}_i), \text{ \AA}$	2.931	2.943	$R(\text{Li}_i-\text{Li}_i), \text{ \AA}$	3.001	2.994
$\omega_1(a_1), \text{ cm}^{-1}$	493 (173)	523	$\omega_1(a_1), \text{ cm}^{-1}$	401 (9)	421
$\omega_2(a_1), \text{ cm}^{-1}$	308 (96)	325	$\omega_2(a_1), \text{ cm}^{-1}$	308 (3)	320
$\omega_3(a_1), \text{ cm}^{-1}$	248 (5)	234	$\omega_3(a_1), \text{ cm}^{-1}$	278 (72)	296
$\omega_4(a_1), \text{ cm}^{-1}$	232 (5)	234	$\omega_4(a_1), \text{ cm}^{-1}$	181 (78)	185
$\omega_5(a_1), \text{ cm}^{-1}$	124 (21)	133	$\omega_5(a_1), \text{ cm}^{-1}$	162 (0)	167
$\omega_6(a_2), \text{ cm}^{-1}$	106 (0)	107	$\omega_6(a_2), \text{ cm}^{-1}$	345 (0)	368
$\omega_7(b_1), \text{ cm}^{-1}$	138 (38)	142	$\omega_7(a_2), \text{ cm}^{-1}$	182 (0)	175
$\omega_8(b_1), \text{ cm}^{-1}$	83 (8)	86	$\omega_8(b_1), \text{ cm}^{-1}$	290 (30)	302
$\omega_9(b_2), \text{ cm}^{-1}$	585 (137)	637	$\omega_9(b_1), \text{ cm}^{-1}$	148 (48)	157
$\omega_{10}(b_1), \text{ cm}^{-1}$	468 (26)	499	$\omega_{10}(b_2), \text{ cm}^{-1}$	447 (82)	475
$\omega_{11}(b_2), \text{ cm}^{-1}$	167 (7)	174	$\omega_{11}(b_2), \text{ cm}^{-1}$	280 (15)	307
$\omega_{12}(b_2), \text{ cm}^{-1}$	108 (14)	115	$\omega_{12}(b_2), \text{ cm}^{-1}$	205 (12)	211

^a The infrared intensities (in km/mol) are given in parentheses. ^b Subscripts "t" and "b" means terminal and bridged; subscript "b" means bridged Li atom located between two Cl atoms.

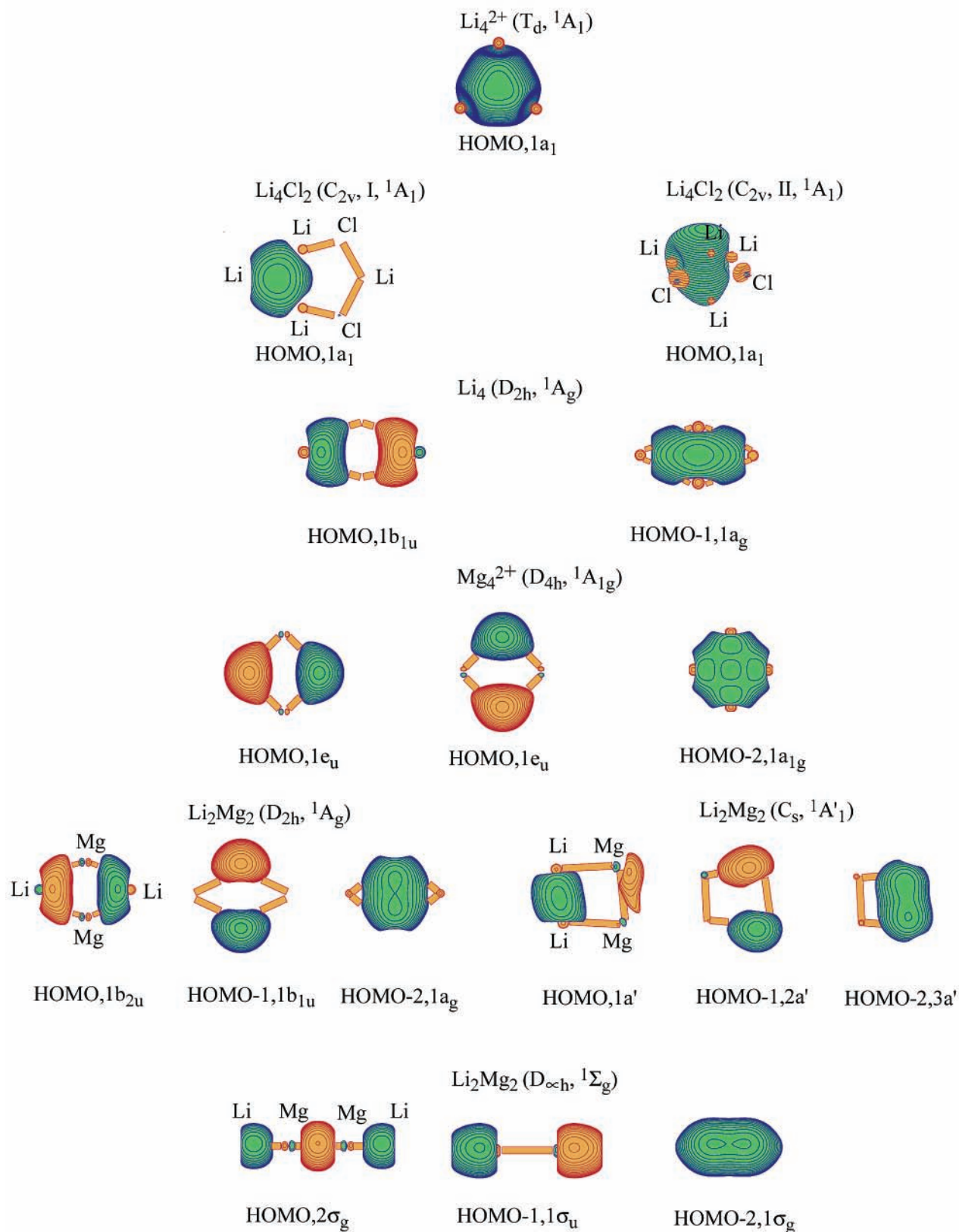


Figure 5. Molecular orbitals of the selected tetraatomic σ -aromatic and σ -antiaromatic clusters.

When two more electrons are added, the neutral Li_4 molecule with four σ -electrons is expected to be antiaromatic and rectangular, as is known for C_4H_4 .³⁵ However, we found that a rhombus structure is the global minimum for Li_4 in agreement with previous calculations.⁴³ Apparently, the σ -frame in C_4H_4 enforces the rectangular distortion. The rhombus structure of Li_4 is expected, on the basis of the Jahn–Teller distortion of

the singlet square structure with the $1a_g^2 1e_u^2$ electronic configuration and the shape of the occupied molecular orbitals (see Figure 5).

The next tetraatomic system with six σ -electrons is Mg_4^{2+} . It is a metastable species with a local minimum at the planar square geometry (Figure 4), which is similar to that of the π -aromatic $\text{C}_4\text{H}_4^{2-}$ hydrocarbon.^{44–46} The linear structure of

Mg₄²⁺ (Figure 4) is, however, more stable because it minimizes the Coulomb repulsion. To avoid dealing with doubly charged species, we studied the Mg₂Li₂ molecule, which also has 6 σ -electrons and is supposed to be σ -aromatic. As is shown in Figure 1, the cyclic Mg₂Li₂ aromatic structures are indeed more stable than the linear Li–Mg–Mg–Li classical structure (Figure 4). The higher stability of the σ -aromatic structures of Mg₂Li₂ provides us with an additional justification for the introduction of the σ -aromaticity concept into metal clusters. The Mg₄ cluster, in analogy with Mg₃, is supposed to be a weakly bound van der Waals complex. However, with the increase of the size of a cluster, the s–p hybridization starts to play more important role, which leads to rather high atomization energy of Mg₄ (22.4 kcal/mol).

4. Discussion

The advance of the aromaticity concept into metal clusters was already very helpful. The triangular structure of the Ga₃²⁻ cluster inside of the large organometallic Na₂[(Mes)₂C₆H₃]₃ (Mes = 2,4,6-Me₃C₆H₂)³ and Na₂[(Mes)₂C₆H₃]₃Ga₃ (Mes = 2,4,6-Me₃C₆H₂)⁴ molecules has been explained on the bases of the presence of π -aromaticity. The presence of the both σ - and π -aromaticity helped us to interpret the presence of the square Al₄²⁻, Ga₄²⁻, and In₄²⁻ clusters in the gas-phase bimetallic MA₄⁻ clusters^{6,9} as well as in the crystal organometallic K₂[Ga₄(C₆H₃-2,6-Trip₂)₂] compound.^{9,47} Also, the presence of the multifold aromaticity in MA₄^{-6,9,10} and MA₆⁻¹² helped us to explain why these species are particularly stable, when other theoretical models such as the “jelly model” and the Wade’s rules failed.¹² Aromaticity helped us to explain the appearance of the cyclic isomer in the series of molecules XAl₃⁻ (X = Si, Ge, Sn, and Pb),⁷ MA₃ (M = P and As),^{16,17} and MGa₃ (M = P and As).¹⁸ Finally, we can point out that the multi-fold aromaticity concept helped us to explain why in Na–Hg amalgams we find planar square Hg₄⁶⁻ clusters.⁸

In this article we extended the aromaticity concept to σ -aromatic alkali metal and alkaline earth metal clusters. We have shown that the introduction of aromaticity and antiaromaticity into Li₃⁺ and Li₃⁻ ions, respectively, can be used to explain their relative stability. It would be interesting to synthesize a Li₃⁺X⁻ molecule and a Li₃⁺X⁻ solid, which would have the σ -aromatic alkali metal cluster as a cation. Probably our most important result is a prediction that the cyclic σ -aromatic structures of Li₂Mg₂ are more stable than the classical linear Li–Mg–Mg–Li structure.

We believe that the concept of aromaticity can be further utilized in studies of metal, nonmetal and mixed metal–nonmetal clusters. However, when atoms with occupied p- and d-orbitals are part of the metal cluster, the chemical bonding becomes more complicated. For example, when p-AOs are involved in bonding, we need to consider two types of p-AOs (radial and tangential) involved in σ -bonding. We plan to discuss how the concept of σ -aromaticity can be extended into such systems in our future publications.

We believe that the aromaticity concept can also be extended into bulk metals. In fact, more than 50 years ago Linus Pauling^{48,49} used the resonance valence bond theory to explain chemical bonding in alkali and transition metals. However, he did this without using the concept of aromaticity. We plan to look at chemical bonding in bulk metals using the aromaticity concept in our future works.

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