The First Principle Study of AlX（X＝4d elements）Dimer*

铝－4d 过渡族金属二聚体的第一性原理计算

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Abstract：【**Objective**】The nature of chemical bond between a transition metal and aluminium is a base of chemistry and materials science. The physical properties of AlX (X＝4d elements) Dimer were studied.【**Methods**】Bond length, vibrational frequency, dissociation energy, ionization potential, energy gap and dipole moment of the title molecules in neutral and charged ions were studied by density functional method B3LYP.【**Results**】For neutral and charged molecules, the bond length decreases from AlY (AlY$^+$ and AlY$^-$) to AlPd (AlPd$^+$ and AlPd$^-$) except AlMo, AlNb$^+$ and AlMo$^+$, and then increases. Opposite trends are observed for dissociation energy and vibrational frequency. The ionization energy through the series increases and reaches the maximum at AlRh and then decreases. The present results are in good agreement with the available experimental and other theoretical values except the vibrational frequency of AlTc. The present calculations show that the late transition metal can combine strongly with aluminum compared with the former transition metal (except AlCd). For cationic dimer, the dissociation procedure of channel AlX$^+$→X ＋ Al$^+$ is easier than that of channel AlX$^+$→Al ＋ X$^+$. However, for anionic dimer, the channel AlX$^-$→Al ＋ X$^-$ is favorable except AlY$^-$, AlPd$^-$ and AlCd$^-$. The ground state spin multiplicity of the charged ions differs by ±1 from that of the corresponding neutral parent. The bond length of AlX$^+$ is larger than that of AlX (except AlPd) and that of AlX$^-$(except AlRu$^-$ and AlPd$^-$). The dissociation energy of charged dimer is bigger than that of neutral counterpart.

Key words：dimer,first-principles,transition metal aluminides,bonding characteristic

摘要：【目的】过渡族金属与铝之间的化学成键特性是化学与材料等领域的基础,对铝－4d 过渡族金属二聚体的物理性能进行研究。【方法】用密度泛函 B3LYP 方法计算铝－4d 过渡族金属二聚体的键长、振动频率、解离能、电离势、能隙和二极矩。【结果】对中性和荷电的二聚体,除 AlMo、AlNb$^+$ 和 AlMo$^+$ 外其键长从 AlY 到 AlPd 先减少后增加,解离能和振动频率的变化趋势与之相反。电离势随原子序数的递增先增加,在 AlRh 处达到极大值后减少。除 AlTc 的振动频率外,计算结果与已有的实验结果和其他的理论计算结果相符。计算结果还显示除 AlCd 外,前过渡族金属与铝的结合强度比后过渡族金属的结合要强。荷电二聚体的自旋多重度比相应的中性二聚体差±1。带正电的二聚体的键长比中性和带负电的二聚体的键长要长,荷电二聚体的解离能大于中性二聚体的解离能,解离方式为 AlX$^+$→X ＋ Al$^+$ 和 AlX$^-$→Al ＋ X$^-$。

关键词：二聚体　第一性原理　过渡族金属铝化物　成键特征

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Understanding the nature of chemical bond between a transition metal and aluminium is of interest in many areas of science, e. g. surface chemistry, catalysis, astrophysics and organometallic chemistry, high temperature chemistry, materials science and astrochemistry. Diatomic metal aluminides are the simplest systems to understand the metal-metal bonding. A thorough understanding of how these species interact is an essential prerequisite to increase our knowledge of more complicated systems. Besides pure transition metal diatomic, the dimers containing transition metal have gotten more and more interests due to their application in catalysis, microelectronics and optical materials. Recently, the structures and stability of AlX and AlX$^-$ species (X=H,Li,B,C,N,O and F) have been reviewed[1]. For transition metal hydrides TMH(TM = Sc — Cu), diverse studies were available. These include theoretical studies by density functional theory (DFT) of both neutral and cations [2], modified coupled-pair functional (MCPF) on both of neutral[3] and cationic species[4], pseudopotential multiconfiguration self-consistent field (MCSCF) on neutral species[5], and local density approximation(LDA) on cations[6]. Some theoretical studies have been done for metal aluminides[7,8]. However, for transition metal aluminides AlTM(TM = 4d elements) and their charged ions, there is a little theoretical study for spectroscopic constants of the neutral dimers[8]. There is no experimental data have been reported on the spectroscopic constants of 4d AlX dimers except AlY[9], AlPd[10,11] and AlAg[12~14].

Density functional theory is currently widely used to determine structures of a wide variety of molecules. Compared to high-level *ab* initio molecular orbital theories, DFT has the advantage of applicability anywhere in periodic table and inherent computational efficiency. In this paper, we examined the 4d-metal aluminides using DFT. The results are compared with the available theoretical and experimental values. It is hoped that our computational results will stimulate further experimental studies on these transition metal aluminides.

1　Computational methods

Bond length(r_e), vibrational frequency(ω),

dissociation energy(D_0), ionization energy(IE) and electron affinity(EA) for neutral and charged dimers(without IE and EA) were determined for the AlX, AlX$^+$ and AlX$^-$(X= 4d metals) using density functional method B3LYP, which includes a mixture of a traditional Hartree-Fock-like exchange energy, the Slater exchange functional, with gradient corrections due to Beck[15], and the correlation potential of Vosko, Wilk and Nusair, with gradient correction due to Lee et al [16]. The calculations presented here were carried out using the GAUSSIAN 03 suit of program [17]. The basis set included: the basis set denoted as 6－311＋＋G(2df) for Al, the ECP used was the ECP28MDF[18] and basis set CC-PVDZ-PP for 4d transition metals from the Stuttgart Group(http://www.theochem.uni-stuttgart.de/index.html). To avoid trapping at local minima of the potential energy curve, a number of different initial geometries(bond lengths) are adopted. Due to the spin polarization, the molecules were calculated at various possible spin multiplicities in order to find the global minimum or ground state for each molecule(neutral and charged species). The calculated energies were corrected by the zero-point vibrational energies(except AlTc which contains radioactive element Tc, and the vibrational frequency is not available by the present method).

The zero-point vibrational energies(Z_{ALX}) are estimated within the harmonic approximation. The dissociation energy was computed as the difference in the total energies and the isolated atoms, for neutral species, the dissociation energy is

$$D_0(AlX) = E_{tot}(Al) + E_{tot}(X) - E_{tot}(AlX) - Z_{ALX}. \tag{1}$$

Within the Born-Oppenheimer approximation, one could evaluate the EA and IE

$$EA = E_{tot}(AlX) + Z_{AlX} - E_{tot}(AlX^-) - Z_{AlX^-}, \tag{2}$$

$$IE = E_{tot}(AlX^+) + Z_{AlX^+} - E_{tot}(AlX) - Z_{AlX}. \tag{3}$$

The energy gap E_G is

$$E_G = E_{Lumo} - E_{Homo}. \tag{4}$$

2　Results and discussion

The calculated spectroscopic constants of the

neutral $4d$ -transition metal aluminides were compiled in Table 1. The calculated spectroscopic constants of charged molecules are given in Tables 2 and 3.

2.1 Neutral dimer

AlY: It can be seen from Table 1 that $^3\Sigma^-$ with electron configuration $7\sigma^2\,3\pi^2$ is the ground state, which is in agreement with experiment [9]. We also found that the bonding is probably described by valence electrons consisting of the $3p$ electron of aluminum and $4d$ electrons of yttrium, which combine to give a ground molecular configuration of $\sigma^2\pi^2$. It appears that the $3p$ orbits of aluminum are heavily involved with the $4d$ orbits. The calculated bond length 2.8429Å and dissociation energy 1.2647eV are close to experimental values 2.8728Å and 1.146eV, respecitvely.

AlZr: $^6\Delta$ with electronic configuration $7\sigma^1 8\sigma^1 3\pi^2\delta^1$ is the ground state. Comparing the e-lectronic configuration of AlZr with AlY, a dramatic bonding pattern change is observed. This is because the $5s$ orbital (main component of molecular orbital 6σ) of Y lies below $4d$, whereas it is opposite for Zr[19]. The calculated dipole moment is the largest value in the neutral molecular AlX (X = $4d$ elements).

AlNb: $^7\Sigma^+$ (with electron configuration $7\sigma^1 8\sigma^1 3\pi^2\delta^2$) is the ground state and AlNb possesses the largest spin polarization among the studied AlX species. From AlY, AlZr to AlNb, the bond length decreases, while the vibrational frequency, dissociation energy and ionization energy increase.

AlMo: The present calculation shows that $^6\Sigma^+$ (with electron configuration $8\sigma^1 3\pi^2\delta^2$) is the ground state. The calculated bond length 2.7390Å of AlMo is only smaller than the values of AlY, but bigger than the values of AlZr and AlNb.

Table 1 Physical parameters of the neutral $4d$ -transition metal aluminide AlX

Neutral dimer	Basis set	State	Electronic configuration	r_e	ω	μ	D_0	IE	EA	E_G
AlY	CC-PVDZ-PP	$^3\Sigma^-$	$7\sigma^2 3\pi^2$	2.8429	247.1	1.7718	1.2647	5.7694	1.0276	1.7886
	Lanl2dz[8]	$^3\Sigma^-$		2.8503	241.3		1.3253			
	Expt[9]	$^3\Sigma^-$		2.8728			1.146			
AlZr	CC-PVDZ-PP	$^6\Delta$	$7\sigma^1 8\sigma^1 3\pi^2\delta^1$	2.6402	292.5	2.3987	1.5219	6.0024	1.2549	1.5551
	Lanl2dz[8]	$^6\Delta$		2.6505	291.4		1.7139			
AlNb	CC-PVDZ-PP	$^7\Sigma^+$	$7\sigma^1 8\sigma^1 3\pi^2\delta^2$	2.5825	296.2	0.9064	1.7964	6.0439	1.0741	1.5970
	Lanl2dz[8]	$^7\Sigma^+$		2.5958	294.3		1.7881			
AlMo	CC-PVDZ-PP	$^6\Sigma^+$	$8\sigma^1 3\pi^2\delta^2$	2.7390	226.0	0.5870	1.3919	6.1107	0.8461	1.8496
	Lanl2dz[8]	$^6\Sigma^+$		2.7564	221.2		1.3519			
AlTc	CC-PVDZ-PP	$^5\Sigma^-$	$7\sigma^1 8\sigma^1 3\pi^4\delta^2$	2.3119		0.2960	2.1012	6.5543	1.1823	1.8868
	Lanl2dz[8]	$^5\Sigma^-$		2.3219			2.1339			
AlRu	CC-PVDZ-PP	$^4\Sigma^-$	$8\sigma^1 3\pi^4\delta^2$	2.2628	342.8	0.5616	2.4146	6.9475	0.8696	1.8994
Lanl2dz[8]		$^4\Sigma^-$		2.2738	357.7		2.4054			
AlRh	CC-PVDZ-PP	$^3\Delta$	$8\sigma^1 3\pi^4\delta^3$	2.2359	377.1	0.1883	2.8169	7.4731	1.1162	1.8240
	Lanl2dz[8]	$^3\Delta$		2.2551	372.9		2.8394			
AlPd	CC-PVDZ-PP	$^2\Sigma^+$	$8\sigma^1 3\pi^4\delta^4$	2.2323	365.9	0.6511	2.7341	6.6699	1.0750	1.6969
	Lanl2dz[8]	$^2\Sigma^+$		2.2509	361.5		2.6771			
	Expt[11]						2.591			
AlAg	CC-PVDZ-PP	$^1\Sigma^+$	$8\sigma^2 3\pi^4\delta^4$	2.5112	248.4	0.8698	1.990	6.9335	0.6519	2.5954
	Lanl2dz[8]	$^1\Sigma^+$		2.5515	237.2		1.8890			
	Expt[12]	$^1\Sigma^+$		2.474	256.1		2.2			
Expt[13]		$^1\Sigma^+$				1.95				
	ICMRCI+Qe[14]	$^1\Sigma^+$		2.5379	240					
AlCd	CC-PVDZ-PP	$^2\Pi$	$8\sigma^2 4\pi^1\delta^4$	2.9157	125.7	0.5504	0.2137	5.6330	0.8236	1.3494
Lanl2dz[8]		$^2\Pi$		3.0794	108.7	0.1700				

Bond length (r_e in Å), vibrational frequency (ω in cm^{-1}), dipole moment (μ in Debye), dissociation energy (D_0 in eV), ionization energy (IE in eV), electron affinity (EA in eV) and energy gaps (E_G in eV).

AlX(X＝Tc,Ru,Rh)：No experimental data are available for these dimers. Our calculations indicate that the ground state spin multiplicities are 5（with electron configuration $7\sigma^1 8\sigma^1 3\pi^4 \delta^2$）for AlTc,4（electron configuration $8\sigma^1 3\pi^4 \delta^2$）for AlRu,3（electron configuration $8\sigma^1 3\pi^4 \delta^3$）for AlRh. For AlTc, vibrational frequency cannot be obtained by the present method. The bond length decreased from AlTc to AlRh,but the dissociation energy and ionization energy increase. Although the ionization energy 6.9475eV of AlRu is smaller than the value 7.4731eV of AlRh,the electron affinity 0.8696eV of AlRu is also smaller than the value 1.1162eV of AlRh. The dissociation energy 2.8169eV and ionization energy 7.4731eV of AlRh are the biggest values, while the dipole moment 0.1883 Debye of AlRh is the smallest in the AlX.

AlPd：$^2\Sigma^+$ with electron configuration $8\sigma^1 3\pi^4 \delta^4$ is the ground state. The bond length 2.2323Å is smallest in AlX,and our calculated dissociation energy 2.7341eV of AlPd agrees with experimental value 2.591eV[11].

AlAg：There are several experimental and theoretical studies available for neutral dimer AlAg[12~14]. Our calculation shows that single state （$^1\Sigma^+$）with electron configuration $8\sigma^2 3\pi^4 \delta^4$ is the ground state. The calculated bond length 2.5112Å, and vibrational frequency 248.4cm^{-1} are in good agreement with the previous experimental values 2.474Å and 256.1cm^{-1}[12]. The calculated dissociation energy （1.990eV）agrees well with experimental value 1.95eV[13]. However,our dissociation energy underestimates experimental value 2.2eV [12] by 0.21eV. The ICMRCI＋Q results[14]（2.5379Å and 240cm^{-1}）for the $^1\Sigma^+$ state of AlAg are in excellent agreement with our results. For the noble metals, the electronic structure of silver is best approximated by the closed shell $d^{10}s^1$ configuration. $^1\Sigma^+$ results from a single bond between the Ag $5s$ and Al $3p$ valence electrons.

AlCd：For AlCd,$^2\Pi$ with electron configuration $8\sigma^2 4\pi^1 \delta^4$ is the ground state. As closed shell of cadmium（（$4d^{10}5s^2$），the bond length 2.9157Å is the largest value，and the vibrational frequency 125.7cm^{-1},dissociation energy 0.2137eV,ionization

energy 5.6330eV and energy gap 1.3494eV are the smallest in AlX,which indicated relatively weak bond.

In a whole,the results calculated in the present are in good agreement with those obtained by B3LYP with Lanl2dz for $4d$-metals[8].

2.2 Cationic dimer

The electron configurations of ground state for AlX$^+$ are given in Table 2. There is a recent ESR（Electron spin resonance）study [20]of AlY$^+$ indicating that both molecules possess $^4\Sigma^-$ ground states deriving from $\sigma^1 \pi^2$ configurations. The difference between the present calculation and experiment maybe result from the basis set for the $4d$ metal used in the present calculation. The calculation was performed by using Lanl2dz instead of ECP28MDF for Y. The results indicate that the ground state is $^4\Sigma^-$. Further experiment is needed to verify it. One can see that the multiplicity of ground state AlX$^+$ differs from the counterpart of neutral one by one. The similar phenomenon was also observed for Al-$3d$ transition metal dimers.

The bond length of AlX$^+$ is larger than that of corresponding AlX except AlRh and AlPd,for which the opposite phenomenon appears. The vibrational frequency of AlX$^+$ is lower than that of corresponding AlX. The bond length of AlPd$^+$ is the shortest in the series of AlX$^+$,while its vibrational frequency is the largest. The bond length of AlZn$^+$ is the largest and the vibrational frequency is the lowest.

The dipole moment of AlX$^+$ is bigger than that of neutral counterpart except AlY and AlZr. As for the energy gap between the Lumo and Homo levels, the values of AlX$^+$ are bigger than those of AlX except AlRh and AlAg.

From Table 2,one can see that the calculated dissociation energies indicate that the dissociation channel of AlX$^+ \rightarrow$X＋Al$^+$ is favorable for AlX$^+$. The dissociation energies of AlX$^+$ are smaller than those of AlX except AlY,AlZr and AlCd. This indicates that neutral dimer is more stable than cationic dimer for most of Al-$4d$ transition metals.

2.3 Anionic dimer

In Table 3, the electronic configurations for AlX$^-$ are compiled. It can be seen that the spin multiplicity of ground state AlX$^-$ differs from the corresponding AlX one by one,which is similar as that for AlX$^+$ mentioned above.

Table 2　Physical parameters of the cation 4d-transition metal aluminide AlX$^+$

Cation dimer	State	Electronic configuration	r_e	ω	μ	D_0 AlX$^+\to$ X$^+$+Al	D_0 AlX$^+\to$ X+Al$^+$	E_G
AlY$^+$	$^2\Pi$	$7\sigma^2 3\pi^1$	3.2379	148.6	0.6994	1.8344	1.5165	1.7296
AlZr$^+$	$^5\Sigma^-$	$7\sigma^1 8\sigma^1 3\pi^2$	2.7347	241.5	0.2717	2.2013	1.5408	1.7560
AlNb$^+$	$^6\Delta$	$7\sigma^1 8\sigma^1 3\pi^2\delta^1$	2.7434	221.0	1.8111	2.9577	1.7737	2.0520
AlMo$^+$	$^7\Sigma^+$	$7\sigma^1 8\sigma^1 3\pi^2\delta^2$	2.7835	191.5	3.0695	2.5461	1.3020	2.2863
AlTc$^+$	$^6\Phi$	$7\sigma^1 8\sigma^1 9\sigma^1 3\pi^3\delta^1$	2.5874		2.9417	2.6586	1.5682	2.0743
AlRu$^+$	$^3\Sigma^-$	$7\sigma^2 3\pi^4\delta^2$	2.3389	283.6	2.4647	3.0975	1.4883	2.0972
AlRh$^+$	$^2\Sigma^+$	$7\sigma^1 3\pi^4\delta^4$	2.2573	351.9	4.5018	3.0850	1.6989	1.4569
AlPd$^+$	$^1\Sigma^+$	$7\sigma^2 3\pi^4\delta^4$	2.2265	349.3	4.2999	4.6521	2.0854	3.5843
AlAg$^+$	$^2\Sigma^+$	$8\sigma^1 3\pi^4\delta^4$	2.5774	188.9	4.4670	3.0012	1.0777	1.8909
AlCd$^+$	$^1\Sigma^+$	$8\sigma^2 3\pi^4\delta^4$	3.1107	127.0	6.2584	3.8400	0.6019	3.8839

Bond length(r_e in Å), vibrational frequency (ω in cm^{-1}), dipole moment (μ in Debye), dissociation energy(D_0 in eV) and energy gaps(E_G in eV)

Table 3　Physical parameters of the anion 4d-transition metal aluminide AlX$^-$

Anion dimer	State	Electronic configuration	r_e	ω	μ	D_0 AlX$^-\to$ X$^-$+Al	D_0 AlX$^-\to$ X+Al$^-$	E_G
AlY$^-$	$^4\Sigma^-$	$8\sigma^1 3\pi^2$	2.8378	252.3	4.3267	2.5801	1.9083	1.7418
AlZr$^-$	$^5\Delta$	$8\sigma^1 3\pi^2\delta^1$	2.7156	267.8	2.6325	2.3139	2.3925	2.0104
AlNb$^-$	$^6\Sigma^+$	$8\sigma^1 3\pi^2\delta^2$	2.6300	288.4	2.6769	2.2586	2.4865	1.7734
AlMo$^-$	$^5\Phi$	$8\sigma^1 9\sigma^1 3\pi^3\delta^1$	2.6247	224.4	4.1319	1.7646	1.8536	1.2574
AlTc$^-$	$^4\Sigma^-$	$8\sigma^1 3\pi^4\delta^2$	2.3942		3.7010	2.6016	2.8993	1.9668
AlRu$^-$	$^3\Delta$	$8\sigma^1 3\pi^4\delta^3$	2.3662	323.7	3.6341	2.4812	2.9003	1.9886
AlRh$^-$	$^2\Delta$	$8\sigma^2 3\pi^4\delta^3$	2.2508	389.1	2.5319	3.0427	3.5258	1.9132
AlPd$^-$	$^1\Sigma^+$	$8\sigma^2 3\pi^4\delta^4$	2.2419	376.6	2.5660	3.5157	3.4252	1.8721
AlAg$^-$	$^2\Pi$	$8\sigma^2 4\pi^1\delta^4$	2.5536	210.4	4.5684	1.6113	2.2580	1.1627
AlCd$^-$	$^3\Sigma^-$	$8\sigma^2 4\pi^2\delta^4$	2.7434	166.5	5.8880	1.9685	0.6534	1.2338

Bond length(r_e in Å), vibrational frequency (ω in cm^{-1}), dipole moment (μ in Debye), dissociation energy(D_0 in eV) and energy gaps(E_G in eV)

The bond lengths of AlX$^-$ are shorter than those of AlX$^+$. By comparing the bond lengths of AlX$^-$ and AlX, the bond length of anionic dimmer is longer for AlZr, AlTc, AlRu, AlPd and AlAg. The vibrational frequencies of AlX$^-$ are higher than that of corresponding AlX$^+$, while only the vibrational frequencies of AlY, AlRu and AlCd are lower than those of the corresponding anionic dimer.

The dipole moments of AlX$^-$ are larger than those of corresponding AlX, while they are less than those of AlX$^+$ except AlRh$^+$, AlPd$^+$ and AlCd$^+$. The energy gap between the Lumo and Homo levels for AlX$^-$ is larger than that of corresponding AlX except for AlY, AlMo, AlAg and AlCd, while it is less than that of corresponding AlX$^+$ except AlY$^+$ and AlZr$^+$.

The dissociation procedure of AlX$^-$ is different from that of AlX$^+$. As for AlX$^-$ (X=Y, Nb, Pd and Cd), the dissociation energy of channel AlX$^- \to$ X$^-$+Al is less than that of channel AlX$^- \to$ X+Al$^-$. Opposite way was observed for the rest of AlX$^-$. The dissociation energy for AlX$^-$ is for larger than that of neutral dimmer and cathonic dimmer except AlAg, while the dissociation energy of anionic AlAg is less than that of neutral AlAg. The dissociation energy of AlCd$^-$ is the least in series of AlX$^-$.

3　Conclusions

Density functional method B3LYP was used to study the spectroscopic constants of 4d-metal aluminides dimers and charged ones. The electronic configuration, bond length, harmonic vibrational frequency, and dissociation energy have been calculated for neutral and charged dimers. The present calculations are in good agreement with the available experimental and other theoretical results. The ground state spin multiplicity of the charged ions differs by ± 1 from that of the corresponding neutral parent. For neutral and charged molecular, the late transition metals (except Ag and Cd) are found to form stronger bonding with aluminum than former tran-

sition metals. The dissociation channel of $AlX^+ \rightarrow X + Al^+$ is favor for AlX^+. However, for anionic dimer, the channel $AlX^- \rightarrow Al + X^-$ is favorable except AlY^-, $AlPd^-$ and $AlCd^-$. The bond length of AlX^+ is larger than that of AlX (except AlPd) and that of AlX^- (except $AlRu^-$ and $AlPd^-$). The dissociation energy of charged dimer is bigger than that of neutral counterpart.

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