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REGULAR ARTICLE

Theoretical study of spectroscopic parameters of alkali -Al and alkaline earth-Al dimers

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Abstract The ground states of alkali-Al dimers (AlLi, AlNa, AlK, AlRb and AlCs) and alkaline earth-Al dimers (AlBe, AlMg, AlCa, AlSr and AlBa) along with their monovalent anions and cations were assigned based on the results of calculations. Bond lengths r_e, harmonic vibrational frequencies ω_e and dissociation energies D_0 of these species were obtained. For neutral dimers, we also calculated adiabatic electron affinities (EA) and adiabatic ionization energies (IE). The present results are in agreement with the available experimental and other theoretical data. The ground state symmetry of AlLi, AlNa, AlK, AlRb and AlCs is $^1\Sigma^+$. The ground state symmetry of AlBe$^+$, AlMg$^+$, AlCa$^+$, AlSr$^+$ and AlBa$^+$ is also $^1\Sigma^+$. The ground state of AlLi$^-$, AlNa$^-$, AlK$^-$, AlRb$^-$ and AlCs$^-$ is $^2\Pi$, and is the same as in the isoelectronic neutral Al-alkaline-earth dimers. For both the alkali-Al and alkaline earth-Al neutral AlX species, the bond length increases monotonously with increasing atomic number of X. For the alkali-Al ions, energies of dissociation via the channels AlX$^-$ $\rightarrow$ Al + X$^-$ and AlX$^+$ $\rightarrow$ Al + X$^+$ are smaller than the energies of dissociation via the channel AlX$^-$ $\rightarrow$ X + Al$^-$andAlX$^+$ $\rightarrow$ X + Al$^+$, respectively. While the opposite dissociation manner is found for alkaline earth-Al anions.

Keywords Dimer · First-principles · Alkali and alkaline earth metal aluminide · Spectroscopic constant

1 Introduction

Understanding the nature of chemical bond between aluminum and other metal is of great interest in many areas of science, such as surface chemistry, catalysis, organometallic chemistry and material science. Diatomic metal aluminides, that is to say, aluminum-containing dimers, are the simplest systems to understand the chemical bonding between aluminium and other metal. A thorough understanding of how these species interact is an essential prerequisite to increasing our knowledge of more complicated system. Indeed, increasing experimental and theoretical efforts have recently been focused on these diatomic systems. Behm and co-workers have systematically investigated AlV [1], AlCr [1], AlMn [2], AlCo [1], AlNi [3], AlCu [4], AlZn [5] and AlCa [6] by resonant two-photon ionization spectroscopy. Among the Al-containing dimers, alkali-Al dimers and alkaline earth-Al dimers are the simplest species, and they have been the subject of many theoretical investigations performed at different levels and with various basis sets. Boldyrev et al. [7] investigated the electronic structures of lithium-containing diatomic LiX, LiX$^+$ and LiX$^-$ (with X = Li through F and Na through Cl) using different correlation levels, including MP2, MP4, and QCISD(T) (quadratic configuration interaction with single and double excitations and triple excitations added perturbatively calculation) method. The ground and very low-lying excited states of all 120 first- and second-row diatomic dimers were also surveyed by Boldyrev et al. [8]. The alkaline earth-alkali metal diatoms BeLi, BeNa, MgLi, MgNa, and AlBe as well as their corresponding negative ions were studied by Bauschlicher et al. [9]. They found that the

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ground states of all the alkaline earth-alkali metal dimers and their negative ions are bound, but the negative ions are more strongly bound than the neutrals. They also found that substituting an alkali atom with Al yielded much stronger bonds. Gutsev et al. [10] have systematically studied the ground and lowest excited states of neutral and negative charged diatomic species formed by Al and second-row atom at the CCSD(T) theory (the infinite-order coupled-cluster method with all singles and doubles and noniterative inclusion of triple excitations, Refs. [11,12]) with a large atomic nature orbital basis of Widmark–Malmqvist–Roos (WMR). Behm et al. [6] investigated AlCa by use of spectroscopic analysis method and ab initio calculation methods. More recently, the equilibrium geometries and energetics of the A_4B_4-type binary clusters consisting of Na, Mg, Al, and Si atoms have been calculated using ab initio molecular-dynamics simulation under the framework of density-functional theory with the plane-wave-based pseudopotential approach [13]. The interaction of hydrogen atom with light metals alloy clusters LiAl and $(\mathrm{LiAl})_2$ have been investigated by using the post–Hartree–Fock (MP2/cc-pVTZ) and density functional theory under the PBE–LYP exchange correlation functional [14].

To the best of our knowledge, the spectroscopic parameters of AlRb, AlCs, AlSr, AlBa and their corresponding charged dimers neither been studied theoretically nor been studied experimentally. In addition, although AlLi, AlNa, AlK, AlBe, AlMg and AlCa and only part of their ions (AlLi^+, AlLi^-, AlCa^+ and AlBe^-) have been studied, the results of CCSD(T) method are very limited, only AlLi, AlLi^-, AlBe (both neutral and charged dimers) were investigated by CCSD(T) method. In this paper, we present a systematically theoretical study of alkali-Al (AlLi, AlNa, AlK, AlRb, AlCs and their corresponding single charged ions) dimers and alkaline earth-Al (AlBe, AlMg, AlCa, AlSr, AlBa as well as their corresponding monovalent anions and cations) dimers. The equilibrium bond length r_e, vibrational frequency ω_e and dissociation energy D_0 were concerned. For the neutral dimers, first adiabatic electron affinities (EA) and adiabatic ionization energies (IE) were also reported.

2 Computational methods

The calculations presented here were carried out using the Gaussian 03 suit of program [15]. In our calculations, different high-level basis sets were used: the 6-311+G(2df) basis set was used for Al, Li, Na, K, Be, Mg and Ca; as for Rb, Cs, Sr and Ba, we chose the small core relativistic effective core potential (RECP) developed by Lim et al. [16,17], namely, ECP28MDF for Rb, Sr and ECP46MDF for Cs, Ba. In this method, 28 inner electrons of Rb, Sr and 46 inner electrons of Cs, Ba are described within the RECP approximation. Both the RECP and the basis sets can be found at the web site of Stuttgart group [18]. The spectroscopic parameters (r_e, ω_e, D_0) for the ground state of neutral AlX (X = Li, Na, K, Rb, Be, Mg, Ca and Sr) dimers and their corresponding ions were determined at the CCSD(T) level of theory. While for AlCs, AlBa and their ions, due to the failure of optimization by CCSD(T) method, the optimization process was performed by using hybrid density functional B3LYP [19,20] method, r_e and ω_e were obtained from B3LYP results, other parameters were calculated with CCSD(T) level based on the structure of B3LYP optimizations.

Each diatomic species is calculated at various possible spin multiplicities in order to find global minimum or ground state. To avoid trapping at local minima of the potential energy curve, different initial structures (the different distance between atoms) were chosen. Dissociation energies are calculated as the difference in total energy of a diatomic and the corresponding constituent atomic species, e.g. for neutral species, it is

$$D_0(\mathrm{AlX}) = E_{\mathrm{tot}}(\mathrm{Al}) + E_{\mathrm{tot}}(X) - E_{\mathrm{tot}}(\mathrm{AlX}) \quad (1)$$

and similar definitions for cations and anions. In the dissociation energy calculations of charged species, we chose two channels for the cations, i.e. $\mathrm{AlX}^+ \to \mathrm{Al} + \mathrm{X}^+$ and $\mathrm{AlX}^+ \to \mathrm{X} + \mathrm{Al}^+$, two channels for anions, i.e. $\mathrm{AlX}^- \to \mathrm{Al} + \mathrm{X}^-$ and $\mathrm{AlX}^- \to \mathrm{X} + \mathrm{Al}^-$. The first electron affinities and ionization energies reported in this work are adiabatic values, that is, the EA and IE are defined as the difference in the total energies of the lowest energy state of ion and the ground state of the neutral dimers. Within the Born–Oppenheimer approximation, one could evaluate the EA and IE as

$$\mathrm{EA} = E_{\mathrm{tot}}(\mathrm{AlX}) - E_{\mathrm{tot}}(\mathrm{AlX}^-) \quad (2)$$

$$\mathrm{IE} = E_{\mathrm{tot}}(\mathrm{AlX}^+) - E_{\mathrm{tot}}(\mathrm{AlX}) \quad (3)$$

where $E_{\mathrm{tot}}(\mathrm{AlX})$, $E_{\mathrm{tot}}(\mathrm{AlX}^+)$ and $E_{\mathrm{tot}}(\mathrm{AlX}^-)$ denote the equilibrium state energy of the neutral dimer, the cation and the anion, respectively. Our results are summarized in Tables 1, 2 and 3 together with the available experimental and other theoretical data.

3 Results and discussion

3.1 AlLi, AlLi^+, and AlLi^-

All of these species have been studied extensively [7,8,10,13]. Brock et al. [21] employed resonant two-photon photoionization (R2PI) to analysis the spectrum, providing the vibrational frequency 318.3 cm^{-1} and dissociation energy 0.75 eV for the AlLi ground state. As for the theoretical studies, several high precise ab initio calculations have been carried out for AlLi. Boldyrev et al. [7] studied three low-lying states ${}^1\Sigma^+, {}^3\Sigma^-$, and ${}^3\Pi_r$ for neutral AlLi at MP2 level with 6-311+G* basis set, they found AlLi had a low-spin

Table 1 Calculated spectroscopic constants [bond length r_e (in Å), vibrational frequency ω_e (in cm^{-1}), dissociation energy D_0 (in eV), adiabatic electronic affinity EA (in eV) and ionization energy IE (in eV)] of the ground states of AlX dimers

X	Method	State	r_e	ω_e	D_0	IE	EA
Li	CCSD(T)/6-311+G(2df)	$^1\Sigma^+$	2.875	309.2	0.9936	5.1752	0.5877
	exp. [21]			318.3	0.75		
	MP2/6-311+G* [7]	$^1\Sigma^+$	2.869	322			
	MP4/6-311+G(2df) [7]	$^1\Sigma^+$			0.9496		
	QCISD(T)/6-311+G(2df) [7]	$^1\Sigma^+$			1.0104		0.62
	CASSCF-MRCISD(Q) [8]	$^1\Sigma^+$	2.859	310			
	CCSD(T)/WMR [10]	$^1\Sigma^+$	2.8381	316	1.06		0.653
Be	CCSD(T)/6-311+G(2df)	$^2\Pi$	2.434	379.6	0.4922	5.8688	1.0677
	CASSCF [9]	$^2\Pi$	2.427	383	0.57		1.09
	CCSD(T)/WMR [10]	$^2\Pi$	2.3981	395	0.59		1.131
Na	CCSD(T)/6-311+G(2df)	$^1\Sigma^+$	3.181	185.3	0.7614	4.8831	0.6305
	MP2/6-311+G* [8]	$^1\Sigma^+$	3.134	196			
	QCISD(T)/6-311+G(2df) [8]	$^1\Sigma^+$	3.182		0.772		
	B3LYP/6-31G* [22]		3.146		0.754		
	LSDA/6-31G* [22]		3.088		1.080		
Mg	CCSD(T)/6-311+G(2df)	$^2\Pi$	2.903	195.5	0.3291	5.3763	0.9089
	MP2/6-311+G* [8]	$^2\Pi$r	2.922	192			
	QCISD(T)/6-311+G(2df) [8]	$^2\Pi$r	2.901		0.34		
	MCSCF/aug-cc-pVDZ [8]	$^2\Pi$r	3.03	131			
K	CCSD(T)/6-311+G(2df)	$^1\Sigma^+$	3.613	139.9	0.5401	4.2739	0.6544
Ca	CCSD(T)/6-311+G(2df)		3.176	179.4	0.3977	4.9297	0.8993
	exp. [6]	$^2\Pi$r	3.1479	189.1 ± 0.8		5.072 ± 0.028	
	exp. [24]	$^2\Pi$	3.14942				
	CASSCF-MRCISD [6]	$^2\Pi$	3.277	172			
	QCISD(T) [6]	$^2\Pi$	3.213				
	CASSCF-MRCISD(Q) [6]	$^2\Pi$	3.268	169	0.47	4.97	
Rb	CCSD(T)	$^1\Sigma^+$	3.752	120.7	0.5231	4.1927	0.6644
	B3LYP	$^1\Sigma^+$	3.810	116.1			
Sr	CCSD(T)	$^2\Pi$	3.330	153.9	0.4716	4.8106	0.9388
	B3LYP	$^2\Pi$	3.371	139.5			
Cs	CCSD(T)[a]	$^1\Sigma^+$	4.048	103.6	0.4865	3.9474	0.6916
Ba	CCSD(T)[a]	$^2\Pi$	3.470	144.7	0.5853	4.6256	0.9582

[a] r_e and ω_e were obtained by using B3LYP method, the rest parameters were calculated with CCSD(T) level of theory

$^1\Sigma^+$ ground state with bond length 2.869 Å and harmonic vibrational frequency 322 cm^{-1}. They calculated dissociation energy of AlLi ($^1\Sigma^+$) into the neutral atoms in their ground states is 23.3 kCal/mol (≈1.0104 eV) at the QCISD(T)/6-311+G(2df) level. Gutsev et al. [10] obtained the ground state of AlLi is $^1\Sigma^+$ at the CCSD(T)/WMR level, they calculated bond length 2.8381 Å, harmonic frequency 316 cm^{-1}, and dissociation energy 1.06 eV. The $^1\Sigma^+$ state of AlLi was also predicted by Boldrev [8] employing rather accurate ab initio method CASSCF-MRCISD(Q) (MRCISD(Q) study based on the CASSCF calculations) level with (17s12p5d4f/7s5p3d2f)Al + (14s9p4d3f /7s5p3d2f) Li basis sets. They found the bond length was 2.859 Å and harmonic frequency 310 cm^{-1}. Furthermore, in Ref. [14], AlLi was investigated by employing various density functional methods, giving bond length from 2.83 to 2.91 Å and bond strength from 0.78 to 1.03 eV. Our CCSD(T)/6-311+G(2df) study found that the ground state symmetry is $^1\Sigma^+$ with a $6\sigma^2 1\pi^4$ electron configuration, which is the same as previous ab initio results. Our calculated bond length 2.875 Å is very close to other theoretical values (MP2: 2.869 Å [7], CASSCF-MRCISD(Q): 2.859 Å [8], and CCSD(T)/WMR: 2.8381 Å [10]). Our calculated frequency 309.2 cm^{-1} are near to the experimental value 318.3 cm^{-1}

Table 2 Calculated spectroscopic constants [bond length r_e (in Å), vibrational frequency ω_e (in cm^{-1}) and dissociation energy D_0 (in eV)] of the ground state of AlX$^-$ dimers

X	Method	State	r_e	ω_e	D_0	
					AlX$^-$ $\rightarrow$ Al + X$^-$	AlX$^-$ $\rightarrow$ X + Al$^-$
Li	CCSD(T)/6-311+G(2df)	$^2\Pi$	2.864	263.7	0.9686	1.2988
	MP2/6-311+G* [7]	$^2\Pi$r	2.832	268		
	CCSD(T)/WMR [10]	$^2\Pi$	2.8346	264	1.09	1.30
	MP4/6-311+G(2df) [7]	$^2\Pi$r				1.2619
	QCISD(T)/6-311+G(2df) [7]	$^2\Pi$r				1.353
Be	CCSD(T)/6-311+G(2df)	$^3\Sigma^-$	2.311	452.3	2.0815	1.2774
	CASSCF [9]	$^3\Sigma^-$	2.315	458		1.36
	CCSD(T)/WMR [10]	$^3\Sigma^-$	2.2839	461		
Na	CCSD(T)/6-311+G(2df)	$^2\Pi$	3.190	158.5	0.8519	1.1094
Mg	CCSD(T)/6-311+G(2df)	$^3\Sigma^-$	2.741	254.4	1.5861	0.9556
K	CCSD(T)/6-311+G(2df)	$^2\Pi$	3.594	119.5	0.7096	0.9120
Ca	CCSD(T)/6-311+G(2df)	$^3\Sigma^-$	3.047	195.1	1.4740	1.0145
Rb	CCSD(T)	$^2\Pi$	3.715	105.1	0.7132	0.9051
	B3LYP	$^2\Pi$	3.819	88.1		
Sr	CCSD(T)	$^3\Sigma^-$	3.177	167.0	1.6972	1.128
	B3LYP	$^3\Sigma^-$	3.175	161.8		
Cs	CCSD(T)[a]	$^2\Pi$	4.004	80.9	0.7178	0.8956
Ba	CCSD(T)[a]	$^3\Sigma^-$	3.575	125.5	1.4813	1.261

[a] r_e and ω_e were obtained by using B3LYP method, the rest parameters were calculated with CCSD(T) level of theory

Table 3 Calculated spectroscopic constants [bond length r_e (in Å), vibrational frequency ω_e (in cm^{-1}) and dissociation energy D_0 (in eV)] of the ground state of AlX$^+$ dimers

X	Method	State	r_e	ω_e	D_0	
					AlX$^+$ $\rightarrow$ Al + X$^+$	AlX$^+$ $\rightarrow$ X + Al$^+$
Li	CCSD(T)/6-311+G(2df)	$^2\Sigma^+$	3.038	236.1	1.1569	1.7471
	MP2/6-311+G* [7]	$^2\Sigma^+$	3.005	242		
	MP4/6-311+G(2df) [7]	$^2\Sigma^+$			1.1751	
	QCISD(T)/6-311+G(2df) [7]	$^2\Sigma^+$			1.1708	
Be	CCSD(T)/6-311+G(2df)	$^1\Sigma^+$	2.831	246.8	3.9063	0.5522
Na	CCSD(T)/6-311+G(2df)	$^2\Sigma^+$	3.401	139.0	0.8223	1.8071
Mg	CCSD(T)/6-311+G(2df)	$^1\Sigma^+$	3.135	190.3	2.4695	0.8815
K	CCSD(T)/6-311+G(2df)	$^2\Sigma^+$	3.879	100.8	0.5269	2.1950
Ca	CCSD(T)/6-311+G(2df)	$^1\Sigma^+$	3.481	163.2	1.4889	1.3968
	QCISD(T) [6]	$^1\Sigma^+$	3.510			1.50
	CASSCF- MRCISD [6]	$^1\Sigma^+$	3.531	158		
	CASSCF- MRCISD(Q) [6]	$^1\Sigma^+$	3.533	156		
Rb	CCSD(T)	$^2\Sigma^+$	4.016	87.1	0.4922	2.2592
	B3LYP	$^2\Sigma^+$	4.086	79.6		
Sr	CCSD(T)	$^1\Sigma^+$	3.640	141.2	e1.3275	1.5898
	B3LYP	$^1\Sigma^+$	3.694	128.6		
Cs	CCSD(T)[a]	$^2\Sigma^+$	4.334	69.2	0.4238	2.4678
Ba	CCSD(T)[a]	$^1\Sigma^+$	3.870	121.7	1.1348	1.8885

[a] r_e and ω_e were obtained by using B3LYP method, the rest parameters were calculated with CCSD(T) level of theory

and previous theoretical results (MP2: 322 cm^{-1} [7], CASSCF-MRCISD(Q): 310 cm^{-1} [8], and CCSD(T)/WMR: 316 cm^{-1} [10]). While for the dissociation energy, all the theoretical results, including the present result, are slightly higher compared with experimental value (0.75 eV), see Table 1. The adiabatic electronic affinity obtained by us 0.5877 eV accord with that of the QCISD(T)/6-311+G(2df) result 0.62 eV [7] and that of the CCSD(T)/WMR result 0.653 eV [10]. The ionization energy of 5.1752 eV for AlLi is the highest in alkali-Al species.

Our calculation found that the ground state of AlLi$^-$ ion is $^2\Pi$ (with a $6\sigma^2 2\pi^1$ electron configuration). The anion AlLi$^-$ is isoelectronic molecule with the neutral AlBe molecule, and AlLi$^-$ has the same ground symmetry as that of AlBe. Boldyrev et al. [7] have studied $^4\Sigma^-, ^4\Pi_r, ^2\Pi_i$, and $^2\Pi_r$ states of AlLi$^-$ at MP2 level with 6-311+G* basis set. They found the $^2\Pi_r$ state of AlLi$^-$ was the most stable one, the bond length and harmonic vibrational frequency of AlLi$^-$ in the ground state is 2.832 Å and 268 cm^{-1}, respectively. The CCSD(T) with WMR basis set approach found the lowest energy state of AlLi$^-$ is $^2\Pi$ [10], which gave the bond length 2.8346 Å, and frequency 264 cm^{-1}. Our calculations indicate the bond length and harmonic frequency for the ground state of AlLi$^-$ are 2.866 Å and 249.9 cm^{-1}, respectively. Our calculated dissociation energy (0.9686 eV) of AlLi$^-$ in channel AlX$^-$ → Al + X$^-$ agrees well with CCSD(T)/WMR calculation (1.09 eV) [10]. The dissociation energy 1.2988 eV of AlLi$^-$ obtained here in channel AlX$^-$ → Al$^-$+X is close to the previous values [7] (QCISD(T)/6-311+G(2df): 31.2 kCal/mol (≈1.353 eV), MP4/6-311+G(2df): 1.2619 eV). On the whole, the present results are in very accordance with previous higher level ab initio calculations.

For the cation AlLi$^+$, the electronic structure have been investigated by MP2, MP4 and QCISD(T) level [7]. We found that the ground state of AlLi$^+$ is $^2\Sigma^+$ with a $6\sigma^1\pi^4$ electronic configuration, which is in accordance with previous theoretical results [7]. Our calculated bond length 3.038 Å, harmonic vibrational frequency 236.1 cm^{-1} are in good agreement with the MP2/6-311+G* results [7] (3.005 Å, and 242 cm^{-1}). As for the dissociation energy of AlLi$^+$, we are unaware of other theoretical data on channel AlX$^+$ → X + Al$^+$, our CCSD(T) method with 6-311+G(2df) basis set gives the dissociation energy of 1.7471 eV. Boldyrev et al. [7] calculated dissociation energy of AlLi$^+$ in channel AlX$^+$ → Al + X$^+$ is 27.1 kCal/mol (≈1.1752 eV) at MP4/6-311+G(2df) level and 27.0 kCal/mol (≈1.1708 eV) at QCISD(T)/6-311+G(2df) level, both results are very in accordance with our CCSD(T) result 1.1569 eV.

3.2 AlBe, AlBe$^-$, and AlBe$^+$

No experimental data are available on these species. The ground state of AlBe is assigned to be $^2\Pi$ (with a $6\sigma^2 2\pi^1$ electronic configuration) based on our calculated results, which is the same as that obtained by complete active space self-consistent field (CASSCF) [9] and CCSD(T)/WMR [10]. Our calculated spectroscopic parameters (bond length 2.434 Å, vibrational frequency 379.6 cm^{-1}) agree well with the CASSCF results [9] (bond length 2.427 Å, vibrational frequency 383 cm^{-1}) and with the CCSD(T)/WMR results [10] (bond length 2.3981 Å, vibrational frequency 395 cm^{-1}). The dissociation energy 0.4922 eV is slightly lower with respect to previous studies, see Table 1. Our calculated first adiabatic electronic affinity of 1.0677 eV is comparable to the CASSCF value 1.09 eV [9] and to the CCSD(T)/WMR value 1.131 eV [10]. The ionization energy of 5.8688 eV for AlBe is the highest in alkaline earth-Al species.

For the anionic dimer AlBe$^-$, the present method gives the $^3\Sigma^-$ (electronic configuration $6\sigma^2 2\pi^2$) ground symmetry with bond length 2.311 Å, harmonic frequency 452.3 cm^{-1}. Our calculated bond length agrees well with CASSCF result (2.315 Å) [9] and CCSD(T)/WMR result (2.2839 Å) [10], and the vibrational frequency obtained by the present method is rather close to the results of CASSCF and CCSD(T), see Table 2. The dissociation energy of AlBe$^-$ in channel AlX$^-$ → X+Al$^-$(1.2774 eV) obtained here is slightly lower compared with the CASSCF value 1.36 eV [9]. The dissociation energy in channel AlX$^-$ → Al+X$^-$ (2.0815 eV) nearly larger than that of channel AlX$^-$ → X+Al$^-$ by 0.8 eV. Both of the two channels give larger dissociation energy than that of the neutral, so AlBe$^-$ is more stable than AlBe thermodynamically. For the cation AlBe$^+$, we are unaware of any theoretical and experimental studies. Our calculations show that the ground state of AlBe$^+$ is $^1\Sigma^+$ with a $6\sigma^2\pi^4$ electronic configuration, which is the same as that of its isoelectronic neutral diatomic AlLi. An electron removed from 2π molecular orbital makes the bond length of AlBe$^+$ (2.831 Å) in $^1\Sigma^+$ state relatively larger than that of AlBe (2.434 Å) and that of AlBe$^-$(2.311 Å), but it is very close to the bond length of AlLi (2.875 Å). The dissociation of AlBe$^+$ in channel AlX$^+$ → X + Al$^+$ is only 0.5522 eV, which is the lowest in the alkaline earth-Al cation species. It is interesting to note that the dissociation energy of AlBe$^+$ in channel AlX$^+$ → Al + X$^+$ is rather high (3.9063 eV), because the ionization energy of Be is rather higher compared with that of Al.

3.3 AlNa, AlNa$^-$, and AlNa$^+$

Experimental molecular constants for AlNa, AlNa$^-$, and AlNa$^+$ are not available. However, high precise ab initio calculations have been carried out for AlNa [8]. Boldyrev et al. [8] found that the low-spin $^1\Sigma^+$ state is the ground state with the bond length 3.134 Å, and vibrational frequency 196 cm^{-1} based on the MP2/6-311+G* level. They used high level electron correlation method QCISD(T) with the 6-311+G(2df) basis set giving the bond length of 3.182 Å and dissociation energy of 17.8 kCal/mol (≈0.772 eV) [8]. The ground electronic state of AlNa obtained in the present method is $^1\Sigma^+(8\sigma^2 2\pi^4)$ with bond length 3.181 Å, vibrational frequency 185.3 cm^{-1}, and dissociation energy 0.7614 eV, which agree well with the MP2 results and QCISD(T) results. The dissociation energy 1.080 eV [22] obtained from LSDA method is larger about 0.25 eV than the results of CCSD(T), MP2 and QCISD(T). For the EA and IE, to the best of our knowledge, there is no any result in literature. Our calculated EA and IE are 0.6305 and 4.8831 eV, respectively.

Both the AlNa$^-$ and AlNa$^+$ are not studied theoretically. Our calculations show that $^2\Pi$ (with a $8\sigma^2 3\pi^1$ electronic configuration) is the ground state for AlNa$^-$, as does the isovalent AlMg molecule, $^2\Sigma^+$(with a $8\sigma^1 2\pi^4$ electronic configuration) for the cation. Compared with neutral AlNa, an additional electron is added to 3π orbital making $8\sigma^2 3\pi^1$ ($^2\Pi$) as the ground state for anion AlNa$^-$. The cation AlNa$^+$ has relatively longer bond length than that of AlNa and AlNa$^-$. The removal of an electron from the bonding 8σ molecular orbital of AlNa ($8\sigma^2 2\pi^4$) increases the bond length of AlNa$^+$($8\sigma^1 2\pi^4$) by 0.211 Å.

3.4 AlMg, AlMg$^-$ and AlMg$^+$

Experimental data are not available for AlMg. Boldrev et al. [8] have studied five low-lying electronic states ($^2\Pi_r$, $^2\Sigma^+$, $^4\Pi_r$, $^4\Sigma^-$ and $^2\Pi_i$) based on the MP2/6-311+G* method, they found $^2\Pi_r$ to be the lowest. They calculated dissociation energy of AlMg ($^2\Pi_r$) is 0.34 eV at the QCISD(T)/6-311+G(2df) level, which is close to our result 0.3291 eV. The rather low dissociation energy of AlMg indicates aluminum combine weakly with magnesium atom. Our CCSD(T) method found the lowest energy state of AlMg is $^2\Pi$ (with a $8\sigma^2 3\pi^1$ electronic configuration), our calculated bond length 2.903 Å and vibrational frequency 195.5 cm^{-1} are in agreement with MP2/6-311+G* values 2.922 Å and 192 cm^{-1}. However, our calculated vibrational frequency is larger than previous MCSCF/aug-cc-pVDZ result [8] (131 cm^{-1}) by 64.5 cm^{-1}, so the harmonic frequency of AlMg needed to be further affirmed by experiment. From Table 1, one can see that calculated bond length in AlMg increases from 2.901 Å at the QCISD(T)/6-311+G(2df) level to 3.03 Å at the MCSCF/aug-cc-pVDZ level. Our calculated adiabatic ionization energy and electronic affinity are 5.3763 and 0.9089 eV, respectively.

Both the AlMg$^-$ and AlMg$^+$ are not studied experimentally and theoretically. Our calculations show that $^3\Sigma^-(8\sigma^2 3\pi^2)$ state is the ground state for AlMg$^-$ with bond length 2.741 Å and vibrational frequency 254.4 cm^{-1}. As for the cation, $^1\Sigma^+(8\sigma^2 2\pi^4)$ give the global minimum, which is the same as the ground assignment of its isoelectronic neutral dimer AlNa. In addition, the ground state bond length 3.135 Å and harmonic vibrational frequency 190.3 cm^{-1} of AlMg$^+$ is very close to that of AlNa (bond length 3.181 Å, vibrational frequency 185.3 cm^{-1}). For the positive charged dimer, channel AlX$^+ \rightarrow$ X + Al$^+$ gives the lowest dissociation energy (0.8815 eV), and the channel AlX$^- \rightarrow$ X + Al$^-$ is preferred for the anion.

3.5 AlK, AlK$^-$ and AlK$^+$

Compared with the above discussed species, these species are studied rarely. The present calculation shows that $^1\Sigma^+$ with a $10\sigma^2 3\pi^4$ electronic configuration is the ground state for the neutral dimer, $^2\Pi(10\sigma^2 4\pi^1)$ for the anion and $^2\Sigma^+$ ($10\sigma^1 3\pi^4$) for the cation. For the ground state of AlK($^1\Sigma^+$), our calculated bond length is 3.613 Å, vibrational frequency 139.9 cm^{-1} and dissociation energy 0.5401 eV. Rao et al. [23] investigated neutral and charged Al$_n$ clusters ($n \leq 8$) decorated with alkali atoms (Li and K) using generalized gradient approximation density functional method BPW91, they found the lowest energy state of AlK was triplet with bond length 3.53 Å. Our calculation found that $^3\Pi$ state with bond length 3.375 Å lie only 0.0367 eV above the ground state $^1\Sigma^+$, this is an indication that $^3\Pi$ state is a strongly competitive candidate for the ground state of AlK. The adiabatic EA and IE of AlK are 0.6544 and 4.2793 ev, respectively.

No previous ab initio calculations and experimental studies were performed for AlK ions. The anion AlK$^-$ is valence isoelectronic with the neutral AlCa dimer, according to our results, $^2\Pi$ electronic state is the lowest energy state for AlK$^-$ and AlCa. The stability of AlK$^+$ is comparable with AlK, because the dissociation energy of AlK$^+$ via channel AlX$^+ \rightarrow$ Al+X$^+$ is 0.5269 eV, which is very close to the dissociation energy 0.5401 eV of AlK. As in the case of AlNa species, the bond length of AlK$^+$ is rather long (3.879 Å) compared with the bond length of AlK (3.613 Å) and with the bond length of AlK$^-$ (3.594 Å).

3.6 AlCa, AlCa$^-$ and AlCa$^+$

The neutral AlCa have been thoroughly studied theoretically and experimentally [6,22]. The spectroscopic analysis of AlCa has been completed by Behm et al. [6] using resonant two-photon ionization spectroscopy. The ground state has been determined as a $^2\Pi_r$ state with bond length 3.1479 ± 0.0010 Å and frequency 189.1 ± 0.8 cm^{-1}. This ground state originates from the interaction of ground Al ($3s^2 3p^1$) and Ca ($3d^0 4s^2$), with the Al $3p$ electron in the $p\pi$ orientation. The ionization energy of AlCa have also been directly determined experimentally as 5.072 ± 0.028 eV [6]. In addition, they also investigated the potential curves of seven low-lying states of AlCa and the $^1\Sigma^+$ ground electronic state of AlCa$^+$ using two sophisticated ab initio techniques: CASSCF-MRCISD(Q) method and QCISD(T) method (see Ref. [6]). Both calculations used large atomic natural orbital basis sets. Their calculations found $^2\Pi_r$ to be the ground state of the neutral dimer. The dissociation energies of AlCa ($^2\Pi_r$) into Al($3s^23p^1, ^2P_0$) + Ca($44s^2, ^1S$) and of AlCa$^+$($^1\Sigma^+$) into Al$^+$($3s^2, ^1S$) + Ca($4s^2, ^1S$) were calculated to be 0.47 and 1.50 eV, respectively. More recently, laser-induced fluorescence spectroscopy have been used to study supersonically cooled AlCa by Fabbi, Langenberg and Morse [24], and they ascertained the bond length of ground state was 3.14942±0.00032 Å, which was very close to early experimental datum 3.1479 ± 0.0010 Å.

The present calculated results together with the results of Behm et al. (both experimental values and theoretical values) are given in Tables 1 and 3. The ground state of AlCa is determined to be a $^2\Pi(10\sigma^2 4\pi^1)$ state based on the present study. With a look at Table 1, as for bond length of AlCa, all the theoretical data are longer than the experimental value. However, our calculated bond length 3.176 Å is more close to experimental results 3.1479±0.0010 Å [6] and 3.14942 ± 0.00032 Å [24] compared with QCISD(T) results (3.21 Å) [6] and with CASSCF-MRCISD(Q) result (3.27 Å) [6]. Our calculated harmonic frequency 179.4 cm^{-1} is more near to experimental value 189.1 ± 0.8 cm^{-1}. The adiabatic ionization energy of 4.9297 eV obtained by CCSD(T) method is very close to previous theoretical result 4.97 eV [CASSCF-MRCISD(Q)] [6] and experimental result 5.072±0.028 eV [6]. The bond length of AlCa$^+$($^1\Sigma^+$) obtained at our CCSD(T) level is 3.481 Å, which underestimates slightly compared with the QCISD(T) result 3.510 Å [6] and with the CASSCF-MRCISD(Q) result 3.533 Å [6]. The bond length of AlCa$^+$ is approximately 0.3 Å longer than that of the $^2\Pi_r$ ground state of AlCa, because an electron is removed from the bonding 4π orbital. Despite this increase in bond length, AlCa$^+$ is more strongly bound than the neutral AlCa dimer, with dissociation energy of AlCa$^+$ in channel AlX$^+$ → X + Al$^+$ is 1.3968 eV. Our calculated the ground symmetry of AlCa$^-$ is $^3\Sigma^-(10\sigma^2 4\pi^2)$ with bond length 3.047 Å, frequency 195.1 cm^{-1}.

3.7 AlRb, AlRb$^\pm$, AlSr, AlSr$^\pm$, AlCs, AlCs$^\pm$, AlBa and AlBa$^\pm$

No experimental data and theoretical results are available for these 12 dimers. The spectroscopic parameters of the ground state of these species are reported here for the first time. All the spectroscopic parameters of AlRb, AlRb$^\pm$, AlSr and AlSr$^\pm$ were obtained from CCSD(T) method directly. While for AlCs, AlCs$^\pm$, AlBa and AlBa$^\pm$, due to the failure of CCSD(T) optimization process, the calculation of bond length and harmonic frequency were calculated by using B3LYP method. In order to determine the effect on bond length and harmonic frequency, we also calculated r_e and ω_e of AlRb, AlRb$^\pm$, AlSr, AlSr$^\pm$ by using of B3LYP with the same basis set, the results were listed in Tables 1, 2 and 3. It can be seen that the bond length of AlRb and AlRb$^\pm$ obtained from B3LYP is slightly larger compared with that of CCSD(T) results, accordingly, the harmonic frequency obtained from B3LYP is slightly lower compared with that of CCSD(T) results. As for AlSr and AlSr$^\pm$, both methods gave nearly equal bond length and frequency. Based on our calculations, the ground symmetry are $^1\Sigma^+(7\sigma^2 2\pi^4)$ for AlRb, AlSr$^+$, AlCs and AlBa$^+$,$^2\Pi(7\sigma^2 3\pi^1)$ for AlRb$^-$, AlSr, AlCs$^-$ and AlBa, $^2\Sigma^+(7\sigma^1 2\pi^4)$ for AlRb$^+$ and AlCs$^+$, and $^3\Sigma^-(7\sigma^2 3\pi^2)$ for AlSr$^-$ and AlBa. The bond lengths of these neutral species are very long, 3.752 Å for AlRb, 4.048 Å for AlCs, 3.330 Å for AlSr and 3.470 Å for AlBa. While for the anions, the dissociation energies are larger than that of corresponding neutral species, see Tables 1 and 2. So AlRb$^-$, AlCs$^-$, AlBa$^-$ and AlSr$^-$ are more stable thermodynamically than their corresponding neutral dimers. In the cation species, we note that the dissociation energies of AlRb$^+$ (0.4922 eV) in the favored channel AlX$^+$ → Al + X$^+$ is lower slightly than that of AlRb (0.5231 eV). Unlike AlBe$^+$, AlMg$^+$ and AlCa$^+$, dissociation of AlSr$^+$ and AlBa$^+$ via channel AlX$^+$ → Al + X$^+$ is preferred to channel $AlX^+ \rightarrow X + Al^+$.

4 Conclusions

AlLi, AlNa, AlK, AlRb and AlCs have the low-spin ground symmetry $^1\Sigma^+$, and the ground state of AlBe, AlMg, AlCa, AlSr and AlBa is $^2\Pi$. As for the alkali-Al ions, the ground electronic states multiplicities are larger by one than the multiplicities of the corresponding alkali-Al neutral dimer, $^2\Pi$ symmetry for anions, and $^2\Sigma^+$ symmetry for cations. AlLi$^-$, AlNa$^-$, AlK$^-$, AlRb$^-$ and AlCs$^-$ have the same ground symmetry as that of neutral alkaline earth-Al dimers. Analogously, the ground state symmetry of AlBe$^+$, AlMg$^+$, AlCa$^+$, AlSr$^+$ and AlBa$^+$ is identical with the ground symmetry of neutral alkaline-Al dimer. While the ground state of AlBe$^-$, AlMg$^-$, AlCa$^-$, AlSr$^-$ and AlBa$^-$ is high-spin $^3\Sigma^-$.

All alkali and alkaline earth metal atoms form chemical bonds with Al. The dissociation energies and harmonic vibrational frequencies of alkali-Al dimers decrease monotonously when alkali metal atom moved from Li to Cs. While for the equilibrium bond length, opposite trend was observed. Compared with alkali-Al dimers, the dissociation energies of alkaline earth-Al neutral dimers are lower, the maximum dissociation energy is 0.5853 eV (AlBa). Because the ns^2 shells are full-filled in alkaline earth metal atoms, so rearrangement to ns^1np^1 is needed in order to form chemical bonds. These promotion energies are high and not adequately compensated by the alkaline earth-Al bonds, alkaline earth-Al are little stable species on the view of thermodynamics.

The ionization energies of alkali-Al decrease monotonously with the increase in atomic number of alkali metal. Although the adiabatic electronic affinities increase monotonously through the alkali metals, the IEs not vary dramatically, AlCs has the maximum EA of 0.6916 eV, and the minimum of EA belongs to AlLi (0.5877 eV). For the alkali-Al anion species, the dissociation energy of channel $AlX^- \rightarrow Al + X^-$ is lower than that of channel $AlX^- \rightarrow X + Al^-$. Except $AlLi^-$, the dissociation energy of anion is higher than the dissociation energy of the corresponding neutral dimer. For the alkali-Al cations, channel $AlX^+ \rightarrow Al+X^+$ is easier than channel $AlX^+ \rightarrow X + Al^+$. We also found that the ionization energies of alkaline earth-Al decrease monotonously with increase of atomic number of alkali earth metal. Unlike the dissociation procedure of alkali-Al anion species, which favors the channel $AlX^- \rightarrow Al + X^-$, channel $AlX^- \rightarrow X+Al^-$ is preferred for alkaline earth-Al anions. As for alkaline earth-Al cations, channel $AlX^+ \rightarrow X+Al^+$ is preferred for $AlBe^+$, $AlMg^+$ and $AlCa^+$, while $AlSr^+$ and $AlBa^+$ favor channel $AlX^+ \rightarrow Al + X^+$.

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