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ELECTRONIC TRANSMUTATION: AN AID FOR THE RATIONAL DESIGN OF
NEW CHEMICAL MATERIALS USING THE KNOWLEDGE OF BONDING AND
STRUCTURE OF NEIGHBORING ELEMENTS

by

Katie A. Lundell

A dissertation submitted in partial fulfillment
of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Chemistry

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2019

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ABSTRACT

Electronic Transmutation: An aid for the rational design of new chemical materials using
the knowledge of bonding and structure of neighboring elements

by

Katie A. Lundell, Doctor of Philosophy

Utah State University, 2019

Major Professor: Alexander I. Boldyrev, D.Sc.

Department: Chemistry and Biochemistry

The concept of electronic transmutation states, “elements, with atomic number Z , begin to have chemical bonding and geometric structure properties of their neighboring element ($Z+1$).” This dissertation reviews this concept since its founding in 2012 and demonstrates the elements from group 13-15 can be electronically transmuted to elements of group 14-16, respectively. The major part of the scientific efforts reported here in focus on further development of the electronic transmutation concept using evidence that the $\text{LiAl}_2\text{H}_4^-$ cluster possess the elusive Al-Al double bond with a geometric structure resembling Si_2H_4 . Introduction of the double electronic transmutation ($Z \rightarrow Z+2$) is also presented with the Al-Al triple bond in the form of the $\text{Al}^{2-} \equiv \text{Al}^{2-}$ kernel, which mimics $\text{P} \equiv \text{P}$ and $\text{N} \equiv \text{N}$ molecules. Chemical bonding analysis confirms the presence of the proposed bonds and indicates the concept’s significant potential in predicting new chemical compounds.

(104 pages)

PUBLIC ABSTRACT

Electronic Transmutation: An aid for the rational design of new chemical materials using the knowledge of bonding and structure of neighboring elements

Katie A. Lundell

Everything in the universe is made up of elements from the periodic table. Each element has its own role that it plays in the formation of things it makes up. For instance, pencil lead is graphite. A series of honeycomb-like structures made up of carbon stacked on top of one another. Carbon's neighbor to the left, boron doesn't like to form such stacked honeycomb-like structures. But, what if there was a way to make boron act like carbon so it did like to form such structures? That question is the basis of the electronic transmutation concept presented in this dissertation. Electronic transmutation states that an element, such as boron, can behave structurally like carbon (form stacked honeycomb structures) if you make them valence (outer most) isoelectronic ("iso" - same; "electronic" - electrons), so both would have the same number of outer most electrons. As a result, chemists would have a new tool to aid in the rational design of new materials.

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CHAPTER 1

INTRODUCTION

1.1 Historic Outline

The purpose of this chapter is to: acknowledge Gilbert Lewis's ideas of the *chemical bond* and *molecular structure* (1916 and 1923); recap the basics of the *isoelectronic concept* as founded by Irving Langmuir (1919) and the concept's evolution to the *isoelectronic principle* by William Penney and Gordon Sutherland (1936); provide a formal definition of the isoelectronic principle as defined by Richard Gillis (1958); introduce Boldyrev and Olson's concept of *electronic transmutation* as a simplified extension of the isoelectronic principle (2012); demonstrate how electronic transmutation can be used in the discovery of novel structures (2012-present).

1.2 Foundations of the Isoelectronic Principle

The modern theories of molecular structure and chemical bonding were first introduced by G. N. Lewis's 1916 paper, "*The Atom and the Molecule* [1]." Three years after Lewis's 1916 paper, Langmuir published an article in an attempt to enlarge on Lewis's ideas [2]. Although a convincing lecturer, Langmuir did not do much to improve upon or extend Lewis's ideas as indicated by Lewis in his 1923 book [3, 4]. Langmuir, in short, truly only introduced terminology we use today (ie. covalent bond, octet rule) and isoelectric species [2, 3]. In 1936 a remarkable discovery about isoelectronic species was made by Penney and Sutherland during an IR Spectroscopy study where they observed that isoelectronic species are usually isostructural [5]. A connection now known as the isoelectronic principle.

The isoelectronic principle, formally described by Gillis as - a certain class x/y defined as those which have x atoms and y valence or outer shell electrons [6] - has been determined to fail as often as it succeeds in the determination of novel structures [6, 7]. Successes such

as carbon monoxide (CO) and dinitrogen (N₂) demonstrate that novel structures could be contrived through molecular analogies. However, comparison of benzene to hexasilabenzene results in a spectacular failure, as hexasilabenzene isn't even a minimum on its potential energy surface [8, 9]. Thus, this dissertation introduces and expands upon a stricter and narrower version of the isoelectronic concept called electronic transmutation.

1.3 Boldyrev and Olson and The Origins of Electronic Transmutation

First proposed in 2012 by Olsen and Boldyrev, electronic transmutation states: “that by acquiring an electron, a certain element with atomic number Z begins to behave similarly as its neighboring element $Z+1$.” The similarities between the transmuted element Z (element Z + electron) and the element $Z+1$ could range from the chemical bonding they possess to the geometries of the compounds they form. An important concept indeed, as many key features that were thought only to belong to element $Z+1$ now belong to element Z [7]. Expansion to clusters with transmuted element Z can thus further be studied to exemplify these features. Thus far, numerous successful accounts of electronic transmutation have been observed and are reported in the Chapter 2 literature review on electronic transmutation. Table 1.1 also offers a brief overview of the simple species reported in chapter 2 and their connection to the isoelectronic principle as defined by Gillis [6, 10].

1.4 Overview

Chapters 3 and 4 will focus on the more recent additions to electronic transmutation beginning with Chapter 3 and the electronic transmutation of Al to produce the elusive Al=Al (Al-Al double bond). Chapter 4 will then proceed with the introduction of the new concept, double electronic transmutation (DET), which states: “that by acquiring two electrons, a certain element with atomic number Z begins to behave similarly as its neighboring element $Z+2$.” The similarities between the transmuted element Z (element Z + two electrons) and the element $Z+2$ could range from the chemical bonding they possess to the geometries of the compounds they form [11]. Experimental and theoretical evidence of highly debated Al≡Al (Al-Al triple bond) will be used to support the validity of the DET

concept. Chapter 5 will conclude this dissertation's literary work with a study classical vs. multi-centered bonding in homocatenated $\text{H}-(\text{Be})_n\text{-H}$ clusters.

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Table 1.1: Collection of electronically transmuted species ($Z \rightarrow Z+1$) and their relationship to the isoelectronic principle.

Isoelectronic to Electronic Transmutation		
Group 2 to Group 13		
Isoelectronic Class	Kernel (element Z)	Kernel (element Z+1)
$n/3n$	Be_n^{n-}	B_n
Group 13 to Group 14		
Isoelectronic Class	Kernel (element Z)	Kernel (element Z+1)
$5n/8n$	$(\text{B}_n\text{H}_{2n+2})^{n-}$	$\text{C}_n\text{H}_{2n+2}$
$5n/8n$	$(\text{Al}_n\text{H}_{2n+2})^{n-}$	$\text{Si}_n\text{H}_{2n+2}$
Group 14 to Group 15		
Isoelectronic Class	Kernel (element Z)	Kernel (element Z+1)
$n/5n$	Si_n^{n-}	P_n
Group 15 to Group 16		
Isoelectronic Class	Kernel (element Z)	Kernel (element Z+1)
$n/6n$	N_n^{n-}	O_n
$n/6n$	P_n^{n-}	S_n

CHAPTER 2

ELECTRONIC TRANSMUTATION: CHEMICALLY TURNING ONE ELEMENT INTO ANOTHER¹

2.1 Abstract

The concept of electronic transmutation (ET) depicts the processes that by acquiring an extra electron, an element with the atomic number Z begins to have properties that were known to only belong to its neighboring element with the atomic number $Z+1$. Based on ET, signature compounds and chemical bonds that are composed of certain elements can now be designed and formed by other electronically transmuted elements. This Minireview summarizes the recent developments and applications of ET on both the theoretical and experimental fronts. Examples on the ET of Group 13 elements into Group 14 elements, Group 14 elements into Group 15 elements, and Group 15 elements into Group 16 elements are discussed. Compounds and chemical bonding composed of carbon, silicon, germanium, phosphorous, oxygen and sulfur now have analogues using transmuted boron, aluminum, gallium, silicon, nitrogen, and phosphorous.

2.2 Introduction

Despite the success of the valence-isoelectronic concept in many examples of predicting reactivity, structures and existence of compounds, such a simple electron counting rule can nevertheless easily fail. For instance, being valence-isoelectronic to benzene (C_6H_6), the planar D_{6h} silabenzene molecule Si_6H_6 is not even a minimum on its potential energy surface [1]. The deformation from this planar structure to its real global minimum is attributable to the pseudo-Jahn–Teller effect. In view of this, a stricter and narrower electronic transmutation (ET) concept [2] was proposed in 2012, stating that by acquiring an

¹Xinxing Zhang, Jared K. Olsen, Kit H. Bowen, Alexander I. Boldyrev

electron, a certain element with the atomic number Z begins to behave similarly as its neighboring element $Z+1$. For example, the transmuted boron, B^- , may well be functioning similarly to carbon. The similarities between the transmuted element Z and the targeted element $Z+1$ could range from the chemical bonding they possess to the geometries of the compounds they form, so that many key features that were thought only belong to element $Z+1$ can now belong to element Z . Alchemists once spent great efforts in transmutating common elements into precious others, which now we know is not possible merely with chemistry, but based on ET, the element Z can now be chemically “turned into” element $Z+1$. After the proposal of the ET concept, a plethora of successful examples, including the transmutation of Groups 13, 14, and 15 elements into Group 14, 15, and 16 elements, have been reported [2–18]. In this Minireview, we will summarize these examples on both the theoretical and experimental fronts, and outlook for wider applications and future research directions of this new concept.

2.3 Electronic Transmutation of Group 13 elements into Group 14 Elements

Group 13 elements, such as boron [19], aluminum [20], and gallium [21], are well known to form clustered compounds through multicenter bonding, which is largely due to their electron-deficient (s^2p^1 electron configuration) nature. The simplest examples are the diborane (B_2H_6) [22], dialane (Al_2H_6) [23], and digallane (Ga_2H_6) [24] molecules, where each of the two bridge hydrogen atoms participates in forming a 3-center 2-electron ($3c-2e$) $M-H_{bridge}-M$ ($M=B, Al, Ga$) bond. Rather distinct from the Group 13 elements, Group 14 elements such as carbon, silicon, and germanium usually form chain or ring compounds as a result of sp^n ($n=1, 2, 3$) hybridizations. With the difference of only one electron, Group 13 and 14 elements behave very differently in chemical bonding and the compounds they can form. In this section, we discuss the theoretical and experimental advances of the electronic transmutation of Group 13 elements into Group 14 elements, where the former yield similar chemical bonding and compounds as the latter after transmutation.

2.3.1 ET of boron into carbon

It is well-known that carbon forms a large variety of hydrocarbons, including aromatic arene, alkane, alkene, and alkyne-based compounds that feature chain (homocatenation) or ring structures. Boron hydrides, or boranes, on the other hand, prefer clustered structures. In order to satisfy the octet rule, the insufficient electrons in boron lead to the formation of 3c-2e bonds, based on which an extension to molecular orbital (MO) theory was developed, known as the polyhedral skeletal electron pair theory (PSEPT) or simply Wade-Mingos rules [19]. In this section, we present the successful examples of homocatenated and aromatic boron compounds when boron is electronically transmuted into carbon.

We first discuss the theoretical predictions of homocatenated boron hydrides where the ET concept was firstly proposed [2]. Alkanes follow the molecular formula C_nH_{2n+2} , suggesting that their boron analogues should have the formula of $(B_nH_{2n+2})^{n-}$, in which each boron atom obtains one negative charge to resemble carbon. These negative charges can be provided by certain electron donors, preferably by alkali metals such as Li, so the first obvious example is the BH_4^- kernel in the $LiBH_4$ salt, which is isoelectronic and isostructural to CH_4 , and already commercially available. Here we focus on the homocatenation of boron, and $Li_2B_2H_6$ seems to be a simple candidate to start with. However, the B-Li, H-Li, and B-H bond dissociation energies are not too far away from each other [25], one would expect a relatively flat potential energy surface and many possible isomers that are close in energy for this molecule, which makes a thorough, unbiased geometrical search indispensable but very expensive in order to find the real global minimum. Here we present the detailed calculation methods used in reference [2] in order to set an example for the search of the global minimum of electronically transmuted molecules. The computational methods for other ET molecules in the rest of this minireview are more or less the same as the case of $Li_2B_2H_6$ unless noted. The search for the global minimum structure of the $Li_2B_2H_6$ molecule was performed using the Coalescence Kick program written by Averkiev [26]. Initially these calculations were performed at a relative low/cheap level of theory (B3LYP/3-21G [27]) to search for a large quantity of isomers, and those

lowest energy isomers ($\Delta E \leq 60$ kcal mol⁻¹) were then reoptimized and frequencies were calculated at B3LYP/6-311++G** [28], and CCSD(T)/6-311++G** [29] and single point calculations were performed using the RCCSD(T)/aug-cc-pVXZ levels of theory (X=D and T) [30]. The final relative energies were obtained through extrapolation of total energies at the CCSD(T) level of theory to the complete basis set limit (CBS) using the Truhlar formula [31] (CCSD(T)/CBS//CCSD(T)/6-311++G**) and corrected for zero-point energies calculated at CCSD(T)/6-311++G**. Chemical bonding analysis (B3LYP/6-311++G**) was performed using the AdNDP method [32]. All calculations were done using GAUSSIAN 03 and GAUSSIAN 09 [33] software packages. Molekel 5.4.0.8 was used for MO visualization, [34] and MOLDEN t3.4 [35] was used for molecular structure visualization.

Figure 2.1A presents the global minimum of Li₂B₂H₆, which contains one 2c-2e B-B σ -bond and six 2c-2e B-H σ -bonds. These σ -bonds are further confirmed by AdNDP analysis (Figure 2.1D). From the structure, the B₂H₆ kernel is indeed very similar to the hydrocarbon analog, ethane. However, the interaction between the Li atoms and the B₂H₆ kernel appears to be critical to determine the existence of electronic transmutation. Calculated effective charges are +0.94 |e| on each Li atom and -1.88 |e| on the B₂H₆ kernel. Thus, the interaction between the Li and the B₂H₆ kernel is ionic, and the B₂H₆ moiety is indeed in the form of B₂H₆²⁻. In other words, electronic transmutation has occurred.

From Li₂B₂H₆ to Li₃B₃H₈ and Li₄B₄H₁₀, the expensiveness of the global minimum search increases exponentially with the number of atoms involved, hence, the authors did not attempt to search for the global minimum, instead, they examined whether or not the propane- and n-butane-shaped molecules were local minima on their potential surfaces. The structures in Figure 2.1B and 2.1C indeed display similar structures as propane and n-butane, manifesting the success of the electronic transmutation in the homocatenation of boron hydrides.

We next discuss the electronically transmuted aromatic boron hydrides, analogues of arenes. Benzene (C₆H₆), cyclopentadienide (C₅H₅⁻), tropylium (C₇H₇⁺), [36] and naphthalene (C₁₀H₈) are planar aromatic hydrocarbons, following the 4n+2 aromaticity rule.

Closo-boranes [19], $B_nH_n^{2-}$ or $(B_nH_{n-2})^{4-}$, feature polyhedral structures (Figure 2.2C, F, I, L). By donating negative charges to these 3-dimensional closo-boranes, is it possible to “flatten” them into aromatic 2-dimensional arene analogues? Alexandrova and Boldyrev [3] examined the calculated global minima of $B_6H_6Li_6$ (Figure 2.2A, B), $B_5H_5Li_6$ (Figure 2D, E), $B_7H_7Li_6$ (Figure 2.2G, H), and $B_{10}H_8Li_{10}$ (Figure 2.2J, K), which are isoelectronic to C_6H_6 , $C_5H_5^-$, $C_7H_7^+$ and $C_{10}H_8$, respectively. All of these B_nH_n kernels are planar, and the formal negative charges on B_nH_n revealed by natural bond orbital (NBO) analysis [37] are close to $-n$, indicating that boron atoms in these molecules are transmuted into carbon. More importantly, are these $B_nH_n^{n-}$ kernels aromatic? Nucleus-independent chemical shifts (NICS) indices were introduced by Schleyer [38] as a simple probe for aromaticity. The NICS index at the center of the $B_6H_6^{6-}$ kernel is -7.2 ppm, very close to that of benzene (-8.0 ppm) calculated at the same level of theory. NICS indices for other species are -2.0 ppm for $B_5H_5Li_6$, -93.2 ppm for $B_7H_7Li_6$, and -54.2 ppm for $B_{10}H_8Li_{10}$, providing evidence of their aromaticity. Figure 2.2M presents the three aromatic π -molecular orbitals of $B_6H_6Li_6$, all of which are similar to that of benzene.

Similarly, Tiznado and co-workers [4] theoretically investigated the $Li_6(BH)_5$ and $Li_7(BH)_5^+$ clusters, and discovered that the $B_5H_5^{6-}$ kernels in the global minima are the transmuted analogues of cyclopentadienide ($C_5H_5^-$). Sol, Teixidor and coworkers [5] examined the intrinsic relationship between the Wade–Mingos rule and $(4n+2)$ π Hückel rule using the electronic confined space analogy (ECSA) method, in which the electronic transmutation concept turned out to be a key factor.

We next present two extreme examples of transmuted boron, the aromatic 2D boron films, which can be viewed as the analogue of graphene. Graphene is one of the allotropes of carbon consisting of a single planar layer of carbon atoms arranged in a hexagonal lattice [39]. Graphene’s boron “cousin” needs to have the stoichiometry of B_n^{n-} . Using powder X-ray diffraction, Akimitsu and co-workers confirm that there are extraordinary 2D layers of honeycomb structures composed of boron atoms with Mg atoms located above and below the boron hexagon (Figure 2.3A) in the well-known high-temperature superconductor

MgB₂ [6]. The 2D-lattice of boron appears to be structurally the same as graphene. Even though not clearly stated by the authors, a complete charge transfer from Mg to B in the form of Mg₂ + B₂²⁻ due to the large electronegativity difference between Mg and B can be anticipated, and the electronic transmutation principle apparently plays a key role in forming this 2D structure. The B_nⁿ⁻ sheet might be the reason for this material’s high-temperature superconducting behavior. During the review process of this minireview, the successful preparation of a honeycomb, graphene-like borophene (Figure 2.3B) by using an Al surface as the substrate and electron donor was reported. [40]. The authors point out that nearly one electron charge is transferred to B from Al, which makes a great example of ET in the application of solid state chemistry. Without electron transfer, the 2D boron film on Ag surface otherwise displays very different structure [41].

2.3.2 ET of aluminum into silicon

As a result of the development of modern gas-phase spectroscopy techniques, many aluminum hydrides (alanes) have been discovered using the pulsed arc cluster ionization source (PACIS) and characterized using the anion photoelectron spectroscopy method [20]. Without ET, aluminum hydrides prefer polyhedral structures, following the Wade–Mingos rule just like boranes [20a]. Similar to the ET of boron into carbon, the ET of aluminum into silicon also involves electron donation to aluminum to make Al⁻.

The first ET example of aluminum is the homocatenation of aluminum hydrides. The stoichiometry Li_nAl_nH_{2n+2} was attempted to theoretically test the viability of ET for aluminum. Figure 2.4A presents the global minimum structures of Li₂Al₂H₆ and Li₃Al₃H₈ [7] and they do have similar structures as corresponding disilane [42]/ethane and trisilane [42]/propane. Figure 2.4B shows the chemical bonds of Li₂Al₂H₆ revealed by AdNDP, including one Al-Al σ -bond and six Al-H σ -bonds, and all of the occupation numbers are more than 1.9 |e|, indicating effective single bonds. The natural population analysis (NPA) charges of Li and the Al₂H₆ kernel are +0.89 and -1.77, suggesting an almost full electron transfer from Li to Al, therefore ET indeed occurs in Li₂Al₂H₆. Figure 2.4C exhibits the chemical bonds of Li₃Al₃H₈, including two Al-Al σ single bonds and eight Al-H σ single

bonds, and all the occupation numbers are more than 1.9 $|e|$, too. The natural population analysis (NPA) charges of Li and the Al_3H_8 kernel are +0.86 and -2.60, manifesting that ET is also present in this case. For the first time it has been shown that ET enables aluminum atoms to homocatenate with the formation of silane/alkane-like species.

To experimentally investigate the existence of these exotic homocatenated aluminum hydrides in the gas phase, it is better to study them in the form of ions. For the $\text{Li}_n\text{Al}_n\text{H}_{2n+2}$ molecules, one could study the $\text{Li}_{n-1}\text{Al}_n\text{H}_{2n+2}^-$ anion by losing one Li^+ counter ion from $\text{Li}_n\text{Al}_n\text{H}_{2n+2}$. When $n=1$, AlH_4^- , the simplest monosilane/methane analogue, was first examined by anion photoelectron spectroscopy [43] in the gas phase. The vertical detachment energy (VDE) of AlH_4^- is as high as 4.4 eV, indicating that it is very stable. Anion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency photon beam and energy-analysing the resultant photodetached electrons. It is governed by the energy-conserving relationship, $h\nu = \text{EBE} + \text{EKE}$, in which $h\nu$ is the photon energy, EBE is the electron binding (transition) energy, and EKE is the electron kinetic energy. The anion photoelectron spectrometer, which has been described previously [44], consists of one of many kinds of ion sources, a linear time-of-flight mass spectrometer, a mass gate, a momentum decelerator, a pulsed Nd:YAG photodetachment laser, and a magnetic bottle electron energy analyzer. Photoelectron spectra were taken with 193 nm (6.42 eV) photon energy and calibrated against the well-known photoelectron spectrum of Cu^- [45]. The AlH_4^- cluster anions were generated in a pulsed arc cluster ionization source (PACIS). During operation, a pulsed valve backed by 200 psi of UHP hydrogen is opened for about 200 microseconds and fills a region between a copper anode and grounded aluminum cathode. A 30 microseconds long, 180 V pulse is applied to the copper anode that discharges through the hydrogen gas and subsequently vaporizes the aluminum cathode. The combination of free atomic hydrogen and vaporized aluminum is entrained with the remaining molecular hydrogen and carried along a 20 cm flow tube where it reacts, cools, and forms AlH_4^- , which is then extracted and mass-selected before photodetachment.

$\text{Li}_2\text{Al}_3\text{H}_8^-$, the aluminum analogue of trisilane/propane, was also interrogated by anion photoelectron spectroscopy but generated in a different laser vaporization source [8]. Briefly, an aluminum rod was coated by a very thin layer of LiAlH_4 powder, and then ablated by a pulsed Nd:YAG laser beam operating at a wavelength of 532 nm. The resulting plasma was cooled by supersonically expanding a plume of helium gas from a pulsed gas valve (backing pressure of 100 psi). Negatively charged anions were then extracted into the spectrometer prior to mass selection and photodetachment. Figure 2.5A presents the photoelectron spectra of $\text{Li}_2\text{Al}_3\text{H}_8^-$ taken with 355 nm (3.49 eV) and 266 nm (4.66 eV) photon energies. Both spectra have an EBE band (X) starting from 2.20 eV and peaking at 2.70 eV. In case of a sufficient Franck–Condon overlap between the ground state of the anion and the ground state of the neutral, the threshold of the first EBE band (2.20 eV) should be the electron affinity (EA) of $\text{Li}_2\text{Al}_3\text{H}_8$. The first experimental VDE, the energy difference between an anion and the corresponding neutral species at the geometry of the anion, corresponds to the peak position of the band X, 2.70 eV. The width of the band X suggests an appreciable geometry change between the ground state of $\text{Li}_2\text{Al}_3\text{H}_8^-$ and that of its neutral. In the 266 nm spectrum, a second band (A) at the higher EBE end peaks at 4.32 eV, corresponding to the transition from the ground state of the anion to the first excited state of the neutral molecule. More importantly, can the $\text{Li}_2\text{Al}_3\text{H}_8^-$ cluster maintain the trisilane/propane-like structure after losing the Li^+ counter ion compared to the neutral $\text{Li}_3\text{Al}_3\text{H}_8$? A thorough unbiased theoretical search finds that the global minimum structure of $\text{Li}_2\text{Al}_3\text{H}_8^-$ still possess the chain structure (Figure 2.5B), and chemical bond analysis does show that the two Al-Al bonds and the eight Al-H bonds are σ -bonds with occupation numbers more than 1.7 |e|. The vertical electronic transition calculations from the anion to the corresponding neutral match the X and A peaks, indicating that the experimentally observed cluster is indeed the calculated global minimum. NPA charges also show a significant electron transfer from the Li atoms to the Al_3H_8 kernel. The discovery of $\text{Li}_2\text{Al}_3\text{H}_8^-$ in the gas phase makes the first successful experimental example of the homocatenation of aluminum.

The above discussions are the ET of aluminum hydrides into saturated silane/alkane analogues, and an obvious question is that can one generate unsaturated aluminum hydrides with the ET concept, such as an Al=Al double bond in the $\text{Al}_2\text{H}_4^{2-}$ kernel? Silicon hydrides are known to have homodinuclear double bonds, such as that in the Si_2H_4 molecule. The Al=Al double bond has been otherwise notoriously difficult to synthesize. A stable neutral compound with an Al=Al double bond was synthesized by Inoue and co-workers using bulky ligands very recently [46]. For the gas phase study, the designed ion is $\text{LiAl}_2\text{H}_4^-$ [9], which was generated and characterized with the same methods as $\text{Li}_2\text{Al}_3\text{H}_8^-$. The measured anion photoelectron spectrum of $\text{LiAl}_2\text{H}_4^-$ is presented in Figure 2.6A, and three EBE bands were observed (X, X' and X''), among which X belongs to the global minimum Isomer I, X' and X'' belong to the second lowest lying Isomer II (Figure 2.6B). The next question is whether the Al=Al double bond exists in the global minimum structure Isomer I? AdNDP analysis shown in Figure 2.6C presents two 2c-2e σ -Al-H bonds ($\text{ON}=2.00 |e|$), two 3c-2e σ -Li-H-Al bonds ($\text{ON}=1.97|e|$) (these four bonds are analogous to the σ -Si-H bonds in Si_2H_4), one σ -3c-2e Al-Li-Al bond ($\text{ON}=1.99 |e|$) (an analogue of the σ -Si-Si bond in Si_2H_4), and one π -Al-Al bond ($\text{ON}=2.00 |e|$) (an analogue of the π -Si-Si bond in Si_2H_4). In order to claim the presence of the Al=Al double bond, one needs to evaluate how much the lithium atom contributes to the σ and π -3c-2e Al-Li-Al bonds. AdNDP reveals that the σ -3c-2e Al-Li-Al bond ($\text{ON}=1.99 |e|$) can be seen as one σ -2c-2e Al-Al bond ($\text{ON}=1.87 |e|$) since the contribution of the lithium atom to this bond is as small as $0.13|e|$. The π -3c-2e Al-Li-Al bond ($\text{ON}=2.00 |e|$) can be seen as one π -2c-2e Al-Al bond ($\text{ON}=1.65 |e|$). That gives the $(1.87+1.65)/2=1.76$ bond order for Al=Al double bond in the cluster. The optimal bond length between the two Al atoms in $\text{LiAl}_2\text{H}_4^-$ structure is 2.46 \AA (PBE0/6-311++G**), which is shorter than the single Al-Al σ -bond (2.59 \AA , PBE0/6-311++ G**) in the H_2AlAlH_2 molecule and the single Al-Al σ -bond (2.55 \AA) in the $\text{H}_3\text{AlAlH}_3^{2-}$ crystal structure [47]. The appreciably shorter Al-Al bond length and the bond order indicate that there is indeed a double bond between the two aluminum atoms. Additionally, the $\text{LiAl}_2\text{H}_4^-$ cluster is slightly distorted from the planar structure, which is

also the case in the Si_2H_4 molecule due to the pseudo Jahn–Teller effect [48].

2.3.3 ET of gallium into germanium

Germanium hydrides (germanes), even though not in a large scale, have been synthesized and shown hydrocarbon-like structures [49]. The ET of gallium into germanium enjoys fruitful experimental discoveries [10–12]. Powders of gallium hydride (gallane)-containing compounds, such as $\text{Cs}_{10}\text{H}[(\text{Ga}_3\text{H}_8)^{3-}]_3$, $(\text{K}_x\text{Rb}_{1-x})_n[(\text{GaH}_2)^-]_n$, $\text{Rb}_8[\text{Ga}(\text{GaH}_3)_4^{5-}]$ and $\text{Rb}_n[(\text{GaH}_2)^-]_n$ have been synthesized and characterized by X-ray diffraction, where K, Rb and Cs are used as the electron donors. In $\text{Cs}_{10}\text{H}[(\text{Ga}_3\text{H}_8)^{3-}]_3$ [10], both ET and the Zintl–Klemm concept [50] are utilized to design the compound, and the $(\text{Ga}_3\text{H}_8)^{3-}$ kernel is isostructural to propane and Ge_3H_8 . In $(\text{K}_x\text{Rb}_{1-x})_n[(\text{GaH}_2)^-]_n$ [11] and $\text{Rb}_n[(\text{GaH}_2)^-]_n$ [12], the $[(\text{GaH}_2)^-]_n$ polyanions feature polyethylene structures, and in $\text{Rb}_8[\text{Ga}(\text{GaH}_3)_4^{5-}]$ [12], the $\text{Ga}(\text{GaH}_3)_4^{5-}$ kernel has similar structure as neopentane. In all these examples, each of the Ga atoms obtain one negative charge for the electronic transmutation.

2.4 Electronic Transmutation of Group 14 Elements into Group 15 Elements

2.4.1 ET of silicon into phosphorous

In this section, we only discuss one example, the transmutation of silicon into phosphorous. Pure silicon forms the diamond cubic crystal structure [42]. Due to the structure and the high bond energy, silicon is hard. Its neighbour, phosphorus, has several types of allotropes [42], one of which is the white phosphorus, or simply tetraphosphorus (P_4), existing as molecules composed of four atoms in a tetrahedral structure. In order to transmutate Si into P, theoretical investigations using Li as the electron donor have been attempted [13, 14]. Figure 2.7 [14] presents the structural evolution of the global minima and charges on the Si_4 moiety with increasing number of Li atoms in the Li_nSi_4^- series ($n=0-5$). According to the ET designing principle, the first Si_4^{4-} kernel mimicking P_4 should occur in the Li_3Si_4^- cluster. Its global minimum indeed shows a tetrahedral Si_4 moiety, and the NPA charge on Si_4 is $-3.43 |e|$, making it effectively a Si_4^{4-} cluster. Surprisingly, by adding more Li atoms

to Li_3Si_4^- , the NPA charges on the Si_4 moieties in the Li_4Si_4^- and Li_5Si_4^- clusters remain around $-3.5 |e|$ (Figure 2.7), suggesting that Si_4 in these clusters have a strong tendency to maintain the ET structure, tetrahedral Si_4^{4-} . The experimental observations of the Si_4^{4-} kernel have been achieved in heavier alkali monosilicides, MSi ($\text{M}=\text{Na}, \text{K}, \text{Rb}, \text{Cs}$) in the solid state [51].

2.5 Electronic Transmutation of Group 15 Elements in to Group 16 Elements

2.5.1 ET of nitrogen into oxygen

The ET of nitrogen into oxygen enjoys both the experimental and theoretical developments. In 2001, Kniep et al. synthesized binary diazenides SrN_2 and BaN_2 [15a, b]. Schnick et al. [15c] experimentally confirmed the stability of the first alkali diazenide Li_2N_2 under high pressure and high temperature conditions, where Sr, Ba and Li function as the electron donors. In these three examples, the existence of the homonuclear dinitrogen anion N_2^{2-} , an analogue of O_2 , are proven by X-ray diffraction, neutron diffraction and infrared spectroscopy. The crystal structures of these examples are displayed in Figure 2.8. In SrN_2 and BaN_2 , each N_2^{2-} kernel is surrounded by an octahedron formed by six Sr^{2+} or Ba^{2+} ions (Figure 2.8A, 2.8B), in Li_2N_2 , each N_2^{2-} kernel is surrounded by a cube formed by eight Li^+ ions (Figure 2.8C).

The attempt of finding the ozone analogue, Li_3N_3 , was performed theoretically [15d]. The bent ozone-like structure of the N_3^{3-} kernel nevertheless is not the global minimum, but it is only slightly higher in energy than the global minimum. Chemical bond analysis of Li_3N_3 and ozone (Figure 2.8D, 2.8E) confirms the similarity in chemical bonding, including two $\text{N}=\text{N}$ double bonds with occupation numbers (ON) of $1.98 |e|$ for σ -bonds and $1.93 |e|$ for π -bonds; one p -lone pair on the central nitrogen ($\text{ON}=1.72 |e|$) and two lone pairs of s and p type on each side nitrogen atom, with ONs ranging from $1.71 |e|$ to $1.86 |e|$. NBO charge on the N_3 moiety is $-2.04 |e|$, suggesting significant charge transfer from Li to N.

2.5.2 ET of phosphorous into sulfur

In search of the transmuted phosphorous, the global minimum search was first performed for Li_xP_x ($x=5-9$) [16]. Remarkably, inorganic double helix structures were found for all of these clusters. Periodic repetition of the LiP infinite double helix chain geometry is shown in Figure 2.9A for illustration. Starting from Li_7P_7 and up to Li_9P_9 , the double helices have a similar chemical bonding pattern: effective charges on Li range from +0.8 to +0.9 |e|; there are no Li-P σ -bonds. Six (Li_7P_7), seven (Li_8P_8), and eight (Li_9P_9) P-P σ -bonds with ON=1.95–1.98 |e| are observed. From this data, it can be concluded that when the bonding between the Li and P atoms is ionic beginning from Li_7P_7 to Li_9P_9 , and the double-helix structures are much more favourable relative to other isomers. NBO analysis does not show any significant direct Li-Li covalent bonding. In the graphical representation of double-helix structures, adjacent Li atoms are connected to make the double-helix structure look more apparent. The helix structure formed by lithium cations is due to the favourable electrostatic interactions with neighbouring phosphorus anions. Further, a theoretical study of $\text{Li}_{90}\text{P}_{90}$ [17], which possesses a circular double-helix structure that resembles the Watson–Crick DNA structure [52] is reported and presented in Figure 2.9B. NBO analysis of the $\text{Li}_{90}\text{P}_{90}$ circular double-helix structure shows that the bonding between lithium and phosphorus atoms is quite ionic with effective atomic charges ranging from -0.4 to -0.8 |e| on P. Additionally, NBO analysis revealed the presence of 90 P-P σ -bonds with occupation numbers (ON) equal to 1.92–1.95 |e|, and two lone pairs of s - and p -type on each phosphorus atom with ONs ranging from 1.72 to 1.84 |e|. The results of the AdNDP analysis are in excellent agreement with the NBO results (Figure 2.9C).

We next provide evidence that the ET of phosphorous into sulfur indeed occurs in these structures. In Li_xP_x ($x=7-9, 90$), the interaction between Li and P atoms are all ionic, and the P atoms obtain enough negative charge to transmute into S. The electronic configurations of P^- and S are $[\text{Ne}]3s^23p^4$, indicating that there should be one s - lone pair, one p - lone pair, and two p - unpaired electrons. Therefore compounds with two σ -bonds formed by these two p - unpaired electrons can be expected. It is indeed the case

in Li_xP_x ($x=7-9, 90$), where each P atom forms two σ -bonds with adjacent two other P atoms and P_n chain structures are observed. However, there are many kinds of sulfur allotropes [42] including various chain and ring structures. The S atoms in these allotropes also possess two σ -bonds formed with adjacent two other S atoms. In 2013, Fujimori et al. [53] synthesized single chains of sulfur encapsulated in carbon nanotubes and characterized them with transmission electron microscopy (Figure 2.9D). Due to the confinement of the nanotube, the sulfur atoms can grow in a single long chain and do not form ring structures. This discovery justifies the ET of phosphorous presented in Figure 2.9A. In view of this confined S-chain, the Li_nP_n chain inside a carbon nanotube channel was also calculated [18]. More recently, first-principles investigations of a series of inorganic double helical XY ($X=\text{Li, Na, K, Rb, Cs}$; $Y=\text{P, As, Sb}$) structures were conducted [54]. Remarkably, the inorganic double helical SnIP semiconductors containing one [SnI] helix and one [P] helix were synthesized by Nilges and co-workers in the solid state (Figure 2.9E) [55]. The Sn atoms in this material function as the electron donor, and both I and P acquire significant negative charges from Sn. Consistent with the ET principle, it is the negative charge that makes the $[\text{P}^-]_\infty$ chain resemble the sulfur chain.

2.6 Outlook

The major development of the ET concept has been *in silico*, where the unbiased global minimum search and the chemical bonding analysis play major roles. The advent of modern gasphase and solid-state synthesis and characterization techniques greatly helps to identify the ET compounds and justify the ET concept. The main spirit of ET is to discover new exotic compounds and chemical bonding. In the near future, we anticipate that more experimental discoveries of electronically transmuted compounds can be achieved. For example, the LiAlH_4 and LiBH_4 salts are currently commercially available, and they can be viewed as SiH_4 and CH_4 analogues. We think the large-scale synthesis of $\text{Li}_n\text{Al}_n\text{H}_{2n+2}$, $\text{Li}_n\text{B}_n\text{H}_{2n+2}$ and $\text{Li}_n\text{Al}_n\text{H}_{2n}$ can come true soon since $\text{Li}_2\text{Al}_3\text{H}_8^-$ [8] and $\text{LiAl}_2\text{H}_4^-$ [9] are observed in the gas phase through the recombination of the plasma generated from the laser vaporization of LiAlH_4 powder.

Another concept, the double electronic transmutation (DET) could play a major role in the near future. By acquiring two electrons, a certain element with the atomic number Z could behave similarly as the element $Z+2$. Based on DET, further examples of transmutation such as B to N, Al to P, C to O is anticipated.

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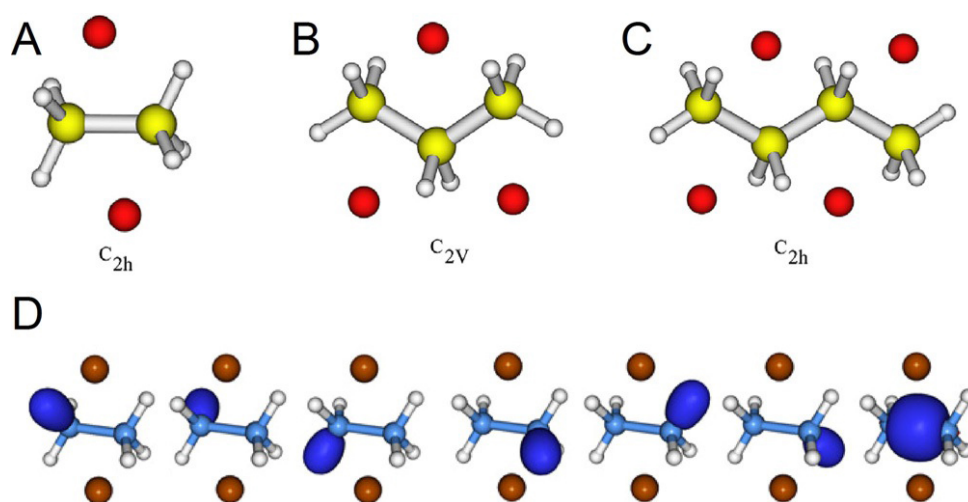


Fig. 2.1: Calculated global minimum structures of $\text{Li}_2\text{B}_2\text{H}_6$ (A), $\text{Li}_3\text{B}_3\text{H}_8$ (B), $\text{Li}_4\text{B}_4\text{H}_{10}$ (C), and the chemical bonding of $\text{Li}_2\text{B}_2\text{H}_6$ recovered by the AdNDP analysis (D).

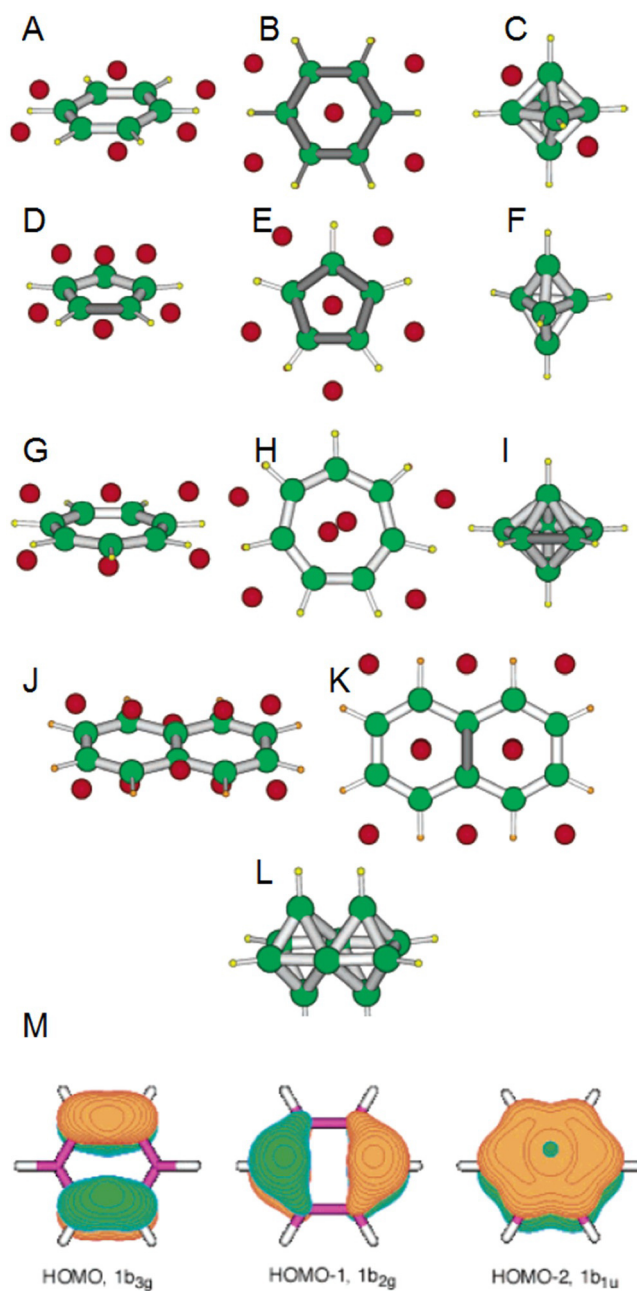


Fig. 2.2: Optimized structures of $B_6H_6Li_6$ (D_{2h} , 1A_g), side view (A); $B_6H_6Li_6$ (D_{2h} , 1A_g), front view (B); $B_6H_6Li_2$ (D_{3d} , $^1A_{1g}$) (C); $B_5H_5Li_6$ (C_s , $^1A'$), side view (D); $B_5H_5Li_6$ (C_s , $^1A'$), front view (E); $B_5H_5^{2-}$ (D_{3h} , $^1A_1'$) (F); $B_7H_7Li_6$ (C_1 , 1A), side view (G); $B_7H_7Li_6$ (C_1 , 1A), front view (H); $B_7H_7^{2-}$ (D_{5h} , $^1A_1'$) (I); $B_{10}H_8Li_{10}$ (D_{2h} , 1A_g), side view (J); $B_{10}H_8Li_{10}$ (D_{2h} , 1A_g), front view (K); and $B_{10}H_8^{4-}$ (D_{2h} , 1A_g) (L). π -molecular orbitals of $B_6H_6Li_6$ (D_{2h} , 1A_g) (M).

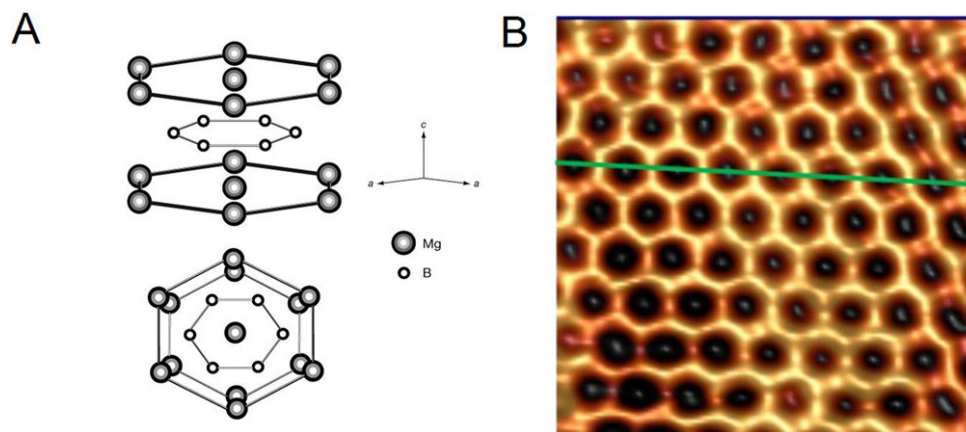


Fig. 2.3: (A) Crystal structure of MgB₂; (B) Scanning tunnelling microscopy image of a graphene-like borophene sheet on an Al substrate.

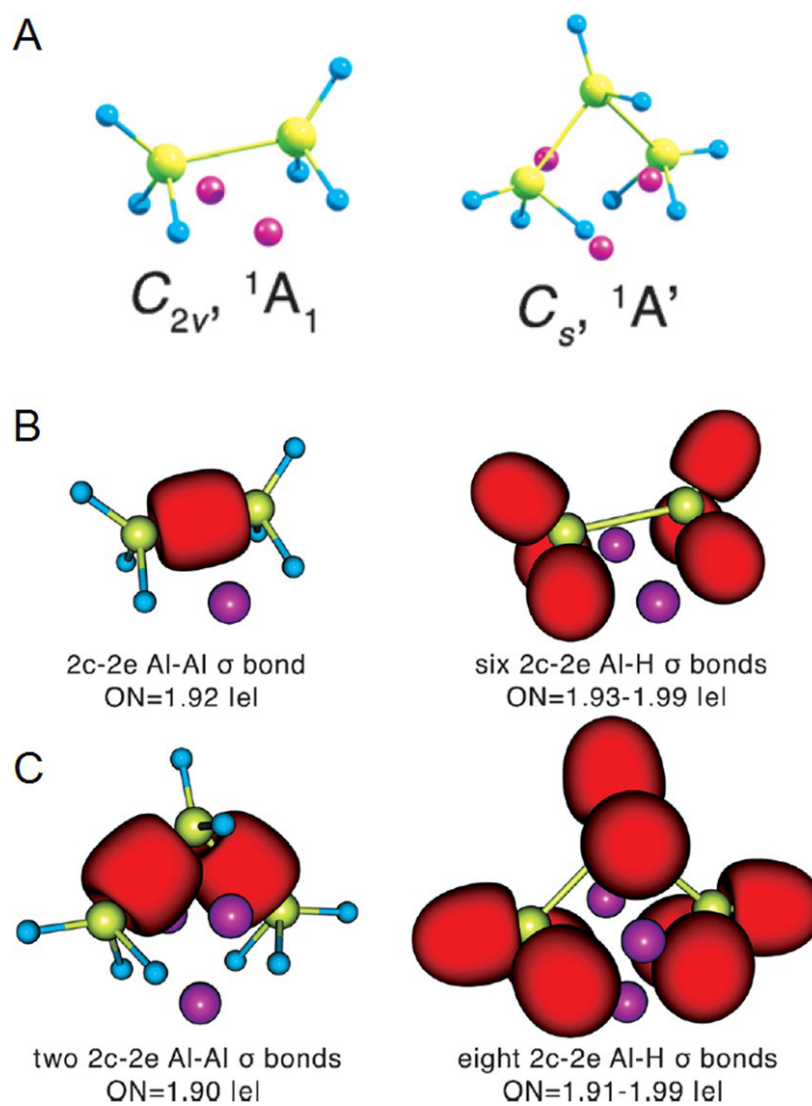


Fig. 2.4: Global minimum structures of $\text{Li}_2\text{Al}_2\text{H}_6$ and $\text{Li}_3\text{Al}_3\text{H}_8$ (A), and the chemical bonds of $\text{Li}_2\text{Al}_2\text{H}_6$ (B) and $\text{Li}_3\text{Al}_3\text{H}_8$ (C) recovered by the AdNDP analyses.

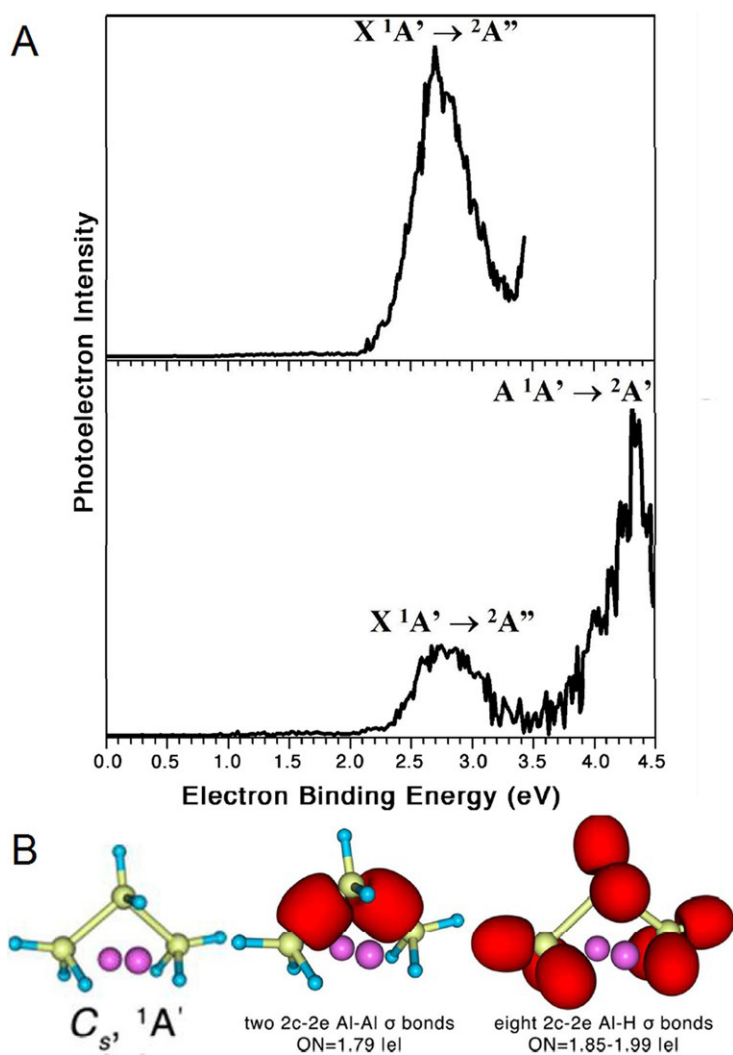


Fig. 2.5: Anion photoelectron spectra of the $\text{Li}_2\text{Al}_3\text{H}_8^-$ anion taken with 355 and 266 nm photons (A) and its global minimum structure and the chemical bonds recovered by the AdNDP analysis (B).

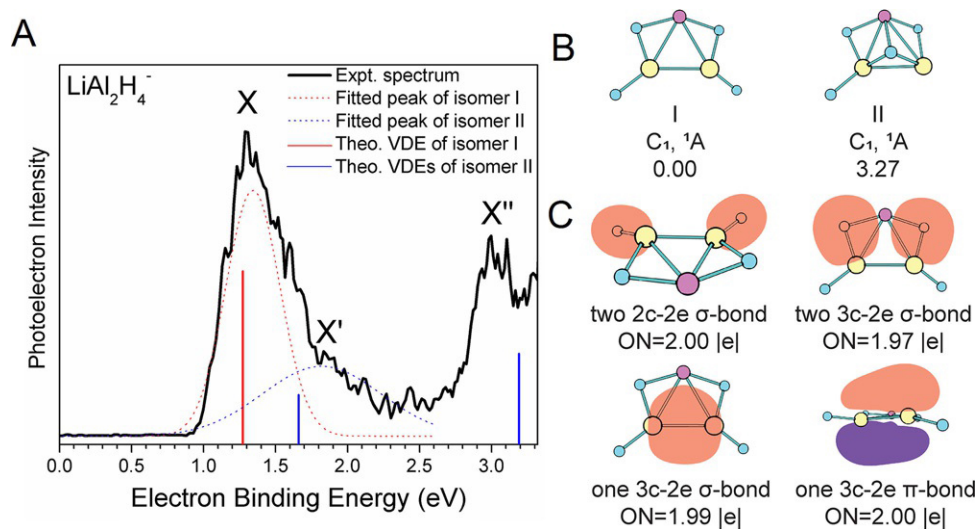


Fig. 2.6: Experimental photoelectron spectrum of $\text{LiAl}_2\text{H}_4^-$ using 355 nm laser (black line), Gaussian fitting of isomers I and II (red and blue dotted lines), and calculated stick spectra of isomers I and II (red and blue vertical lines) (A); the structures of the two lowest-energy isomers I and II (B), and the chemical bonds of the global minimum structure recovered by the AdNDP analysis (C).

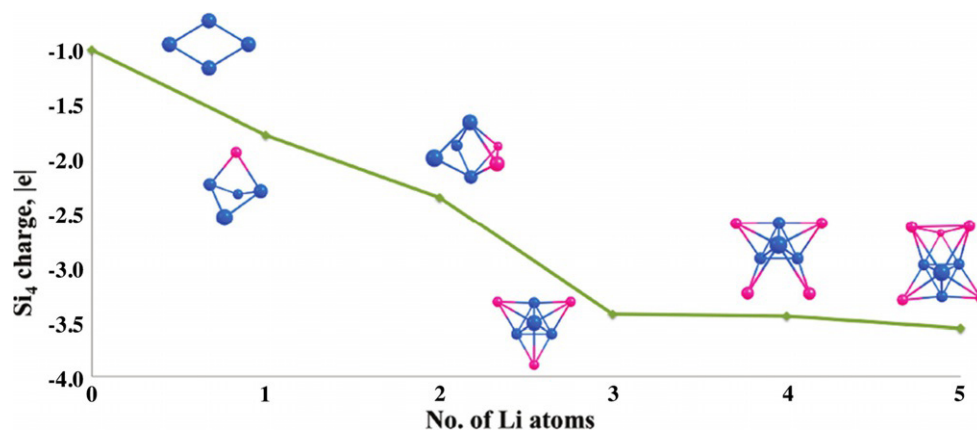


Fig. 2.7: Structural evolution and charge on the Si₄ moiety with increasing number of Li atoms in the Li_nSi₄⁻ series (n=0–5).

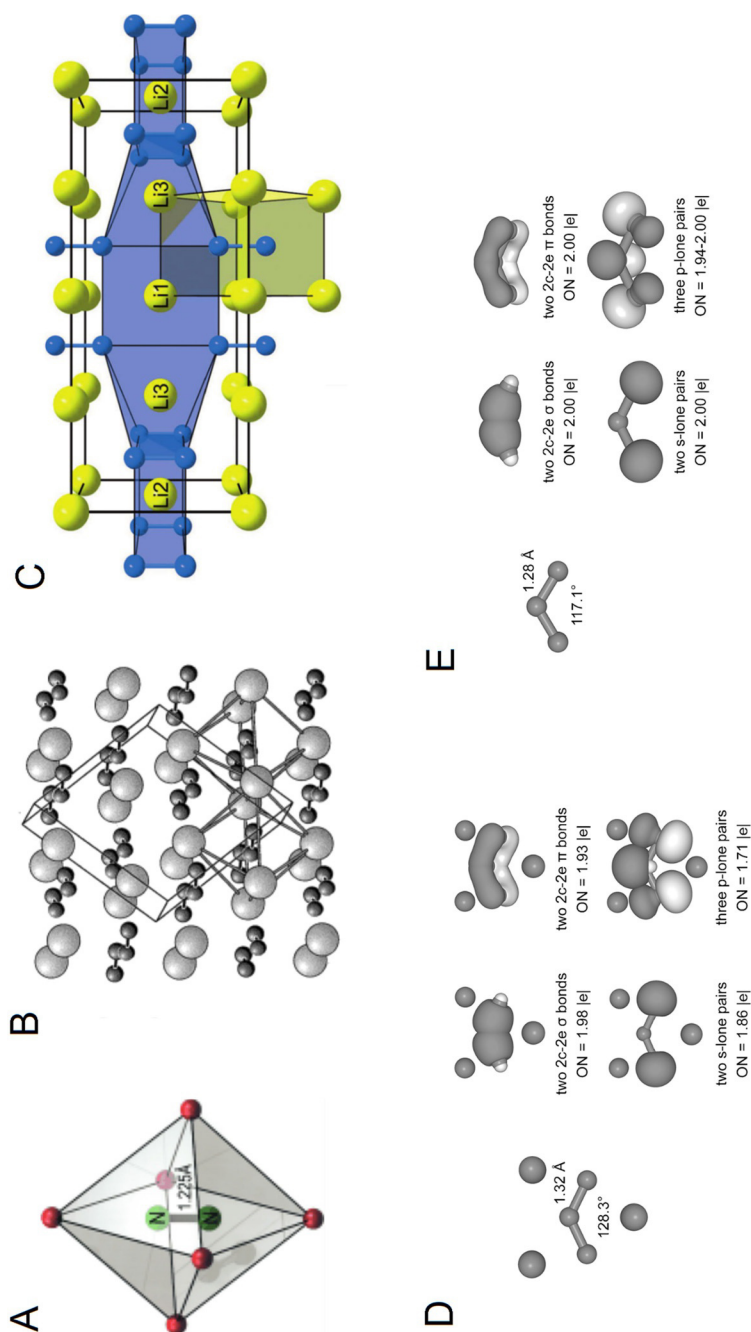


Fig. 2.8: Crystal structures of SrN_2 (A, Sr in red, N in green), BaN_2 (B, Ba in grey, N in black), and Li_2N_2 (C, Li in yellow, N in blue), as well as the chemical bonding of Li_3N_3 (D) and O_3 (E) revealed by the AdNDP analysis.

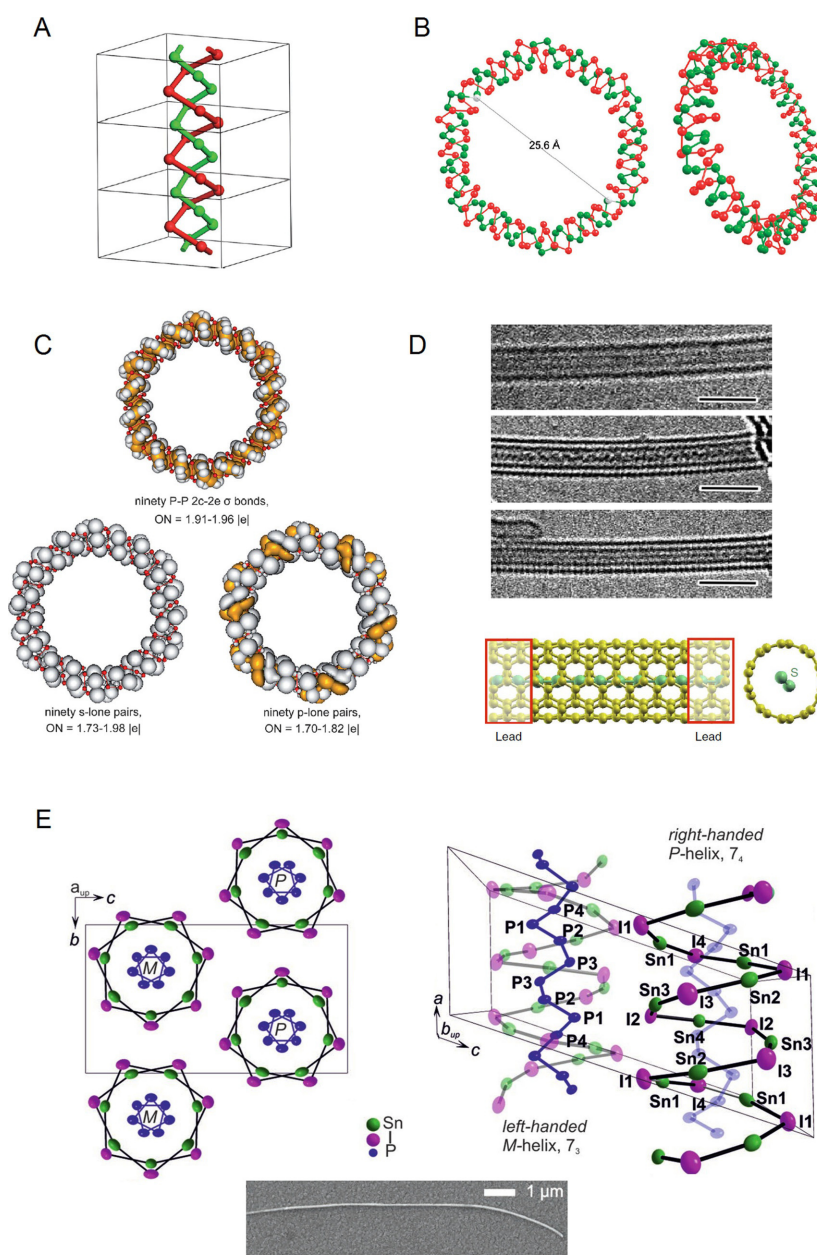


Fig. 2.9: Periodic repetitions of the LiP infinite double-helix chain geometry (A, P in green, Li in red), optimized Li₉₀P₉₀ double-helical toroid structure with internal diameter of 25.6 Å (B, P in green, Li in red), chemical bonding pattern of Li₉₀P₉₀ shown by the AdNDP analysis (C), the high resolution transmission electron microscopy images and graphical representation of single-walled or double-walled carbon nanotubes encapsulated sulfur chains (D), and crystal structure sections projected along the *a* and *b* axis of SnIP, as well as the scanning electron microscopy (SEM) image of exfoliated SnIP (E).

CHAPTER 3

ON THE EXISTENCE OF DESIGNER Al=Al DOUBLE BOND IN THE $\text{LiAl}_2\text{H}_2^-$
CLUSTER VIA ELECTRONIC TRANSMUTATION¹**3.1 Abstract**

The Al=Al double bond is elusive in chemistry. Herein we report the results obtained via combined photoelectron spectroscopy and ab initio studies of the $\text{LiAl}_2\text{H}_4^-$ cluster that confirm the formation of a conventional Al=Al double bond. Comprehensive searches for the most stable structures of the $\text{LiAl}_2\text{H}_4^-$ cluster have shown that the global minimum isomer I possesses a geometric structure which resembles that of Si_2H_4 , demonstrating a successful example of the transmutation of Al atoms into Si atoms by electron donation. Theoretical simulations of the photoelectron spectrum discovered the coexistence of two isomers in the ion beam, including the one with the Al=Al double bond.

3.2 Introduction

Aluminum–hydrogen clusters are known to be stabilized by multicenter bonding [1–6]. Yet, it was recently shown that formation of conventional Al–Al bonds is possible in clusters [7,8] and in solid-state compounds [9,10]. Reports of double Al=Al and triple Al≡Al bonds are scarce [11–13,15–21]. Chesnut [21] performed topological study in di- and tetra-hydrides Al_2H_2 and Al_2H_4 molecules. Based on the ELF analysis, he concluded that in the trans-bent HAlAlH isomer (though not a global minimum structure), chemical bonding can be described as a resonance between a no-bond and double bond situation between two the aluminum atoms. In 1988 Uhl [15] synthesized the R_2AlAlR_2 ($\text{R}=\text{CH}(\text{SiMe}_3)_2$) compound containing an Al–Al bond. In the early 1990s it was shown that this compound could be

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reduced to $[\text{R}_2\text{AlAlR}_2]^-$ anions ($\text{R}=\text{CH}(\text{SiMe}_3)_2$ [16, 22] or $\text{C}_6\text{H}_2\text{-2,4,6-iPr}_3$) [17, 18], which had Al-Al bonds of formal order 1.5 owing to the occupation of a π -orbital by a single electron. In 2003, Power and coworkers [17] reported the [2+4] Diels–Alder cycloaddition product of a probable dialuminene, $\text{Ar}'\text{AlAlAr}'$ ($\text{Ar}'=\text{C}_6\text{H}_3\text{-2,6-Dipp}_2$; $\text{Dipp}=\text{C}_6\text{H}_3\text{-2,6-iPr}_2$), with toluene. However, the dialuminene was not isolated. Three years later, Power [20] synthesized and characterized a stable $\text{Na}_2[\text{Ar}'\text{AlAlAr}']$ compound with the Al-Al bond order of 1.13. Very recently, Inoue and co-workers reported an Al=Al containing compound stabilized by the N-heterocyclic carbene ligands [23]. The utilization of electron-donating, bulky ligands forced the s and p valence electrons of Al to hybridize and form homodinuclear multiple bonds to fulfill the octet rule, which is in a similar way that the $\text{B}\equiv\text{B}$ triple bonds were synthesized by Zhou [24] and Braunschweig [25].

Our strategy for designing an Al=Al double bond is different. Herein we adopt the electronic transmutation method that was developed by our group [26]; briefly, when an atom acquires an extra electron, it starts to behave as the isoelectronic, neighboring element. We have discovered many examples that such approach indeed works [7, 8, 26–31]. Based on this, it could be anticipated that by adding one electron to each Al atom in the H_2AlAlH_2 molecule, Al might be transmuted into Si, yielding a molecule that is isoelectronic to the $\text{H}_2\text{Si}=\text{SiH}_2$ molecule. The doubly charged $\text{H}_2\text{AlAlH}_2^{2-}$ anion is not expected to be stable in the isolated state owing to the Coulomb repulsion between the two excess electrons. Indeed a crude evaluation shows that the $\text{Al}_2\text{H}_4^{2-}$ dianion is not stable owing to electron autodetachment (vertical electron detachment energy is -3.1 eV). To stabilize this dianion we counter the $\text{Al}_2\text{H}_4^{2-}$ dianion with the Li^+ cation. The final $\text{LiAl}_2\text{H}_4^-$ anion is expected to be stable due to the electrostatic stabilization from the Li^+ cation.

3.3 Experimental Details

The photoelectron spectrum of $\text{LiAl}_2\text{H}_4^-$ taken with a 3.49 eV (355 nm) laser is presented in Figure 3.1. Details of the experiment and the apparatus are given in the Supporting Information. The spectrum has an electron binding energy (EBE) band starting from about 1.0 eV and peaks at 1.30 eV. In case of a sufficient Franck–Condon overlap between

the ground state of the anion and the ground state of the neutral species, and given there is not much hot band signal, the threshold of the first EBE band (ca. 1.0 eV) should be the electron affinity (EA). The first experimental vertical detachment energy (VDE) is the photodetachment transition at which the Franck–Condon overlap between the wavefunctions of the anion and its neutral counterpart is maximal, corresponding to the peak position, 1.30 eV. The width of the band suggests an appreciable geometry change between the ground state of $\text{LiAl}_2\text{H}_4^-$ and that of its neutral.

3.4 Methods of Calculation

To find the experimentally observed structure, we initially performed an unbiased search (10000 trial structures) for the singlet configuration of the $\text{LiAl}_2\text{H}_4^-$ stoichiometry using the coalescence-kick method [32] with the Gaussian09 program [33] at the PBE0 [34]/3-21G [35] level of theory. Afterwards, the lowest-lying isomers ($\Delta E \leq 20 \text{ kcal mol}^{-1}$) were recalculated at the more expensive PBE0/6-311++G** level of theory [36] with geometry optimization and frequency analysis to ensure that each structure was a minimum on the potential energy surface. Single-point couple cluster calculations (CCSD(T) [37]/ 6-311+G** and CCSD(T)/aug-cc-pVTZ [38, 39]) at the DFT optimized geometry were subsequently performed to give more precise relative energies. VDEs of the lowest isomers were calculated as the energy difference between the ground states of the anions and different states of the neutral counterparts at the same geometry of the anions using three different levels of theory: TD-DFT [40], OVGF [41, 42], and CCSD(T), and compared with experimental results. The chemical bonding analysis of the two lowest isomers, isomers I and II, via Adaptive Natural Density Partitioning (AdNDP) [43] method at the PBE0/6-311++G** level of theory is also presented. Chemcraft v1.8 (build 165) [44] was used for structural and molecular orbital visualization.

3.5 Results and Discussion

The lowest ten isomers found at PBE/6-311++G** and CCSD(T)/aug-cc-pVTZ level of the $\text{LiAl}_2\text{H}_4^-$ stoichiometry are presented in Figure 3.2. The 3D coordinates of all of these

structures are provided in the Supporting Information. As designed, the global minimum structure I is similar to the Si_2H_4 structure. Because of an imaginary frequency, the planar C_{2v} ($^1\text{A}_1$) structure is not a minimum. Geometry optimization following this imaginary frequency mode leads to a slightly non-planar structure C_2 (^1A) symmetry with hydrogen atoms lying above and below the Al-Li-Al plane by 0.27 and 0.35 Å. However, the barrier for planarization is very small ($0.01 \text{ kcal mol}^{-1}$) and thus this structure is effectively planar if we include ZPE corrections. The similar distortion is known for the Si_2H_4 molecule. According to our calculations, the planar Si_2H_4 molecule is not a minimum at the planar D_{2h} symmetry and undergoes the pseudo Jahn–Teller distortion towards a trans-bent structure (see the Supporting Information for details). However, as in the case of $\text{LiAl}_2\text{H}_4^-$, the barrier for the planarization in Si_2H_4 is small ($0.14 \text{ kcal mol}^{-1}$ at PBE0/6–311++G**) and the vibrationally averaged structure is effectively planar. The optimal bond length between the two Al atoms in $\text{LiAl}_2\text{H}_4^-$ structure is 2.46 Å (PBE0/6–311++G**), which is shorter than the single Al-Al σ -bond (2.59 Å, PBE0/6–311++G**) in the H_2AlAlH_2 molecule and the single Al-Al σ -bond (2.55 Å) in the $\text{H}_3\text{AlAlH}_3^{2-}$ crystal structure [9,10]. The appreciably shorter Al-Al distance in structure I indicates that there could be a double bond between the two aluminum atoms.

Before further analysis of the chemical bonding, we need to confirm that the calculated VDEs agree with the experimentally observed values. Table 1 summarizes the calculated and experimental VDE data. First, calculated VDEs for both isomers I and II using three different methods are in a reasonable agreement among themselves. The first calculated VDE from HOMO 3b for the global minimum structure I is 1.27 eV (CCSD(T)), in excellent agreement with the experimentally observed 1.30 eV value (Figure 3.1, peak X, fitted by a red dotted line), confirming that the Si_2H_4 -like structure for $\text{LiAl}_2\text{H}_4^-$ was indeed observed in the ion beam. However, the experimental EBE intensity at around 1.8 eV (X', fitted by a blue dotted line) and the peak at 3.0 eV (X') do not agree with the other calculated VDE (HOMO-1, 3a) of isomer I. They might correspond to coexisting low-lying isomers, which is not uncommon for laser vaporization generated ion beams. According to the

calculations, the first VDE (HOMO 6a) of isomer II at 1.64 eV (CCSD(T)) is in reasonable agreement with the PES intensity at 1.8 eV (X'). The next experimental EBE band at 3.0 eV (X') is also in good agreement with the second VDE (HOMO-1, 5a) of isomer II at 3.19 eV (CCSD(T)). Thus, from the comparison of theoretical and experimental data, we can confirm that two isomers were experimentally observed in the ion beam. Since the third isomer was found to be very close in energy to isomer II, we performed VDE calculations for it as well (Supporting Information, Table S1). The two first VDEs have energies at 2.4–2.5 eV and there are no corresponding peaks in the experimental spectrum. Most importantly, our expectation of the Si_2H_4 -like $\text{LiAl}_2\text{H}_4^-$ isomer was indeed produced by experiment.

The next obvious question is whether the Al=Al double bond exist in the global minimum structure. To answer this question, we performed AdNDP analysis for the global minimum isomer I (Figure 3.3) and isomer II (Supporting Information, Figure S1). From Figure 3.3, two 2c–2e σ Al–H bonds (ON=2.00 |e|), two 3c–2e σ Li–H–Al bonds (ON= 1.97 |e|; these four bonds are analogous to the σ Si–H bonds in Si_2H_4), one σ 3c–2e Al–Li–Al bond (ON=1.99 |e|; an analogue of the s Si–Si bond in Si_2H_4), and one π Al–Li–Al bond (ON=2.00 |e|) (an analogue of the π Si–Si bond in Si_2H_4) can be observed. To claim the presence of the Al=Al double bond we need to evaluate how much the lithium atom contributes to the σ 3c–2e Al–Li–Al and π 3c–2e Al–Li–Al bonds. The AdNDP method allows us to view this bond as a 2c–2e bond. We found that the σ 3c–2e Al–Li–Al bond (ON=1.99 |e|) can be seen as one σ 2c–2e Al–Al bond (ON=1.87 |e|) and the π 3c–2e Al–Li–Al bond (ON=2.00 |e|) can be found as one π 2c–2e Al–Al bond (ON=1.65 |e|). That gives us the 1.76 bond order for Al=Al double bond in our cluster. Therefore, the global minimum isomer I does have an Al=Al double bond. This is further supported by each Al demonstrating an electronic transmutation of their natural charge from +0.7 in H_2AlAlH_2 to +0.0 in $\text{LiAl}_2\text{H}_4^-$ through the addition of one electron and one Li atom to the system (see the Supporting Information, Table S3 for full natural population analysis charges).

3.6 Summary

In summary, on the basis of the electronic transmutation model, we have designed and

observed a $\text{LiAl}_2\text{H}_4^-$ cluster with a global minimum that has a Si_2H_4 -like structure and an $\text{Al}=\text{Al}$ double bond. Photoelectron spectroscopy study and the comparison with the theory reveal that the $\text{LiAl}_2\text{H}_4^-$ ion beam consists of two isomers, including the calculated global minimum (isomer I) and the second low-lying isomer (isomer II). The AdNDP analysis indicates that the $\text{Al}=\text{Al}$ double bond of isomer I possesses one σ and one π bond. Our results provide the viability of the electronic transmutation strategy in designing Al-Al multiple bonds, and shed light on the future discovery of the $\text{Al}\equiv\text{Al}$ triple bond. Also, molecules with the $\text{Al}=\text{Al}$ double bonds are important for further synthesis of new unusual molecules through [2+2] or [2+4] reactions.

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Table 3.1: Calculated and experimental VDEs (eV) of isomers I and II of the $\text{LiAl}_2\text{H}_4^-$

Isomer I	$\text{VDE}_{EXPT.}$	$\text{VDE}_{TD-DFT}^{[a]}$	$\text{VDE}_{OVGF}^{[b]}$	$\text{VDE}_{CCSD(T)}^{[c]}$
HOMO (3b)	1.3	1.224	1.178	1.273
HOMO-1 (3a)	NA	3.685	4.059	3.852
HOMO-2 (2b)	NA	5.465	6.720	6.225
Isomer II	$\text{VDE}_{EXPT.}$	$\text{VDE}_{TD-DFT}^{[a]}$	$\text{VDE}_{OVGF}^{[b]}$	$\text{VDE}_{CCSD(T)}^{[c]}$
HOMO (6a)	1.8	1.615	1.632	1.649
HOMO-1 (5a)	3.0	3.3034	3.009	3.187

[a] TD-DFT/6-311++G**. [b] OVGF/aug-cc-pvTZ. [c] CCSD(T)/aug-cc-pvTZ

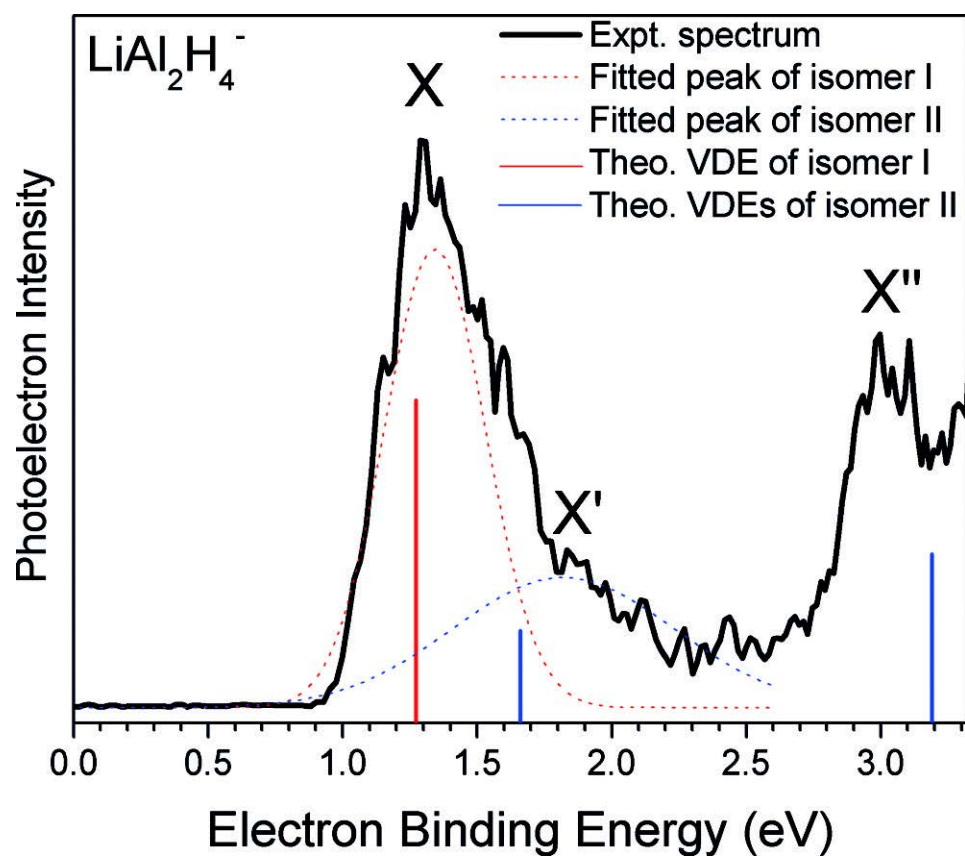


Fig. 3.1: Experimental photoelectron spectrum of $\text{LiAl}_2\text{H}_4^-$ using 355 nm laser (black line), Gaussian fitting of isomer I and II (red and blue dotted lines), and calculated stick spectra of isomer I and II (red and blue vertical lines).

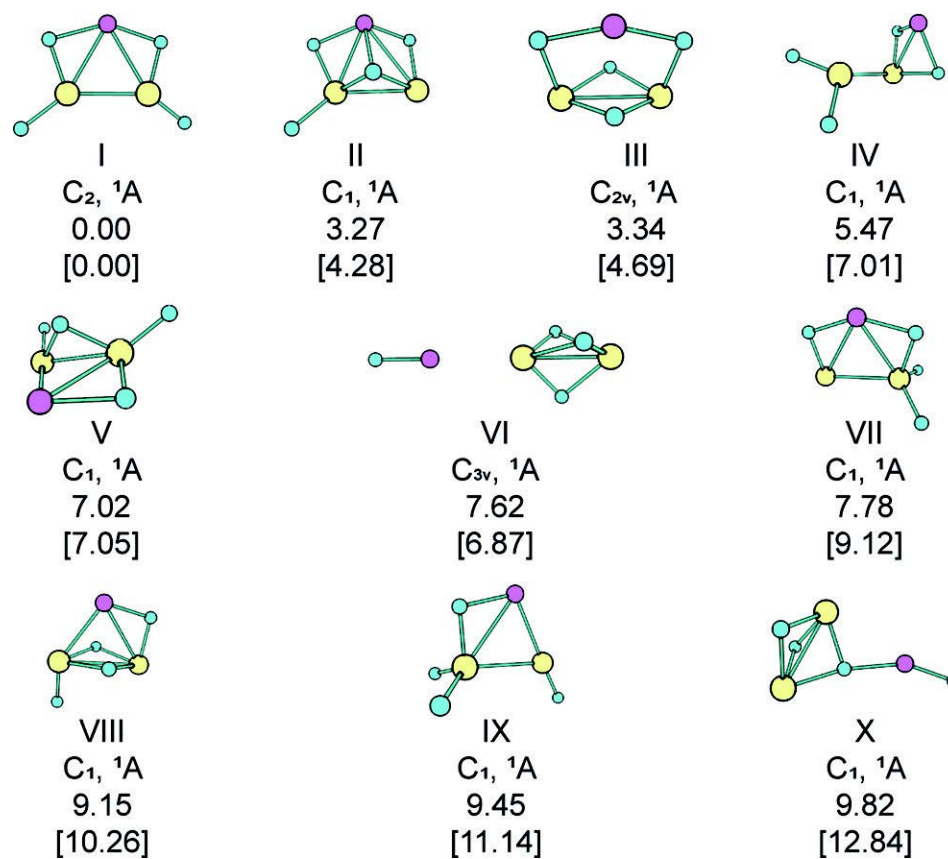


Fig. 3.2: Lowest energy isomers of $\text{LiAl}_2\text{H}_4^-$, their point group symmetries, ground electronic states, and ZPE corrected relative energies [kcal mol⁻¹] at the CCSD(T)/aug-cc-pVTZ (in parentheses) and PBE0/6-311+ +G** (in square brackets) levels of theory. The solid rods-between atoms help visualize and do not necessarily represent σ -bonds here and elsewhere. H blue, Al yellow, Li pink.

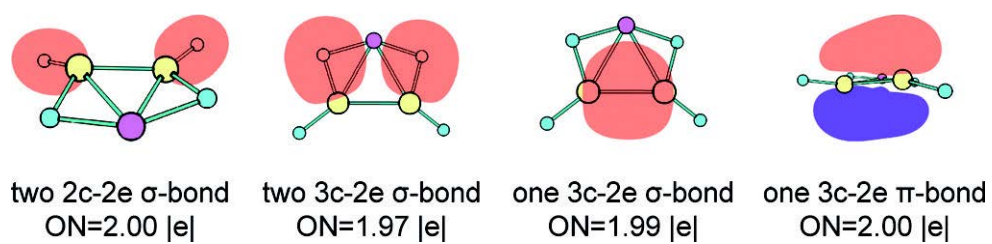


Fig. 3.3: Chemical bonds recovered by the AdNDP analysis for isomer I.

CHAPTER 4

 REALIZATION OF AN $\text{Al}\equiv\text{Al}$ TRIPLE BOND IN THE GAS-PHASE Na_3Al_2^-
 CLUSTER VIA DOUBLE ELECTRONIC TRANSMUTATION¹
4.1 Abstract

The discovery of homodinuclear multiple bonds composed of Group 13 elements represents one of the most challenging frontiers in modern chemistry. A classical triple bond such as $\text{N}\equiv\text{N}$ and $\text{HC}\equiv\text{CH}$ contains one σ bond and two π bonds constructed from the p orbitals perpendicular to the σ bond. However, the traditional textbook triple bond between two Al atoms has remained elusive. Here we report an $\text{Al}\equiv\text{Al}$ triple bond in the designer Na_3Al_2^- cluster predicted in silico, which was subsequently generated by pulsed arc discharge followed by mass spectrometry and photoelectron spectroscopy characterizations. Being effectively Al^{2-} due to the electron donation from Na, the Al atoms in Na_3Al_2^- undergo a double electronic transmutation into Group 15 elements, thus the $\text{Al}^{2-}\equiv\text{Al}^{2-}$ kernel mimics the $\text{P}\equiv\text{P}$ and $\text{N}\equiv\text{N}$ molecules. We anticipate this work will stimulate more endeavors in discovering materials using $\text{Al}^{2-}\equiv\text{Al}^{2-}$ as a building block in the gas phase and in the solid state.

4.2 Introduction

Other than the well-known dinitrogen ($\text{N}\equiv\text{N}$), diphosphorus ($\text{P}\equiv\text{P}$), and acetylene ($\text{HC}\equiv\text{CH}$) molecules, homodinuclear triple bonds composed of main-group elements are extremely scarce [1, 2], and the synthesis of such species imposes a great challenge to modern chemistry. The narrative of homodinuclear triple bonds composed of Group 13 elements started with Robinson and co-workers' synthesis of the famous digallyne molecule $\text{Na}_2[\text{ArGaGaAr}]$ ($\text{Ar}=\text{C}_6\text{H}_3\text{-2,6-}(\text{C}_6\text{H}_2\text{-2,4,6-iPr}_3)_2$) featuring the shortest Ga-Ga bond on

¹Xinxing Zhang, Ivan A. Popov, Haopeng Wang, Chaonan Mu, Wei Wang, Hansgeorg Schnöckel, Alexander I. Boldyrev, Kit H. Bowen

record [3]. Even though the $[\text{ArGaGaAr}]^{2-}$ kernel is valence isoelectronic to acetylene, its X-ray crystallography reveals a trans-bent structure. The nature of the Ga-Ga bond in this digallyne has attracted considerable debate afterwards [4,5]. Cotton et al. offered an opposing opinion by density functional theory (DFT) calculations that the Ga-Ga bond had a π -type nonbonding orbital, and the short bond length was a result of the $\text{Ar-Na}^+-\text{Ar}$ attractions [6]. Power and co-workers provided similar arguments that the bonding in $[\text{RGaGaR}]^{2-}$ ions had considerable Lewis base character at the Ga centers where electron density was accumulated [7]. In a model system $[\text{PhGaGaPh}]^{2-}$, Frenking and co-workers pointed out that two of the three electron pairs of the Ga-Ga bond had partial lone-pair character, hence the calculated bond order had a value typical for single bonds [8]. Grunenberg and Goldberg pointed to the mechano-chemical weakness of this bond by calculating relaxed force constants (FCs) [9]. According to their calculations of the inverted Hessian matrix, the Ga-Ga bond ($0.87 \text{ aJ } \text{\AA}^{-2}$) in a “gallyne” model compound $\text{Ga}_2\text{H}_2\text{Na}_2$ was found to be weaker than the Ga-Ga double bond ($1.20 \text{ aJ } \text{\AA}^{-2}$) in $\text{Ga}_2\text{H}_4\text{Na}_2$. However, according to Schaefer, Schleyer, Robinson and co-workers’ calculations [10], the $\text{Ga}\equiv\text{Ga}$ triple bond was composed of two dative bonds and one π bond, thus constituting a non-classical but genuine triple bond. Using a simplified model $[\text{Ga}_2\text{H}_2]^{2-}$, Klinkhammer [11] supported the existence of the $\text{Ga}\equiv\text{Ga}$ triple bond, which was claimed to be a combination of a σ bond, a π bond, and a nonclassical “slipped” π bond. These studies in this phenomenal “digallyne debate” have been significant contributions to Group 13 chemistry. However, due to the trans-bent nature, the Ga-Ga bonding situation of these compounds does not correspond to the classical triple bond that is composed of one σ bond and two π bonds constructed from the p orbitals perpendicular to the σ bond, such as that in the linear $\text{HC}\equiv\text{CH}$.

The discovery of the $\text{B}\equiv\text{B}$ triple bond has more fruitful results, which starts from the isolation of the $\text{OC}\rightarrow\text{B}\equiv\text{B}\leftarrow\text{CO}$ molecule in an argon matrix at 8 K by Zhou et al. [12], followed by a plethora of theoretical and experimental studies of the B_2 molecule stabilized by diatomic Lewis bases such as CO, CS, N_2 , NHC (N-heterocyclic carbene), BO^- [13–17], Braunschweig et al. synthesized the unprecedented $\text{NHC}\rightarrow\text{B}\equiv\text{B}\leftarrow\text{NHC}$ crystal featured the

first ambient-temperature isolable diboryne [18]. Köppe and Schnöckel questioned this triple bond based on electronic interactions between the B-B bond and the two B-(NHC) bonds [19]. However, later Grunenberg’s [20] and Frenking’s calculations [20], Braunschweig’s Raman [20] and NMR [21] spectroscopic measurements as well as chemical reactions [21] supported the existence of the $B\equiv B$ triple bond in $NHC\rightarrow B\equiv B\leftarrow NHC$.

The search for multiple Al-Al bonds has proceeded in a step-by-step manner. In 1988, Uhl [22] synthesized the R_2AlAlR_2 ($R=CH(SiMe_3)_2$) compound containing an Al-Al single bond. In the early 1990s, it was shown that this compound could be reduced to $[R_2AlAlR_2]^-$ anions with an increased formal bond order of 1.5 [23–26]. Recently, Inoue and co-workers [27] reported the synthesis of a dialumene compound $RR'AlAlRR'$ ($R=tBu_2MeSi$, $R'=NHC$) stabilized by N-heterocyclic carbenes, featuring a double $Al=Al$ bond. Immediately after Inoue’s work, the $LiAl_2H_4^-$ cluster [28] produced in an ion beam was also found to exhibit an $Al=Al$ double bond, with an $Al_2H_4^{2-}$ kernel mimicking the isoelectronic Si_2H_4 molecule. In 2006, Power [29] synthesized and characterized a stable $Na_2[Ar'AlAlAr']$ ($Ar'=C_6H_3-2,6-(C_6H_2-2,4,6-iPr_3)_2$) compound named dialuminyne, which was similar to digallyne [3] and featured a trans-bent structure, where the Al-Al triple bond was described to contain a slipped π bond.

In view of the above discussions, we aim to design a ligandless $Al\equiv Al$ triple bond that is similar to $N\equiv N$ and $P\equiv P$, so that it can rule out the possibilities of resonance structures, trans-bent geometry, and any non-classical bonding interactions such as the slipped π bond. Hence, we used the concept of double electronic transmutation (DET), which depicts the process that by acquiring two extra electrons, an element with the atomic number Z begins to have properties that were known to only belong to the element with the atomic number $Z+2$. Based on DET, $Al^{2-}\equiv Al^{2-}$ should be similar to $P\equiv P$. Being a stricter and narrower notion of the widely used valence-isoelectronic principle, single electronic transmutation (SET) has been successfully applied for predicting structures of various compounds as reviewed elsewhere [30], including those with single [30] and double [28] Al-Al bonds. However, no compounds have been reported so far based on the DET

concept.

To experimentally examine the $\text{Al}^{2-}\equiv\text{Al}^{2-}$ prototype, we designed a Na_3Al_2^- cluster in the hope that each Na atom could function as an electron donor, and the fourth electron is in the form of a negative charge. Na-Al clusters of various stoichiometries were generated with a pulsed arc cluster ionization source (PACIS) [31] in the gas phase by discharging an Al/Na mixture target with about 1500 A, 180 V, 20 μs pulsed arc. Experimental details are provided in the Supporting Information. The resulting mass spectrum is presented in Figure 1A, where $\text{Na}_x\text{Al}_{5-x}$ ($x=0-4$), NaAl_3O^- and Al_4O^- cluster anions are observed. Oxygen atoms are from the natural oxidation of sodium. Na_3Al_2^- is a magic number species with a reproducibly intense mass peak among its neighboring clusters, indicating an unusually high stability. Indeed, if the Al-Al core is successfully “transmuted” into $\text{P}\equiv\text{P}$, the Na_3Al_2^- cluster might well be very stable due to the closed-shell configuration and the triple $\text{Al}^{2-}\equiv\text{Al}^{2-}$ bond.

The bonding situation of Na_3Al_2^- can be better interpreted by photoelectron spectroscopy, a direct means to investigate the electronic structures of the occupied molecular orbitals (MOs). In Figure 1B, several electron binding energy (EBE) peaks at 0.89, 1.84 and 2.25 eV are assigned as the vertical detachment energies (VDE). If Na_3Al_2^- is a transmuted version of $\text{P}\equiv\text{P}$, these three peaks should correspond to the photoelectrons detached from the three frontier orbitals, these being one s bonding orbital and two p bonding orbitals, which is a direct observation of the $\text{Al}\equiv\text{Al}$ triple bond.

Isolated and well-defined gas-phase systems are ideally suited for simulations employing state-of-the-art quantum theoretical methods. The unmatched high complementarity and comparability of experiment and theory in the case of gas-phase investigations bear an enormous potential for modeling challenging tasks such as global minimum (GM) search and chemical bonding analysis. To find the most thermodynamically stable structure of Na_3Al_2^- , we employed an unbiased search for the GM on the potential energy surface, which was expected to be the main contributor to the photoelectron spectrum. Using the Coalescence Kick (CK) program, 10000 trial structures (in singlet and triplet states) underwent geometry

optimizations at PBE0/6-311+G*, subsequently the lowest structures were recalculated at higher levels of theory (CCSD(T)/6-311+G* and CCSD-(T)/aug-cc-pVTZ//CCSD(T)/6-311+G*), and further ranked according to their relative energies (Figure S1 and Table S1 in the Supporting Information). The GM structure of Na_3Al_2^- (C_{2v} , 1A_1) exhibits a direct Al-Al contact of 2.49 Å (CCSD-(T)/6-311+G*) with three surrounding Na atoms, which define a plane passing through the center of the Al_2 core. The slight deviation from the perfect D_{3h} symmetry is stipulated by the pseudo-Jahn-Teller effect, which lowers the symmetry to C_{2v} (origin of the pseudo-Jahn-Teller distortion is presented in the Supporting Information). To verify that the GM structure of Na_3Al_2^- describes the photoelectron spectrum, VDEs were computed at three levels of theory (DFT, OVGF, and CCSD(T)). As shown in Table 1, the first three VDEs unambiguously coincide with the experimental VDEs, thus confirming the computationally predicted GM structure.

The GM of the neutral Na_4Al_2 cluster (other isomers and their Cartesian coordinates are provided in Figure S2 and Table S2), which has four Na atoms positioned around the Al_2 core in the D_{4h} manner, also possesses a quite short Al-Al bond length of 2.45 Å. Being isoelectronic, both clusters are expected to form a triple $\text{Al}^{2-}\equiv\text{Al}^{2-}$ bond, which might be the shortest for dialuminum-containing species. However, they are comparable to the Al=Al double bond $\text{LiAl}_2\text{H}_4^-$ (2.46 Å) [28], and somewhat longer than that of the ditertbutyl(methyl)silyl-substituted dialumene (2.39 Å) [27]. We opine that it is because Al atoms carry large negative charges, which repulse each other. Other than the Al-Al distances, the Al-Al force constants $\text{FC}(\text{Al-Al})$ reflect a better measure of the bond order. According to our calculations at the PBE0/Def2-SVP level of theory employing normal coordinates within Gaussian 09 program, $\text{FC}(\text{Al-Al})$ of Na_4Al_2 is 2.30 mDyneÅ⁻¹, and $\text{FC}(\text{Al-Al})$ of Na_3Al_2^- is 2.02 mDyneÅ⁻¹. These values are in excellent agreement with the coupled cluster values at CCSD(T)/6-311+G*, that is, 2.41 mDyneÅ⁻¹ and 2.00 mDyneÅ⁻¹. Corresponding DFT values for the bulkier $\text{R}_2\text{Al-AlR}_2$ ($\text{R}=\text{CH}(\text{SiMe}_3)_2$) [22] and $\text{RR}'\text{Al}=\text{AlRR}'$ ($\text{R}=\text{tBu}_2\text{MeSi}$, $\text{R}'=\text{NHC}$) [27] complexes, for which single and double Al-Al bonds have been reported, are found to be 0.68 mDyneÅ⁻¹ and 1.00 mDyneÅ⁻¹, respectively, thus

supporting our interpretation of the $\text{Al}\equiv\text{Al}$ triple bond in Na_3Al_2^- and Na_4Al_2 . This argument is further confirmed by the relation of $\text{FC}(\text{P-P})$ of molecules with single, double and triple P-P bonds: 1.9:3.4:5.5 $\text{mDyne}\text{\AA}^{-1}$ [32]. All these data are in accordance with the magic status of Na_3Al_2^- in the mass spectrum (Figure 1A). Contrary to the “real space” FCs, which are not invariant to the choice of the used coordinate system, relaxed FCs (compliance constants) were previously shown to provide a better measurement of the interaction strength between two atoms [9,33]. To get more insight into the Al–Al interaction in the Na_3Al_2^- and Na_4Al_2 clusters, we calculated the relaxed $\text{FC}(\text{Al-Al})$ values using the compliance 3.0.2 program [34] at the PBE0/Def2-SVP level of theory for Na_3Al_2^- , Na_4Al_2 , $\text{R}_2\text{Al-AlR}_2$ ($\text{R}=\text{CH}(\text{SiMe}_3)_2$) [22], $\text{RR}'\text{Al=AlRR}'$ ($\text{R}=\text{tBu}_2\text{MeSi}$, $\text{R}'=\text{NHC}$) [27] systems as well as for some other prototypical model clusters where single ($\text{Al}_2\text{H}_6^{2-}$), double ($\text{Al}_2\text{H}_4\text{Na}_2$), and triple ($\text{Al}_2\text{H}_2\text{Na}_2$) Al-Al bonds are expected, in accordance with previous considerations of the corresponding Ga counterparts [9]. The relaxed $\text{FC}(\text{Al-Al})$ values (in $\text{mDyne}\text{\AA}^{-1}$) of Na_3Al_2^- (0.95) and Na_4Al_2 (1.08) are higher than those of the single-bonded $\text{Al}_2\text{H}_6^{2-}$ (0.61) and $\text{R}_2\text{Al-AlR}_2$ (0.80) systems, as well as of the triple-bonded $\text{Al}_2\text{H}_2\text{Na}_2$ (0.79), and are comparable to that of the double bonded $\text{Al}_2\text{H}_4\text{Na}_2$ (1.03). Similarly to the case of model “gallyne” $\text{Ga}_2\text{H}_2\text{Na}_2$ cluster [9], the triple bond in $\text{Al}_2\text{H}_2\text{Na}_2$ is found to be weaker than in its double-bonded counterpart $\text{Al}_2\text{H}_4\text{Na}_2$. However, the relaxed FCs of Na_3Al_2^- and Na_4Al_2 are lower than that of the $\text{RR}'\text{Al=AlRR}'$ molecule (1.43).

Apparently, somewhat larger relaxed FC values of the species in solid state ($\text{R}_2\text{Al-AlR}_2$ [22] and $\text{RR}'\text{Al=AlRR}'$ [27] in comparison to the corresponding model clusters ($\text{Al}_2\text{H}_6^{2-}$ and $\text{Al}_2\text{H}_4\text{Na}_2$) are associated with the presence of the bulky stabilizing ligands, which help increase the Al-Al bond strength. Hence, comparison of these numbers should be made with caution.

To further investigate the $\text{Al}\equiv\text{Al}$ triple bond, we perform the Adaptive Natural Density Partitioning (AdNDP) analysis [35] of chemical bonding in P_2 , Na_3Al_2^- and Na_4Al_2 at the $\omega\text{B97XD/Def2-TZVP}$ level of theory (Figure 2). In both Na_3Al_2^- and Na_4Al_2 , the bonding pattern is similar to P_2 , though Na atoms contribute to the lone pair (LP) on each Al atom

as well as to the σ - and π -bonds. According to AdNDP, there are two s-type lone pairs on the two Al atoms (one on each) with occupation numbers (ONs) equal to 1.64 |e| in Na_3Al_2^- and 1.63 |e| in Na_4Al_2 . The Al-Al σ -bond is found as a pure two-center two-electron (2c-2e) σ -bond with ON=1.85 |e| in Na_3Al_2^- and 1.97 |e| in Na_4Al_2 . The two 2c-2e π bonds have somewhat lower ON values: 1.30 |e|, 1.51 |e| in Na_3Al_2^- , and 1.60 |e|, 1.60 |e| in Na_4Al_2 . It is noted that the deviation of the ON values of the π -bonds from the ideal value of 2.00 |e| is in agreement with the relaxed FC(Al-Al) values for Na_3Al_2^- and Na_4Al_2 , which are comparable to that of the $\text{Al}_2\text{H}_4\text{Na}_2$ cluster exhibiting Al=Al double bond. The analogous bonds in P_2 have ON values close to 2.00 |e| (Figure 2A). Indeed, the remaining electron density in Na_3Al_2^- and Na_4Al_2 is found on the Na atoms. Inclusion of the Na atoms into the bond search produces multicenter bonds with ON=2.00 |e|, thus allowing to assess the contribution of Na atoms (Figure 2B,C).

4.3 Summary

In summary, we have applied the DET concept to design two clusters, Na_3Al_2^- and Na_4Al_2 , which are found to possess classical Al \equiv Al triple bonds, although with somewhat low ON values of the direct Al-Al π bonds. Excellent agreement between the experimental and calculated VDEs for the most stable isomer of Na_3Al_2^- confirms the proposed structure. Presence of the triple bond in Na_3Al_2^- is also supported by its reproducibly intense mass peak among the neighboring clusters, which indicates an unusually high stability. Similarity of the canonical MOs of the P \equiv P molecule with Na_3Al_2^- and Na_4Al_2 , along with the AdNDP results, further confirm that Na atoms can “transmutate” Al into P, and therefore, aid in the formation of the Al \equiv Al triple bonds. The $\text{Al}^{2-}\equiv\text{Al}^{2-}$ core may serve as a building block in other gas-phase clusters, and it also holds potential to be realized in periodically extended solid-state compounds. Similarly, the valence-isoelectronic triple bonded C_2^{2-} already functions as a building block of a large family of carbide compounds [36]. Furthermore, highly charged species of the heavier homologs of Al, such as the Tl_4^{8-} and In_4^{8-} cluster anions, represent more examples of experimentally observed building blocks, which are stabilized as solid-state Zintl phases via strong Coulomb interactions with Na^+ [37]. Hence, this

work will not only serve as a general guideline for predicting novel DET clusters, but also stimulate synthesis of the unprecedented chemical solids featuring $\text{Al}^{2-}\equiv\text{Al}^{2-}$ triple bonds.

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Table 4.1: Experimental and Calculated VDEs (eV) for global minimum of Na_3Al_2^- at three levels of theory.^[a]

MO	VDE			
	EXPT.	OVGF	TDB3LYP	CCSD(T)
HOMO (3a_1)	0.89	0.82	0.67	0.87
HOMO-1 (2a_1)	1.84	1.74	1.50	_[b]
HOMO-2 (1b_1)	2.25	2.23	2.54	_[b]

[a] aug-cc-pVTZ basis set was employed for all three methods. [b] This VDE could not be obtained at this level of theory.

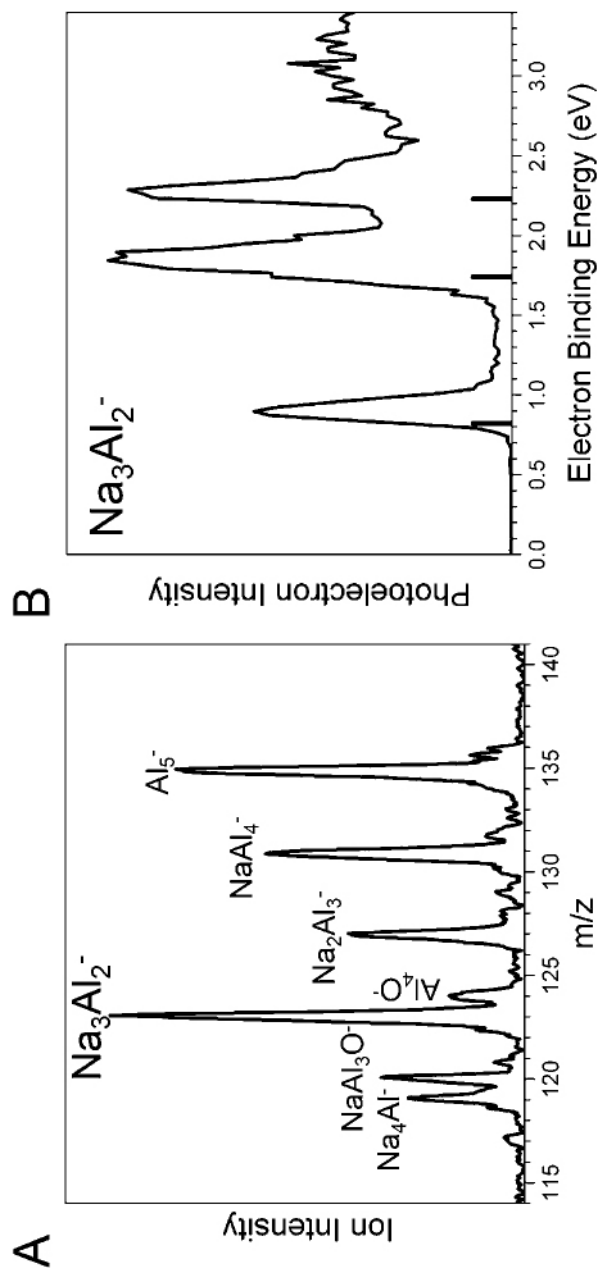


Fig. 4.1: The mass spectrum containing Na_3Al_2^- as the highest peak (A) and the anion photoelectron spectrum of Na_3Al_2^- taken with 355 nm photons. The vertical bars denote the calculated VDEs from the OVGF calculations (B).

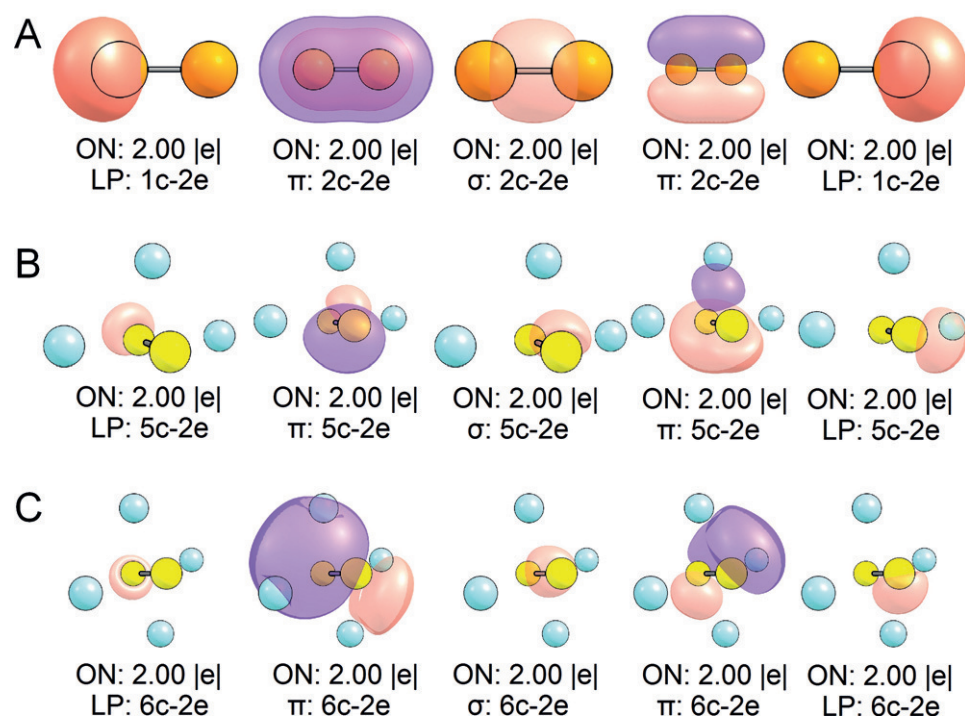


Fig. 4.2: Summary of the AdNDP analysis of the P_2 (A), $Na_3Al_2^-$ (B) and Na_4Al_2 (C) clusters.

CHAPTER 5

TUG-OF-WAR BETWEEN CLASSICAL AND MULTICENTERED BONDS IN H-(Be)_n-H SPECIES

5.1 Abstract

Quantum chemical calculations were performed for beryllium homocatenated compounds [H-(Be)_n-H]. Global minimum structures were found using machine searches (Coalescence Kick method) with density functional theory. Chemical bonding analysis was performed with the Adaptive Natural Density Partitioning method. It was found that H-(Be)_n-H and H-(Be)₃-H clusters are linear with classical two-center two-electron bonds, while for $n > 3$, three-dimensional structures are more stable with multicenter bonding. Thus, at $n = 4$, multicenter bonding wins the tug-of-war vs. classical bonding.

5.2 Introduction

The capacity of an atom to form bonds with itself producing chain-like structures is called homocatenation. The most notable element that fits this description is carbon with its ability to form extended C_nH_{2n+2} chains. For example, the current record for the longest continuous C_nH_{2n+2} chain belongs to the 390 carbon [CH₃(CH₂)₃₈₈CH₃], so called, super-long alkane [1]. The other group XIV congeners are also able to form similar chains, although not to the same extent as carbon due to lower dissociation energy of the M-M bonds, where M is an arbitrary atom designation. Additional accounts of homocatenation beyond group XIV are as follows: Wörle and Nesper demonstrated the existence of pure-phase LiB_x samples (with the approximate range $0.82 < x < 1.0$) possessing chains of boron atoms surrounded by a lithium shell which illustrates the structural analogy between borynide chains in LiB_x and isoelectronic polyyne and polycumulene chains [2]. Fahlquist et al. have shown the viability of this concept for gallium containing species: a hydroge-

nous Zintl-phase $\text{Cs}_{10}\text{H}[\text{Ga}_3\text{H}_8]_3$ featuring the propane-like polyanions [3] $[\text{Ga}_3\text{H}_8]^{3-}$ and $(\text{K}_x\text{Rb}_{1-x})_n[\text{GaH}_2]_n$ ($0 \leq x \leq 1$) composed of $[\text{GaH}_2]_n^{n-}$ anionic chains with a polyethylene structure [4, 5]. Additionally, six indium atoms were previously found to arrange into one line upon treatment of indium(I) iodide with a protonated N-xylyl b-diketiminate and a strong potassium base in tetrahydrofuran [6]. Further examples of the main-group homocatenated compounds are reported elsewhere [7–13].

With numerous accounts of homocatenation present in transition metals, metalloids and nonmetals [7–13], it can be thought that alkaline earth elements of group II could also form long $\text{H}-(\text{M})_n\text{-H}$ chains since such species can be predicted using classical chemical bonding. Indeed, those elements may form M-M two-center two-electron (2c-2e) σ -bonds through the *sp* hybridization of the M atom. One molecule from this series, H-Be-Be-H , has been experimentally observed under the matrix isolation condition [14]. In principle, additional Be atoms could be inserted into this chain under the assumption that classical bonding in these chains will insure that the linear molecules are minima. Based on this assumption, this study will explore the possibility of homocatenation in beryllium chains.

5.3 Methods of Calculations

The search for global minimum structures of the $\text{H}-(\text{Be})_n\text{-H}$ ($n = 2\text{--}5$) molecules was performed by an unbiased Coalescence Kick method [15] through the generation of 2500–10,000 trial structures. Initial geometry optimization for all structures was conducted at the PBE0/3-21G [16, 17] level of theory, via the Gaussian 09 program [18]. The lowest energy isomers ($\Delta E \leq 20$ kcal/mol) were reoptimized and frequencies were calculated at PBE0/6-311++g(d,p) [16, 19] and CCSD(T)/6-311++G(d,p) [19, 20]. Single point calculations were performed using CASSCF/6-311++G(d,p)//CCSD(T)/6-311++G(d,p) [19–21] and CCSD(T)/aug-cc-pVTZ//CCSD(T)/6-311++G(d,p) [19–23] levels of theory. Chemical bonding analysis was implemented using the Adaptive Natural Density Partitioning (AdNDP) method [24]. Chemcraft 1.8 [25] was used for visualization of bonds and molecular structure.

5.4 Results and Discussion

The global minimum structures of $\text{H}-(\text{Be})_2\text{-H}$, $\text{H}-(\text{Be})_3\text{-H}$ and $\text{H}-(\text{Be})_4\text{-H}$, here in reported as H_2Be_2 , H_2Be_3 , and H_2Be_4 , respectively, from this study are shown in Fig. 5.1. The second lowest-lying for H_2Be_2 , H_2Be_3 and the linear isomer for H_2Be_4 are also illustrated in Fig. 5.1.

The relative energies reported in this article are at the CCSD(T)/aug-cc-pVTZ//CCSD(T)/6-311++G(d,p) level of theory unless otherwise specified. Additionally, CASPT2/6-311++G(d,p)//CCSD(T)/6-311 + G(d,p) calculations were performed for all isomers discussed above to test the wave functions for multi-configurational character since it is known that beryllium has a quasi-degenerate 2s- and 2p-AOs. In all cases, the coefficient of the leading Hartree-Fock determinant in the CASSCF expansions were always above 0.9. Norm(A) was also evaluated in coupled cluster calculations and found to always be less than 1.21, which provided another indication that the CCSD(T) calculations were reliable. Thus, supporting the validity of the statements about H_2Be_2 , H_2Be_3 and H_2Be_4 in the following paragraphs.

The global minimum search for H_2Be_2 revealed that the linear isomer (Fig. 5.1, I) was the lowest energy isomer with the next isomer (Fig. 5.1, IV) in the series being 30.2 kcal/mol. It was determined for the H_2Be_3 stoichiometry that the linear isomer (Fig. 5.1, II) was also the global minimum structure and the subsequent isomer (Fig. 5.1, V) was 33.3 kcal/mol higher in energy. Evaluation of the H_2Be_4 stoichiometry revealed that the linear isomer (Fig. 5.1, III) was no longer the lowest energy isomer. In fact, the linear isomer was now fifth in the series, with a relative energy equal to 23.3 kcal/mol, and the global minimum structure instead a three-dimensional isomer with two hydrogen atoms coordinated to the opposite sides of the distorted tetrahedron (Fig. 5.1, VI). This data suggests that homocatenation stops at $n = 4$ for the linear $\text{H-Be}_n\text{-H}$ structures. A global minimum search for the H_2Be_5 stoichiometry was performed at the PBE0/6-311++G(d,p) level of theory to support this conclusion, and it was determined that three-dimensional structure is the global minimum with the linear $\text{H-Be}_5\text{-H}$ isomer now 41.2 kcal/mol higher

in energy. The findings support that homocatenation does stop at $n = 4$ for the linear $\text{H}(\text{Be})_n\text{-H}$ structures. Thus, higher levels of calculations were not performed for the $\text{H}(\text{Be})_5\text{-H}$ isomer since this study was only interested in finding the transition from linear to three-dimensional isomer in the $\text{H}(\text{Be})_n\text{-H}$ series.

Evaluation of why the linear structures failed to remain the global minimum for the $\text{H}(\text{Be})_n\text{-H}$ series ($n = 2\text{--}4$) was conducted by AdNDP analysis. It was determined that the linear H_2Be_2 structure I (Fig. 5.1) exhibited classical 2c-2e σ -bonding for the two Be-H bonds and one Be-Be bond with occupation numbers (ON) greater than 1.9 |e| in all cases (Fig. 5.2a). Small deviation from the exact Lewis number 2.00 |e| occurs due to the localization scheme [24]. Our results for H_2Be_2 are similar to the classical Lewis structure model that contains exactly two electrons for every 2c-2e σ -bond (Be-H and Be-Be). Extension of the AdNDP analysis to H_2Be_2 isomer IV (Fig. 5.1) resulted in the finding of two Be-H 2c-2e σ -bonds and one Be-Be 2c-2e σ -bond (Fig. 5.2b).

Analysis of the chemical bonding found in linear structure II (Fig. 5.1) and second most stable isomer V (Fig. 5.1) of the H_2Be_3 stoichiometry revealed two 2c-2e Be-H and two Be-Be σ -bonds for the linear structure (Fig. 5.3a), which is similar to the H_2Be_2 stoichiometry. The second lowest isomer (Fig. 5.3b), however, only demonstrated three of its four bonds to follow the classical 2c-2e scheme ($\text{ON} = 1.98|\text{e}|$). The remaining bond was found to be multicenter with a 3c-2e Be_3 σ -bond ($\text{ON} = 2.00|\text{e}|$).

Evaluation of the chemical bonding for the three-dimensional isomer III (Fig. 5.1) and linear isomer VI (Fig. 5.1) of the H_2Be_4 stoichiometry was also performed and the results are presented in Fig. 5.4.

The bonding in the linear isomer continues to remain classical with two 2c-2e Be-H and three Be-Be σ -bonds ($\text{ON} = 1.93|\text{e}|$). However, for the three-dimensional isomer VI, we did not find 2c-2e σ -bonds. The hydrogen atoms in this structure are bound to the Be_4 cluster through 3c-2e σ -bonds ($\text{ON} = 1.99|\text{e}|$). The bonding inside the Be_4 cluster also exhibits multicentered bonding with one 4c-2e σ -bond ($\text{ON} = 1.96|\text{e}|$) and two 4c-2e π -bonds ($\text{ON} = 2.00|\text{e}|$). Thus, according to our calculations, three-dimensional structures

with multicenter bonding become global minima at $n = 4$ in the $\text{H}-(\text{Be})_n\text{-H}$ clusters.

5.5 Summary

In summary, the homocatenation for the Be-Be bonding in the $\text{H-Be}_n\text{-H}$ clusters ends at $n = 3$. Thus, this study has demonstrated that multicentered bonding will win the tug-of-war in the competition between multicentered bonding. Additionally, all theoretical predictions presented in this study can be tested experimentally either under matrix isolation conditions or by negative photoelectron spectroscopy.

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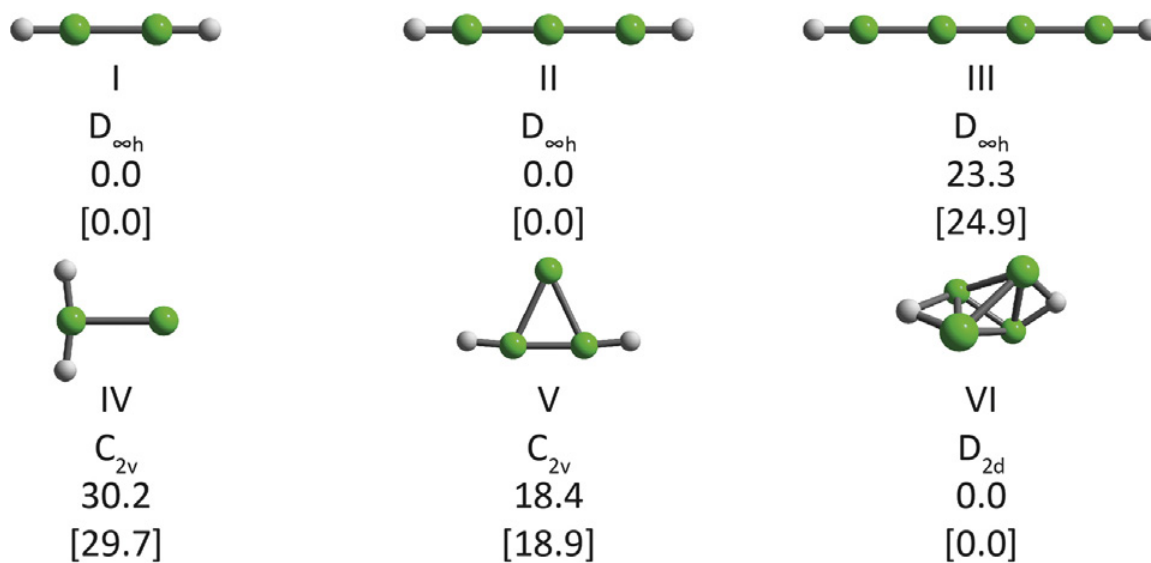


Fig. 5.1: Lowest energy linear structures and isomers with multicenter bonding of $H-(Be)_n-H$ ($n = 2-4$), their point group symmetries and ZPE correct relative energies (in kcal/mol) at the CCSD(T)/aug-cc-pVTZ and PBE0/6-311++G(d,p) (in square brackets) levels of theory. H is white, and Be is green (here and elsewhere).

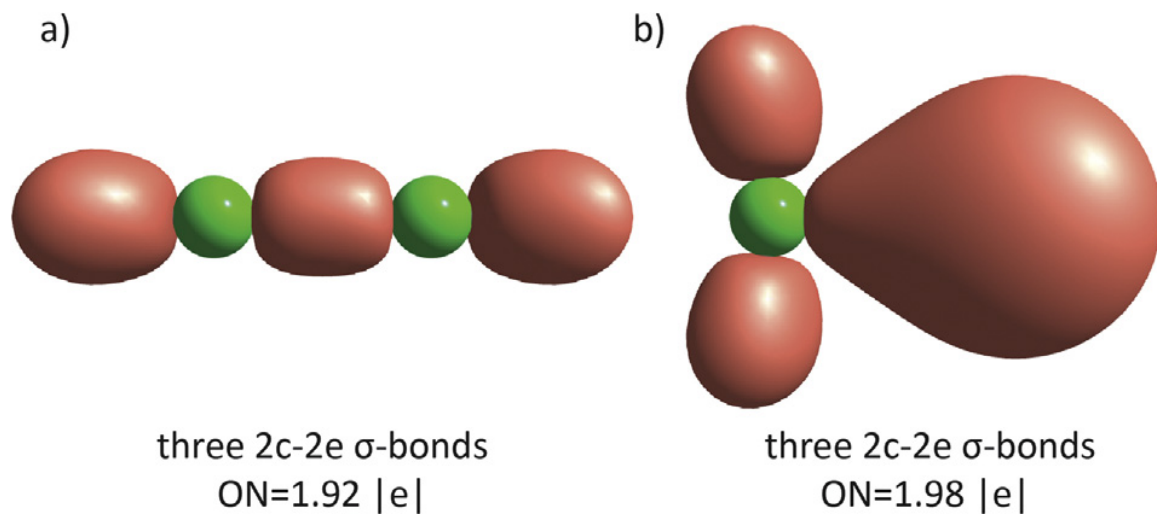


Fig. 5.2: Chemical bonds recovered for H_2Be_2 by AdNDP analysis for the (a) linear isomer and (b) the second lowest isomer.

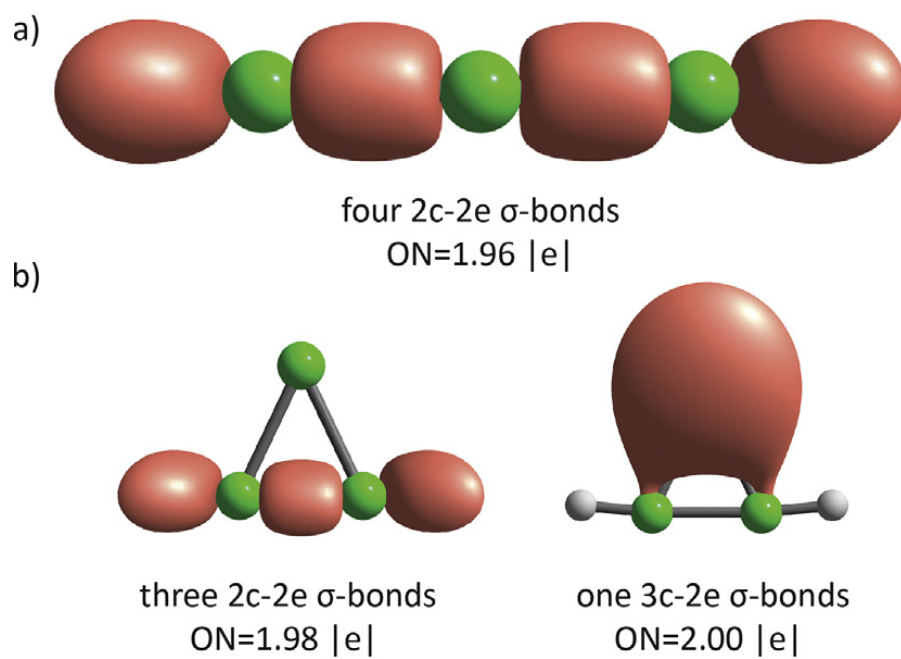


Fig. 5.3: Chemical bonds recovered for H_2Be_3 by AdNDP analysis for the (a) linear isomer and (b) lowest isomer with multicenter bonds.

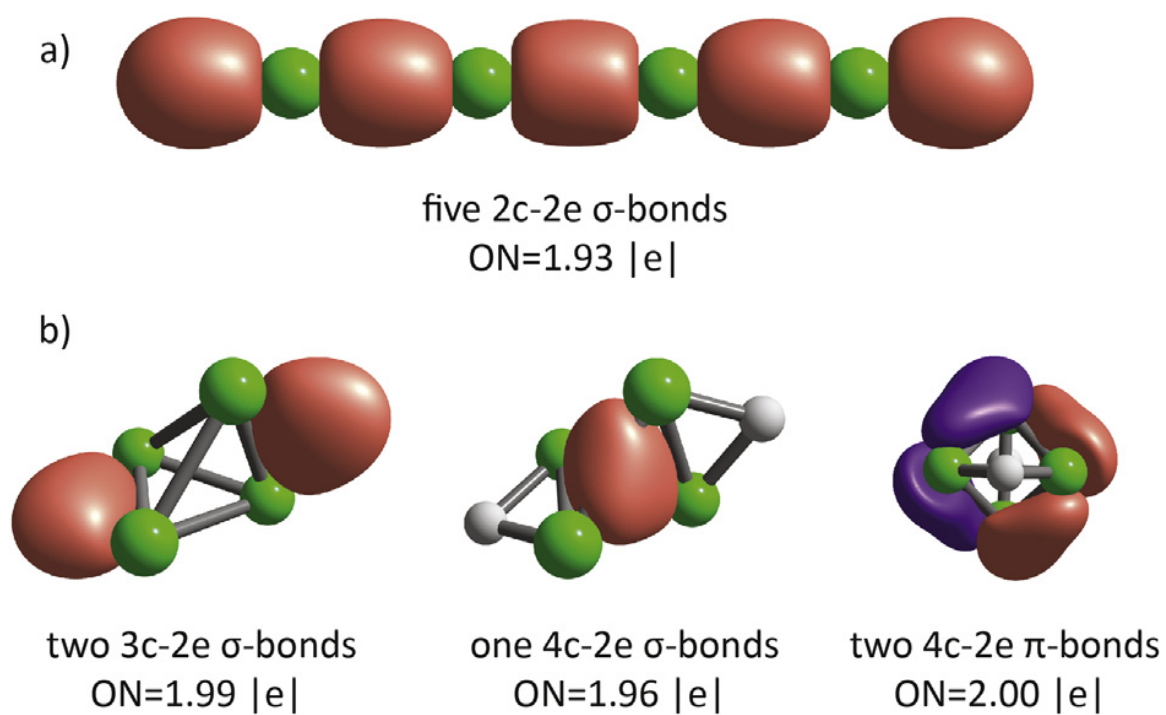


Fig. 5.4: Chemical bonds recovered for H_2Be_4 by AdNDP analysis for the (a) linear isomer and (b) lowest isomer with multicenter bonds.

CHAPTER 6

SUMMARY

The main spirit of electronic transmutation (ET) is to discover new exotic compounds and chemical bonds. As of 2012 [1], the major development in these discoveries have majorly been *in silico* where unbiased global minimum search and chemical bond analysis lay a foundation for experimentalists. Advancement in modern matrix isolation and negative photoelectron spectroscopy techniques greatly help in the synthesis and characterization of ET compounds. This in turn provides backing for the ET concept, which assumes that a certain element with atomic number Z will behave similar to its neighboring element ($Z+1$) through the addition of an electron [1].

Historically, the ET concept has been applied to the elements B, Al, Ga, Si, N, and P, which have demonstrated successful “transmutation” to C, Si, Ge, O, and S, respectively [1–17]. Exploration of the ET concept throughout the remainder of the Periodic Table is the aspiration of the Boldyrev group. However, the scope of this dissertation was limited to the advancements of Al “transmutations.”

The basis of the ET model for the Al-analog of the Si_2H_4 global minimum cluster was designed around $\text{LiAl}_2\text{H}_4^-$. The $\text{LiAl}_4\text{H}_4^-$ cluster presented a global minimum that mimics the Si_2H_4 structure with an $\text{Al}=\text{Al}$ double bond comprised of one σ - and one π -bond. The results of this study provide evidence that ET is a viable strategy in designing molecules with Al-Al multiple bonds. Discovery of the $\text{Al}\equiv\text{Al}$ triple bond being of particular interest.

Pursuit of the $\text{Al}\equiv\text{Al}$ triple bond required that the ET concept’s acquisition of one electron in $Z \rightarrow Z+1$ be broadened to the acquisition of two electrons, $Z \rightarrow Z+2$ [18]. This modification became known as the double electronic transmutation (DET) concept. Application of the DET concept to design the clusters Na_3Al_2^- and Na_4Al_2 resulted in an Al cluster which possessed a classical $\text{Al}\equiv\text{Al}$ triple bond (one σ - and two π -bonds). Presence of the triple bond in both cluster was supported by agreement in vertical detachment energies

between theoretical and experimental data. Additional, similarity between the canonical molecular orbitals and natural localized molecular orbitals, used by AdNDP, of the $\text{P}\equiv\text{P}$ molecule and the Na_3Al_2^- and Na_4Al_2 further supports that Na atoms can doubly “transmute” Al into P. These chemical bonding analyses have proven throughout this dissertation to be invaluable in discerning new chemical species designed by ET and also can aid in determining when classical bonding breaks down.

In the classical Lewis description of a bond, it is expected that two atoms will be joined by two electrons or a two center-two electron bond [19–21]. Some instances this description indeed holds true. For example the 390 carbon super-alkane $[\text{CH}_3(\text{CH}_2)_{388}\text{CH}_3]$ follows the classical description [22]. However, in lieu of Chapter 5, this should not be taken for granted for every molecule. As the findings of Chapter 5 conveyed, “it could be dangerous to use classical bonding arguments to predict global minimum structures containing metals. As metals may favor multi-center bonds.” Just as $\text{H}-(\text{Be})_n-\text{H}$ favored multi-bonding after $n=3$ [23].”

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Katie Lundell

(208) 431-3854

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“Realization of an $\text{Al}\equiv\text{Al}$ Triple Bond in the Gas-Phase Na_3Al_2^- Cluster via
Double Electronic Transmutation Angew. Chem. Int. Ed. 57, 14060-14064.

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04-30-2019

W. Wang
Collaborative Innovation Center of Chemical Science and
Engineering, College of Chemistry, Nankai University
Tianjin 300071 (China)

Dear Wei Wang:

I am in the process of preparing my dissertation in the Chemistry department at Utah State University. I hope to complete my degree program in 05/2019.

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Double Electronic Transmutation Angew. Chem. Int. Ed. 57, 14060-14064.

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CURRICULUM VITAE

Katie. A. Lundell

(April 2019)

Professional Preparation

Institution	Degree	Date
<i>Utah State University</i>	Ph.D. Chemistry	2019
<i>Idaho State University</i>	B.S. Chemistry (High Honors)	2015
	B.S. Biochemistry (High Honors)	2015
<i>College of Southern Idaho</i>	A.S. Biology (Honors)	2011

Teaching Preparation

Courses	Role	Number of Sections	Date
CHEM1010 (Introduction to Chemistry)	Instructor	1	Summer 2019
CHEM2315 (Organic Chemistry Lab I)	TA*	2	Fall 2018
CHEM5100 (Computational Chemistry)	TA*	1	Fall 2018
CHEM1210 (General Chemistry Recitation)	TA*	7	Spring 2018
CHEM5650 (Instrumental Analysis Lab)	TA*	1	Spring 2017
CHEM3005 (Quantitative Analysis Lab)	TA*	2	Fall 2016
CHEM-5650 (Instrumental Analysis Lab)	TA*	1	Spring 2016
CHEM-3005 (Quantitative Analysis Lab)	TA*	2	Fall 2015

*Teaching Assistant

Awards and Scholarships

Majorie H. Gardener Teaching Award	2018
NSF Chemistry/Biochemistry Scholarship	2012-2015
Chemistry Alumni Endowment Award Scholarship	2014-2015
ASC Outstanding Undergraduate in Organic Chemistry	2014
Patty Family Scholarship	2013-2014
Eugene H. Magleby Foundation Scholarship	2012-2013
ACS Polymer Education Award for Organic Chemistry	2012
Brightest and Best of ISU Chemistry Department	2012
Idaho INBRE Summer Fellow	2012
Idaho INBRE Summer Scholar	2011

Publications

1. Lundell, K. A.; Olson, J. K.; Boldyrev, A. I. "Exploring the Limits of Electronic Transmutation: *ab initio* Study of Li_nBe_n ($n = 3-5$)" **In progress**.
2. Xinxing Zhang, Ivan A. Popov, Katie A. Lundell, Haopeng Wang, Chaonan Mu, Wei Wang, Hansgeorg Schöckel, Alexander I. Boldyrev, and Kit H. Bowen "Realization of an an $\text{Al}\equiv\text{Al}$ Triple Bond in the Gas-Phase Na_3Al_2^- Cluster via Double Electronic Transmutation" *Angew. Chem. Int. Ed.* (2018) DOI:10.1002/anie.201806917
3. Xinxing Z.; Lundell, K. A.; Olsen, J.; Boldyrev, A. I.; Bowen, K. H. "Electronic Transmutation (ET): Chemically Turning One Element into Another" *Chem. Eur. J.* (2018) DOI: 10.1002/chem.201800517
4. Lundell, K. A.; Xanxing, Z. Boldyrev, A. I.; Bowen, K. H. "On the Existence of Designer $\text{Al}=\text{Al}$ double bonds in the $\text{LiAl}_2\text{H}_2^-$ Cluster via Electronic Transmutation" *Angew. Chem. Int. Ed.* 56, 16593-16596 (2017) DOI: 10.1002/anie.201710338
5. Lundell, K. A. Boldyrev, A. I. "Tug-of-war-between classical and multicentered bonds in $\text{H}-(\text{Be})_n-\text{H}$ species" *Chem. Phys. Lett.* 699, 85-87 (2018) DOI: 110.1016/j.cplett.2018.03.044