

Electronic States of Al_3As_2 , Al_3As_2^- , Al_3As_2^+ , Al_2As_3 , Al_2As_3^- , and Al_2As_3^+

Ping Yi Feng,^{†‡} Dingguo Dai,[‡] and K. Balasubramanian^{*,‡}

State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Metallurgy, Academia Sinica, Shanghai 200050, China, and Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604

Received: August 30, 1999; In Final Form: November 1, 1999

We have computed the optimized geometries and energy separations for the electronic states of Al_3As_2 , Al_2As_3 , and their positive and negative ions using complete active-space MCSCF (CASSCF) followed by multireference singles + doubles configuration interaction (MRSDCI) calculations which included up to 3.9 million configurations. The $^2\text{A}_1(\text{C}_{2v})$ state is the lowest electronic state of Al_3As_2 among seven states with distorted trigonal bipyramid structures. The $^2\text{A}_1$ state and another distorted $^2\text{B}_1(\text{C}_{2v})$ state are formed from the undistorted $^2\text{E}'$ and $^2\text{E}''(\text{D}_{3h})$ states, respectively, as a consequence of Jahn–Teller effect. The $^2\text{A}_2''(\text{D}_{3h})$ state is found to be the ground state of Al_2As_3 with an undistorted trigonal bipyramid structure (D_{3h}). Four electronic states of Al_3As_2^+ and Al_2As_3^+ were computed and their ground states are undistorted $^3\text{A}_2'$ and $^1\text{A}_1'(\text{D}_{3h})$ states for Al_3As_2^+ and Al_2As_3^+ , respectively. The $^1\text{A}_1'(\text{D}_{3h})$ state is the ground state for both Al_3As_2^- and Al_2As_3^- . The atomization energies, adiabatic ionization potentials, and other properties for the electronic states of Al_3As_2 and Al_2As_3 and a comparison with the Ga analogues are provided. The Al_3As_2 cluster is shown to differ from Ga_3As_2 in some states due to a greater charge transfer from $\text{Al}(3s)$ to $\text{As}(4p)$ in Al_3As_2 .

I. Introduction

Spectroscopic and geometrical properties of group III–V (group 13–15) and other related mixed main group clusters^{1–32} have been investigated intensely not only due to their intrinsic merit but also due to their technological importance. The III–V materials find applications in the emerging semiconductor technology of fast devices and light-emitting diodes. It is of great experimental and theoretical interest to study how the clusters evolve as a function of their sizes to the bulk, as smaller clusters exhibit dramatic variations in their properties and relative abundance compared to larger clusters.

Early interest in group III–V clusters arose from the pioneering work of Smalley and co-workers¹ on Ga_xAs_y ; they showed that while the relative abundance of larger clusters followed a binomial distribution, the abundance of smaller clusters deviated strongly from the anticipated binomial distribution. Subsequently, driven by the technological importance of these species and the availability of experimental techniques to generate these species, such as the supersonic jet expansion method, spectroscopic studies of many III–V clusters have been carried out. In the supersonic jet method, a source material of the III–V compound, such as a foil of the material, is laser-evaporated. The vapor thus formed is passed through a supersonic nozzle, which results in cooling and formation of copious amounts of clusters of various sizes.⁶ The clusters can be mass-analyzed and a variety of spectroscopic techniques could then be utilized to probe the low-lying electronic states of these clusters as a function of their sizes.

Negative ion photoelectron spectroscopy is a powerful method to probe the ground and excited electronic states of the neutral clusters since mass analysis of the generated anionic clusters

would confirm the cluster sizes unequivocally. In addition, the technique has reasonable spectral resolution. Newmark and co-workers^{4–5,7,8} have studied a number of III–V clusters, especially Ga_xP_y , In_xP_y , Ga_xAs_y , etc. Experimental studies of other III–V clusters such as Al_xP_y , Al_xAs_y , etc., are in progress.¹⁵ These experimental results have revealed several fascinating trends for the measured electron affinities and other properties of the low-lying electronic states of the neutral clusters. The experimental studies have yielded electron affinities, term values, and vibrational frequencies of the neutral and anionic clusters. In a recent experimental study, Taylor et al.¹⁵ have demonstrated that vibrationally resolved anion photoelectron spectra of III–V clusters, such as GaP_2^- and GaP_3^- anions, could be obtained, thus providing more accurate term values, electron affinities, and vibrational frequencies of such species.

Weltner and co-workers^{11–13} have used a matrix-isolation technique to study a few group III–V clusters. Subsequently, ESR or far-IR spectroscopic methods have been used to probe the ground states of the matrix-isolated clusters. On the basis of the hyperfine patterns, the spin multiplicities, and the geometries of the ground states of these species can be deduced. These authors¹¹ have obtained the far-infrared spectra of Ga/P , Ga/As , and Ga/Sb clusters in rare gas matrices at 4 K. Few vibrational spectroscopic studies of the group III–V clusters have been performed; at present such studies are restricted to GaP , GaAs , and GaSb in a rare gas matrix. As noted before, Taylor et al.¹⁵ have reported vibrationally resolved spectra on larger clusters including pentamers.

Van Zee et al.¹² have studied a pentamer cluster related to the title cluster of our current study. They have obtained the hyperfine interaction and structure of Ga_2As_3 using the matrix-isolation method. These authors have employed a laser vaporization technique for GaAs crystals followed by aggregation at a relatively high pressure of Ar/Kr prior to condensation of the matrices at 4 K, which yielded a pentameric Ga_2As_3 cluster.

* To whom correspondence should be addressed. E-mail: kbalu@asu.edu.

[†] Shanghai Institute of Metallurgy.

[‡] Arizona State University.

Electron spin resonance revealed a doublet ground state with a hyperfine pattern that suggested a trigonal bipyramid structure (tbp) in a probable ground state of ${}^2\text{A}_2''$.

Duncan and co-workers^{18–20} have studied several mixed main group cluster cations, such as In_xSb_y^+ , using the photoionization and photodissociation techniques. Such studies have revealed interesting information on the photofragmentation patterns as well as spectroscopic data on the excited states of their cations. The current theoretical study is aimed at the excited states of not only neutral clusters but also the cations.

Stimulated by experimental studies on these clusters, several theoretical studies were directed toward the geometrical and electronic properties of group III–V clusters.^{14–24} These studies have varied from molecular dynamics methods to relativistic *ab initio* CASSCF and MRSDCI techniques. However, to the best of the present authors' knowledge, the low-lying electronic states of the clusters containing Al and As have not been studied before at the level of theory considered here. The present paper deals with the low-lying electronic states of Al_3As_2 and Al_2As_3 and their positive and negative ions using high-level relativistic *ab initio* CASSCF and MRSDCI techniques that included up to 3.91 million configurations.

II. Method of Computations

In the present study, we use a relativistic CASSCF/MRSDCI method to compute the electronic properties of the neutral, cationic, and anionic clusters. Geometries were fully optimized at the CASSCF level and the MRSDCI technique was employed for further geometry optimization and term energies. We employed relativistic effective core potentials (RECPs) that retained the outer $3s^23p^1$ and $4s^24p^3$ shells of the Al and As atoms explicitly in the valence space, replacing the remaining electrons by RECPs. The RECPs together with the valence Gaussian basis sets were taken from ref 33. These basis sets were augmented with a set of 3d polarization functions with exponent $\alpha_d = 0.3084$ for Al and $\alpha_d = 0.22$ for As, respectively.

The CASSCF technique was used to generate the molecular orbitals for higher-order MRSDCI calculations. In the CASSCF calculations, five *s* orbitals of Al and As were kept in the core in that excitations were not allowed from these orbitals, but they were allowed to relax as a function of geometries. The computations were carried out in the C_{2v} group, although many of the relevant electronic states have D_{3h} symmetries. The CASSCF wave function that included $i a_1, j b_2, k b_1, l a_2$ orbitals in the active space is labeled *ijkl*-CAS. On the basis of the results of several trial computations and the previous work on other isovalent pentameric clusters,³¹ we adopted a 3232-CAS method for the Al_3As_2 , Al_2As_3 , and their ions. Thus, nine active electrons for Al_3As_2 (eight electrons for Al_3As_2^+ and 10 electrons for Al_3As_2^-) and 11 active electrons for Al_2As_3 (10 electrons for Al_2As_3^+ and 12 electrons for Al_2As_3^-) were distributed in all possible ways among the chosen set of active orbitals in the CASSCF.

It is anticipated that some of the electronic states with the D_{3h} geometry would be subjected to Jahn–Teller distortion, if the electronic states under consideration were E' or E'' states. This is consistent with a previous study on the electronic states of Ga_3P_2 and Ga_2P_3 ,³¹ which has revealed two distorted states with C_{2v} symmetries, although the extent of distortion was rather small. Consequently, we optimized the geometries using a quasi Newton–Raphson technique at the CASSCF level of theory. For this purpose, the GAMESS³⁴ molecular computational package was employed. Two distorted electronic states of the neutral clusters, namely ${}^2\text{A}_1$, ${}^2\text{B}_1(C_{2v})$ of Al_3As_2 and ${}^2\text{A}_2$, ${}^2\text{A}_1-$

(C_{2v}) for Al_2As_3 were found to arise from Jahn–Teller distortion of the ${}^2E'$ and ${}^2E''$ states, respectively. However, the ground states of the anion and cation are found to be undistorted. The geometries of all possible low-lying doublet and quartet electronic states for Al_3As_2 and the doublet states of Al_2As_3 were searched and optimized.

We have also considered an isomer of Al_3As_2 in which the As atoms are in tetra coordination. One may visualize this as an isomer of the distorted tbp structure considered above, but one of the axial As atom switched to the equatorial position such that there would be two As and an Al at the equatorial position and two Al atoms at the axial sites. However, geometry optimization of such a structure would rearrange the structure so that the Al atoms move away from the center of the triangle above the plane so as to form a direct As–Al–As bridge. This results in a capped rhombus structure in which two As and two Al atoms form a planar rhombus structure, wherein the As–As bond is the shorter diagonal of the rhombus, the Al–Al bond is the longer diagonal, and the four equal sides are the Al–As bonds. The third Al atom is above the plane of the rhombus at the middle of the As–As bond so as to form a As–Al–As bridge with Al–As bond lengths being the same as the other four Al–As bonds in the rhombus structure. The resulting structure exhibits C_{2v} symmetry. We considered two low-lying states (${}^2\text{A}_1$ and ${}^2\text{B}_1$) for this structure, and the geometries were optimized at the CASSCF level. Among the two states, the ${}^2\text{B}_1$ state was found to be lower and thus it was considered for higher level of theory. However, it is clear that this structure is not a viable candidate for Al_2As_3 since the As atoms tend to cling together and it would take significant energy to break the As–As bonds, while in the case of Al_3As_2 , the Al–Al bonds are weaker than the Al–As bonds.

The multireference singles + doubles configuration interaction (MRSDCI) calculations were carried out following the CASSCF computations to introduce higher-order electron correlation effects. All configurations in the CASSCF with absolute coefficients larger than 0.07 were included as reference configurations in the MRSDCI computations. This created up to 3 909 883 configuration spin function (CSFs) in the MRSDCI computations. Furthermore, a multireference Davidson correction technique for uncoupled quadruple clusters to the MRSDCI energy was invoked and the resulting energy separation was labeled as MRSDCI+Q, which is considered to be a full-CI estimate.

As noted earlier, it would be useful to compute the ground and excited electronic states of the Al_3As_2^+ and Al_2As_3^+ ions, as the results of such computations would be useful in photoionization studies of these species. Likewise, anions of these species are of interest in the anion photoelectron spectroscopic studies carried out by Neumark and co-workers.^{15,16} Consequently, computations on the Al_3As_2^- and Al_2As_3^- anions as well as four low-lying electronic states of Al_3As_2^+ and Al_2As_3^+ were carried out. Furthermore, the atomization energies to dissociate the Al_3As_2 and Al_2As_3 clusters into aluminum (${}^2\text{P}$) and arsenic atoms (${}^4\text{S}$) were computed as supermolecular calculations.

The CASSCF/MRSDCI calculations were made using a version of ALCHEMY II codes³⁶ modified by one of the authors³⁵ to include relativistic ECPs (RECPs).

III. Results and Discussion

A. Electronic States of Al_3As_2 , Al_3As_2^+ , and Al_3As_2^- . The first part of Table 1 shows the optimized geometries, energy separations, and dipole moments for two of the lowest Jahn–

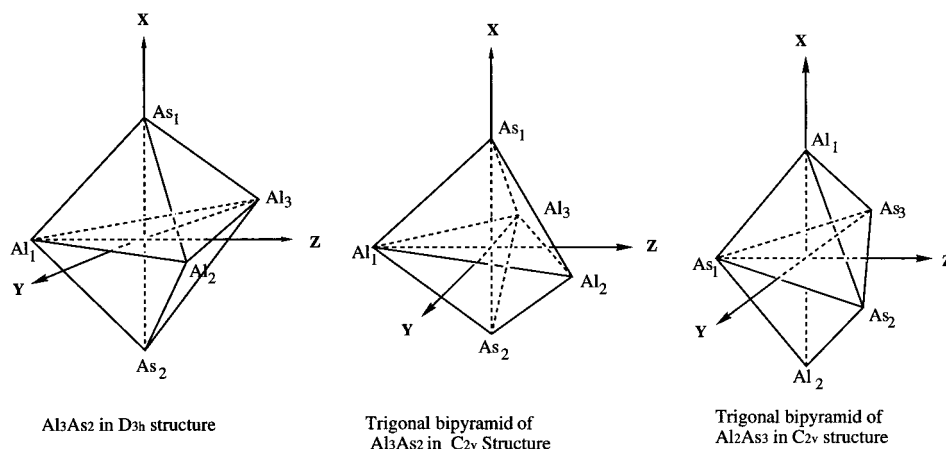


Figure 1. Geometries of regular trigonal bipyramid (tbp), distorted tbp structures of Al_3As_2 , and the regular tbp structure of Al_2As_3 .

TABLE 1: Geometries and Energy Separations for the Electronic States of Al_3As_2 with Distorted Tbp and Capped Rhombus and Al_2As_3 with Distorted Tbp Structures

species		distorted tbp states (C_{2v})		capped rhombus states (C_{2v})	
		2A_1	2B_1	2B_1	2A_1
Al_3As_2	$\text{Al}_2-\text{Al}_1-\text{Al}_3$ (deg)	69.5	71.7	45.0	45.0
	$\text{As}_1-\text{Al}_1-\text{As}_2$ (deg)	67.9	51.1	53.0	60.5
	$\text{As}_1-\text{Al}_2-\text{As}_2$ (deg)	59.9	53.8	53.0	60.5
	Al_1-Al_2 (Å)	3.641	3.902	4.833	4.469
	Al_2-Al_3 (Å)	4.153	4.568	3.417	3.160
	Al_1-As_1 (Å)	2.384	2.793	2.700	2.587
	Al_2-As_1 (Å)	2.667	2.661	2.700	2.587
	As_1-As_2 (Å)	2.663	2.410	2.409	2.607
	dipole moment (D)	-5.42	-1.29	-0.14(X)	
	$E(\text{CASSCF})$ (eV)	0.00	0.51	0.76	1.04
	$E(\text{MRSDCI})$ (eV)	0.00	0.63	0.46	
	$E(\text{MRSDCI}+Q)$ (eV)	0.00	0.58	0.54	
species		distorted tbp states (C_{2v})			
		2A_2	2A_1		
Al_2As_3	$\text{As}_2-\text{As}_1-\text{As}_3$ (deg)	55.6	49.6		
	$\text{Al}_1-\text{As}_1-\text{Al}_2$ (deg)	136.0	90.7		
	$\text{Al}_1-\text{As}_2-\text{Al}_2$ (deg)	110.8	88.6		
	As_1-As_2 (Å)	2.485	3.184		
	As_2-As_3 (Å)	2.319	2.672		
	As_1-Al_1 (Å)	2.624	2.442		
	As_2-Al_1 (Å)	2.956	2.487		
	Al_1-Al_2 (Å)	4.865	3.475		
	dipole moment (D)	-0.63	-0.21		
	$E(\text{CASSCF})$ (eV)	0.41	1.05		
	$E(\text{MRSDCI})$ (eV)	0.69	0.94		
	$E(\text{MRSDCI}+Q)$ (eV)	0.80	0.92		

Teller distorted electronic states of Al_3As_2 , namely 2A_1 and 2B_1 (C_{2v}), and also two states for the isomer with capped rhombus structure described before. Figure 1 illustrates the actual locations for the atoms. Table 2 exhibits all undistorted doublet and quartet electronic states of Al_3As_2 with their ideal trigonal bipyramid geometries (D_{3h}), and their energy separations. As can be seen from Table 2, the first two low-lying electronic states of Al_3As_2 with regular D_{3h} structures are the $^2E'$ and $^2E''$ states which would be subjected to Jahn–Teller distortion. Among the undistorted D_{3h} states, the $^2E'$ state is the lowest in energy. The $^2E''$ state is 0.35 eV above the $^2E'$ state, and all of the quartet states are higher at both CASSCF and MRSDCI levels of theory. The geometries of the distorted 2A_1 and 2B_1 (C_{2v}) states of Al_3As_2 can be visualized as the derivatives of the $^2E'$ and $^2E''$ states by Jahn–Teller effect. Consequently, the distorted 2A_1 and 2B_1 (C_{2v}) states of Al_3As_2 in Table 1 are the lowest C_{2v} Jahn–Teller components arising from the $^2E'$ and

$^2E''$ states, respectively. Consequently, the 2A_1 (C_{2v}) state is 0.27 eV lower than the corresponding $^2E'(D_{3h})$ state, while the 2B_1 (C_{2v}) state is only 0.06 eV lower than the $^2E''(D_{3h})$ state at the MRSDCI level of theory. Thus, the Jahn–Teller stabilization energy is rather small, especially for the $^2E''(D_{3h})$ state. This is further confirmed by a small geometry change between the distorted and undistorted structures. At all levels of theory, the 2A_1 (C_{2v}) state prevails as the ground state of Al_3As_2 , while the 2B_1 (C_{2v}) state is 0.56 eV above the 2A_1 state at the MRSDCI level.

As seen from Table 2, the three Al atoms form an equilateral triangular base for the $^2E'(D_{3h})$ state. The three Al atoms depart from the equilateral triangular position in the $^2A_1(C_{2v})$ state due to Jahn–Teller distortion, resulting in two contracted Al_1-Al_2 and Al_1-Al_3 (3.641 Å) bonds, and an elongated Al_2-Al_3 (4.153 Å) bond. However, the average Al–Al bond length of 3.812 Å for the $^2A_1(C_{2v})$ state is close to the Al–Al distance (3.748 Å) in the $^2E'(D_{3h})$ state. The As_1-As_2 bond length in the $^2A_1(C_{2v})$ state is 2.663 Å, which is quite comparable to 2.704 Å in the $^2E'(D_{3h})$ state (see, Tables 1 and 2). Likewise, the average Al–Al bond length of the three Al–Al bonds, namely Al_1-Al_2 , Al_1-Al_3 (3.902 Å) and Al_2-Al_3 (4.568 Å) in the $^2B_1(C_{2v})$ state is 4.124 Å, which is near the Al–Al bond length (4.142 Å) in the $^2E''(D_{3h})$ state. On the other hand, the As_1-As_2 bond length of 2.410 Å in the $^2B_1(C_{2v})$ state is close to 2.469 Å in the $^2E'(D_{3h})$ state. These features suggest that the Al atoms move from their ideal equilateral triangular locations in the D_{3h} structures of Al_3As_2 due to Jahn–Teller effect, but the As atoms do not change their axial positions substantially.

The As–As bond length of the As_2 dimer is 2.164 Å in the $^1\Sigma_g^+$ ground state.³⁷ The As–As bond distances in the first two low-lying electronic states of Al_3As_2 are near 2.50 Å, similar to those in the excited states of As_2 . However, the Al–Al distances exhibit a different behavior. The Al_1-Al_2 and Al_2-Al_3 bond lengths in the 2A_1 ground state of Al_3 are 2.521 and 2.559 Å,³⁸ respectively. These values are much shorter than the Al–Al bond lengths (3.2–4.6 Å) in Al_3As_2 . Evidently the interactions among the three Al atoms in Al_3As_2 are weakened by the bonding between Al and As atoms in Al_3As_2 .

It is noticeable that the $\text{As}_1-\text{Al}_1-\text{As}_2$ and $\text{As}_1-\text{Al}_2-\text{As}_2$ bond angles in the 2B_1 state (51.1° and 53.8°, respectively) are considerably smaller than the corresponding values of 67.9° and 59.9° in the 2A_1 state, respectively. This suggests a stronger As–As bonding in the 2B_1 state compared to that in 2A_1 . This is consistent with the fact that the As–As bond length in the 2B_1 state is 2.410 Å which is shorter than 2.663 Å for 2A_1 . However, the Al_1-As_1 bond length is 2.384 Å, while the Al_1-

TABLE 2: Electronic States of Al₃As₂, Al₂As₃ and Their Ions: *D*_{3h} Tbp Structures

species	state		MRSDCI			
	<i>C</i> _{2v}	<i>D</i> _{3h}	Al–Al (Å)	Al–As (Å)	As–As (Å)	<i>E</i> (eV) ^a
Al ₃ As ₂	² A ₁ , ² B ₂	² E'	3.748	2.552	2.704	0.27 (0.22)
	² B ₁ , ² A ₂	² E''	4.142	2.691	2.469	0.61 (0.58)
	⁴ A ₂	⁴ A ₁ '	3.205	2.499	3.360	0.73 (0.58)
	⁴ B ₁ , ⁴ A ₂	⁴ E''	3.193	2.517	3.427	1.48 (1.45)
	⁴ A ₁ , ⁴ B ₂	⁴ E'	3.549	2.611	3.236	2.35 (2.16)
	Al ₃ (² A ₁) + 2As(⁴ S)					5.58 (5.69)
	3Al(² P) + 2As(⁴ S)					8.90 (9.27)
Al ₃ As ₂ ⁺	³ B ₂	³ A ₂ '	3.748	2.552	2.704	6.84 (6.77)
	¹ A ₁ , ¹ B ₂	¹ E'	3.748	2.552	2.704	7.02 (7.11)
	³ B ₁ , ³ A ₂	³ E''	3.748	2.552	2.704	8.09 (8.03)
	¹ B ₁ , ¹ A ₂	¹ E''	3.748	2.552	2.704	8.74 (8.62)
Al ₃ As ₂ [−]	¹ A ₁	¹ A ₁ '	3.839	2.574	2.616	−2.33 (−2.37)

species	state		MRSDCI			<i>E</i> (eV) ^a
	<i>C</i> _{2v}	<i>D</i> _{3h}	As–As (Å)	As–Al (Å)	Al–Al (Å)	
Al ₂ As ₃	² B ₁	² A ₂ '	2.556	2.560	4.184	0.00 (0.00)
	² A ₂ , ² B ₁	² E''	2.457	2.800	4.828	1.02 (1.01)
	² A ₁ , ² B ₂	² E'	2.950	2.456	3.539	1.49 (1.45)
	As ₃ (² A ₂) + 2Al(² P)					7.59 (7.71)
	3As(⁴ S) + 2Al(² P)					12.77 (13.12)
Al ₂ As ₃ ⁺	¹ A ₁	¹ A ₁ '	2.556	2.560	4.184	6.61 (6.87)
	³ B ₁	³ A ₂ '	2.556	2.560	4.184	7.66 (8.00)
	³ B ₂ , ³ A ₁	³ E'	2.556	2.560	4.184	7.96 (8.29)
	¹ B ₁	¹ A ₂ '	2.556	2.560	4.184	8.92 (8.93)
Al ₂ As ₃ [−]	¹ A ₁	¹ A ₁ '	2.495	2.658	4.468	−2.05 (−1.94)

^a The values in the parentheses are the Davidson corrected energies.

Al₂ and Al₂–Al₃ bond distances in the ²A₁ state are 3.641 and 4.153 Å, respectively. All these distances are shorter than their corresponding values of 2.793 (Al₁–As₁), 3.902 (Al₁–Al₂), and 4.568 Å (Al₂–Al₃) in the ²B₁ state. The ²A₁ state remains as the ground state of Al₃As₂ at all levels of theory, while the ²B₁ state is 0.56 eV higher than the ²A₁ state at the MRSDCI level, suggesting that the interaction between the Al and As atoms has a greater influence on the term energies and geometries of the electronic states of Al₃As₂. Likewise, the As₁–Al–As₂ bond angle of the ²E'' state (54.6°) for the undistorted structure is smaller than the corresponding angle of 64.0° in the ²E' state. This is caused by a shorter As–As bond length (2.469 Å) in the ²E'' state compared to the As–As bond (2.704 Å) in the ²E' state. Thus, the As–As bonding in the ²E'' state is stronger than that in the ²E' state. However, the ²E' state is 0.35 eV lower than the ²E'' state because both Al–As and Al–Al bonds of ²E' are stronger than those of ²E''. As seen from Table 2, all of the quartet states of the undistorted *D*_{3h} structure were also computed, but these states, namely ⁴A₂', ⁴E'', and ⁴E', are higher in energy than ²E''.

The capped rhombus structures shown in Table 1 for Al₃As₂ can be envisaged as derivatives from the Al₂As₂ molecule, which exhibits a rhombus ground state with the As–As bond being the shorter diagonal of the rhombus. The As–Al bonds are the four equal sides of the rhombus. The capped rhombus structure is derived from this by adding the third Al atom above the center of the As–As bond (As–As edge capping) such that the Al–As bond distances are the same as those of the four sides of the rhombus. As seen from Table 2, two low-lying electronic states arise from this isomer, the ²B₁ being the lower of the two. However, this state is 0.76 and 0.46 eV higher than the distorted tbp ²A₁ state at the CASSCF and MRSDCI levels, respectively. While it falls slightly below the distorted tbp ²B₁ state at the MRSDCI level, it is still higher than the distorted tbp ²A₁ state. The capped rhombus and distorted tbp structures are nearly degenerate for the ²B₁ state at the MRSDCI+Q level (Table 1). Hence this state should be considered as an excited isomer

for Al₃As₂. It should be noted that the ²B₁ state with the capped rhombus structure is multireference in character in that three reference configurations have coefficients larger than 0.1 and 12 reference configurations have coefficients of 0.07 or more. This is reflected in the MRSDCI energy separation of this state, which is lower than the CASSCF energy separation.

The nature of bonding in the electronic states can be comprehended through the leading configurations, compositions of the orbitals, and the Mulliken populations. Table 3 shows the leading configurations for the electronic states of Al₃As₂ and its ions. The distorted electronic states of Al₃As₂ with *C*_{2v} geometries (²A₁ and ²B₁) have (1a₁22a₁23a₁24a₁21b₂22b₂21b₁–21a₂) portion of the configuration in common for both states. Likewise, all of the undistorted electronic states with *D*_{3h} symmetries have (1a₁'22a₁'21e'⁴1a₂'²) in common. We describe the compositions of the *D*_{3h} molecular orbitals (MOs), which can be correlated into the *C*_{2v} group. The 1a₁' (1a₁ in *C*_{2v}) orbital is predominantly As₁(s) + As₂(s). The 2a₁' (3a₁ in *C*_{2v}) orbital is a bonding combination of Al₁(s) + Al₂(s) + Al₃(s). The 3a₁' orbital (4a₁ in *C*_{2v}) is a bonding orbital composed of As₁(p_x) and As₂(p_x) in which the two As atoms furnish p orbitals overlapping with same sign along the *x* axis. The two degenerate components of the 1e' orbital (2a₁ and 1b₂ in *C*_{2v}) are 2Al₁(s) – [Al₂(s) + Al₃(s)] and Al₂(s) – Al₃(s) linear combinations, respectively. The 2e' orbital (5a₁ and 2b₂ in *C*_{2v}) consists of two parts, viz., [2Al₁(s) – [Al₂(s) + Al₃(s)]] mixed with [As₁–(p_y) + As₂(p_y)] and [Al₂(s) – Al₃(s)] + [As₁(p_z) + As₂(p_z)], respectively. Likewise, the two degenerate components of the 1e'' orbital (2b₁ and 1a₂ in *C*_{2v}) are [As₁(p_y) – As₂(p_y)] combined with [2Al₁(p_x) – Al₂(p_x) – Al₃(p_x)] and [As₁(p_z) – As₂(p_z)] + [Al₂(p_x) + Al₃(p_x)], respectively. The 1a₂' orbital (1b₁ in *C*_{2v}) is an antibonding As₁(s) – As₂(s) orbital. The 2a₂' orbital (3b₁ in *C*_{2v}) is composed of As₁(p_x) + As₂(p_x), which is antibonding with respect to the As atoms. As indicated in Table 3, the primary difference between the ²A₁ and ²B₁ states (*C*_{2v}) is in the electronic occupancies of the 5a₁ and 2b₁ orbitals. Both 5a₁ and 2b₁ orbitals exhibit antibonding character, the former relative

TABLE 3: Leading Configurations of the Electronic States of Al₃As₂, Al₂As₃, and Their Ions^a

system	state		weight	configuration				
	<i>C</i> _{2v}	<i>D</i> _{3h}		4a ₁	5a ₁	2b ₂	2b ₁	1a ₂
Al ₃ As ₂	² A ₁		96	2	1	2	2	2
	² B ₁		96	2	2	2	1	2
				3a ₁ '	2e'	1e''	2a ₂ ''	
	² A ₁ , ² B ₂	² E'	96	2	3	4	0	
	² B ₁ , ² A ₂	² E''	96	2	4	3	0	
	⁴ A ₂	⁴ A ₁ ''	96	2	2	4	1	
	⁴ B ₁ , ⁴ A ₂	⁴ E''	93	1	3	4	1	
	⁴ B ₂ , ⁴ A ₁	⁴ E'	94	2	3	3	1	
	³ B ₂	³ A ₂ '	96	2	2	4	0	
	¹ A ₁ , ¹ B ₂	¹ E'	94	2	2	4	0	
Al ₃ As ₂ ⁺	³ B ₁ , ³ A ₂	³ E''	96	2	3	3	0	
	¹ B ₁ , ¹ A ₂	¹ E''	96	2	3	3	0	
	¹ A ₁	¹ A ₁ '	96	2	4	4	0	
				4a ₁	5a ₁	2b ₂	3b ₁	1a ₂
Al ₂ As ₃	² A ₂		96	2	2	2	2	1
	² B ₁		96	2	2	2	1	2
				2a ₁ '	3a ₁ '	3e'	1e''	2a ₂ ''
	² B ₁	² A ₂ ''	96	2	2	0	4	1
	² A ₂ , ² B ₁	² E''	96	2	2	0	3	2
	² B ₂ , ² A ₁	² E'	95	2	2	1	4	0
	¹ A ₁	¹ A ₁ '	95	2	2	0	4	0
	³ B ₁	³ A ₂ ''	96	2	1	0	4	1
	³ B ₂ , ³ A ₁	³ E'	96	2	2	0	3	1
	¹ B ₁	¹ A ₂ ''	95	2	1	0	4	1
Al ₂ As ₃ ⁻	¹ A ₁	¹ A ₁ '	96	2	2	0	4	2

^a The 1a₁²2a₁²3a₁²1b₂²1b₁² configuration part for Al₃As₂ (or 1a₁²2a₁²3a₁²1b₂²1b₁²2b₁² for Al₂As₃) is same for all states in *C*_{2v} structure. Likewise, the 1a₁²2a₁²1e⁴1a₂² configuration part for Al₃As₂ and its ions (or 1a₁²1e⁴2e⁴1a₂² for Al₂As₃ and its ions) is common to all states in *D*_{3h} group.

to the Al atoms, and the latter relative to the As atoms. Consequently, a doubly occupied 2b₁ orbital and a singly occupied 5a₁ orbital in the ²A₁ state lead to longer As–As bond (2.663 Å) and relatively shorter Al₁–Al₂ (3.641 Å) and Al₂–

Al₃ (4.153 Å) bonds compared to the corresponding parameters for the ²B₁ state. This in turn leads to larger As₁–Al₁–As₂ (67.9°) and As₁–Al₂–As₂ (59.9°) bond angles for the ²A₁ state. In contrast to the ²A₁ state, the ²B₁ state has a doubly occupied 5a₁ orbital and a singly occupied 2b₁ orbital leading to shorter As–As bond length (2.410 Å) and very acute As₁–Al₁–As₂ (51.1°) and As₁–Al₂–As₂ (53.8°) bond angles. However, in the ²B₁ state, both Al₁–Al₂ (3.902 Å) and Al₂–Al₃ (4.568 Å) bonds are longer than those in the ²A₁ state.

As expected, the main distinction between the ²E' and ²E'' states of the undistorted Al₃As₂ cluster (*D*_{3h}) is in the electronic occupations of the 2e' and 1e'' orbitals. Thus, the compositions of these two orbitals determine the geometries of the two states. As described above, the 2e' orbital exhibits π bonds between the As atoms, while the 1e'' orbital is antibonding relative to the As atoms, but the interactions between the Al and As atoms are favorable. The 1e'' orbital of the ²E' state is fully occupied, but the 2e' orbital is only partially occupied leading to a longer As–As bond length (2.704 Å) but relatively shorter Al–As bond lengths (2.552 Å). On the other hand, the 2e' orbital is fully occupied, but the 1e'' orbital is partially occupied in the ²E'' state. This leads to a shorter As–As bond length (2.469 Å) and relatively longer Al–As bonds (2.691 Å) in the ²E'' state.

All of the quartet electronic states have an occupied 2a₂'' orbital, which consists of an antibonding interaction between the p_x orbitals of the two axial As atoms. Consequently, all of the quartet states are higher in energy.

As seen from Table 4, which displays the Mulliken populations of the electronic states of Al₃As₂, the total populations on the Al atoms are between 2.55 and 2.66, while the total As populations are about 5.51–5.61 for all of the states considered here. The depletion of the Al populations compared to the isolated Al atom and uniformly excessive As populations compared to the atomic As are attributed to charge transfers from the aluminum atoms to the As atoms leading to ionic Al⁺As⁻ bonding in the Al₃As₂ cluster. However, it is noted that

TABLE 4: Mulliken Populations for the Low-lying Electronic States of Al₃As₂, Al₂As₃, and Their Ions

system	state		total			gross population								
	<i>C</i> _{2v}	<i>D</i> _{3h}	Al ₁	Al ₂	As	Al ₁			Al ₂			As		
						s	p	d	s	p	d	s	p	d
Al ₃ As ₂	² A ₁		2.547	2.623	5.605	1.233	1.209	0.105	1.822	0.731	0.070	1.815	3.615	0.175
	² B ₁		2.554	2.643	5.581	1.859	0.640	0.055	1.844	0.729	0.079	1.851	3.560	0.170
	² A ₁ , ² B ₂	² E'	2.622		5.568	1.648	0.892	0.082				1.804	3.581	0.183
	² B ₁ , ² A ₂	² E''	2.615		5.577	1.843	0.707	0.065				1.847	3.554	0.176
	⁴ A ₂	⁴ A ₁ ''	2.661		5.509	1.559	1.008	0.094				1.771	3.561	0.177
	⁴ B ₁ , ⁴ A ₂	⁴ E''	2.645		5.531	1.398	1.160	0.087				1.817	3.557	0.157
	⁴ A ₁ , ⁴ B ₂	⁴ E'	2.659		5.512	1.690	0.893	0.076				1.840	3.513	0.159
	³ B ₂	³ A ₂ '	2.355		5.466	1.539	0.737	0.079				1.800	3.473	0.193
	¹ A ₁ , ¹ B ₂	¹ E'	2.349		5.477	1.487	0.783	0.079				1.806	3.480	0.191
	³ B ₁ , ³ A ₂	³ E''	2.444		5.334	1.727	0.637	0.080				1.807	3.318	0.209
Al ₃ As ₂ ⁺	¹ B ₁ , ¹ A ₂	¹ E''	2.437		5.345	1.647	0.707	0.083				1.805	3.325	0.215
	¹ A ₁	¹ A ₁ '	2.866		5.701	1.750	1.036	0.080				1.817	3.719	0.166
system	state		total			gross population								
	<i>C</i> _{2v}	<i>D</i> _{3h}	As ₁	As ₂	Al	As ₁			As ₂			Al		
						s	p	d	s	p	d	s	p	d
Al ₂ As ₃	² A ₂		5.402	5.219	2.581	1.862	3.382	0.158	1.867	3.171	0.181	1.857	0.661	0.063
	² A ₁		5.307	5.303	2.545	1.871	3.329	0.107	1.888	3.294	0.121	1.278	1.137	0.130
	² B ₁	² A ₂ ''	5.277		2.586	1.876	3.247	0.154				1.537	0.939	0.110
	² A ₂ , ² B ₁	² E''	5.273		2.591	1.878	3.223	0.172				1.855	0.671	0.065
	² B ₂ , ² A ₁	² E'	5.321		2.520	1.886	3.315	0.120				1.256	1.128	0.136
	¹ A ₁	¹ A ₁ '	5.192		2.212	1.883	3.146	0.163				1.272	0.828	0.112
Al ₂ As ₃ ⁺	³ B ₁	³ A ₂ ''	5.244		2.135	1.875	3.201	0.168				1.007	1.013	0.115
	³ B ₂ , ³ A ₁	³ E''	5.058		2.413	1.903	3.004	0.151				1.608	0.698	0.106
	¹ B ₁	¹ A ₂ ''	5.061		2.410	1.894	3.015	0.152				1.543	0.755	0.112
	¹ A ₁	¹ A ₁ '	5.424		2.864	1.853	3.401	0.170				1.739	1.034	0.091

both Al(s) and As(s) populations of all the electronic states are smaller than 2.0, implying small hybridization. Thus, most of the charge transferred from the Al atoms is mainly received by the As(p) orbitals.

The $^2\text{A}_1(\text{C}_{2v})$ ground state of Al_3As_2 is composed of $\text{Al}_1(\text{s}^{1.233}\text{p}^{1.209})$, $\text{Al}_2(\text{s}^{1.822}\text{p}^{0.731})$, and $\text{As}(\text{s}^{1.815}\text{p}^{3.615})$ Mulliken populations, while the corresponding populations for the $^2\text{B}_1(\text{C}_{2v})$ state are $\text{Al}_1(\text{s}^{1.859}\text{p}^{0.640})$, $\text{Al}_2(\text{s}^{1.844}\text{p}^{0.729})$, and $\text{As}(\text{s}^{1.851}\text{p}^{3.560})$, where we have omitted the d populations as they are <0.21 . The primary difference in the populations between these two states is in the s and p populations of the Al_1 atom. This is a consequence of the various electronic occupancies for the $5a_1$ and $2b_1$ orbitals. The $5a_1$ orbital has $\text{Al}_1(\text{s})$ as its principal component, while the $2b_1$ orbital contains a large contribution from $\text{Al}(\text{p}_x)$. Since the $2b_1$ orbital is fully occupied in the $^2\text{A}_1$ state, it comprises a large $\text{Al}_1(\text{p})$ population (1.209) together with an $\text{Al}_2(\text{p})$ population of 0.731 in the $^2\text{A}_1$ state compared to the corresponding populations of $\text{Al}_1(\text{p})$ (0.640) and $\text{Al}_2(\text{p})$ (0.729) in the $^2\text{B}_1$ state. On the other hand, a doubly occupied $5a_1$ orbital (and a singly occupied $2b_1$ orbital) in the $^2\text{B}_1$ state results in noticeably large $\text{Al}_1(\text{s})$ population (1.859) compared to the $\text{Al}_1(\text{s})$ population (1.233) of the $^2\text{A}_1$ state. Likewise, the compositions of the $2e'$ and $1e''$ orbitals and their occupancies determine the populations of the $^2\text{E}'$ state. This state exhibits a larger Al(p) population (0.892) and a smaller Al(s) (1.648) population. On the other hand, the $^2\text{E}''$ state has a larger Al(s) population of 1.843 and a smaller Al(p) (0.707) population. As can be seen from Table 1, the dipole moment of the $^2\text{A}_1(\text{C}_{2v})$ state is (-5.42 D) , which is larger in magnitude than that of the $^2\text{B}_1$ state (-1.29 D) . This is consistent with a greater charge transfer from Al to As in the former compared to the latter, as evidenced from the total Mulliken populations.

As seen from Table 2, the $\text{Al}_3\text{As}_2^+(D_{3h})$ positive ion exhibits four low-lying electronic states, namely $^3\text{A}_2'$, $^1\text{E}'$, $^3\text{E}''$, and $^1\text{E}''$. We kept the geometry of the positive ion fixed at the neutral $^2\text{E}'$ geometry, as we do not expect geometry relaxation to make a significant impact on the computed ionization energy. Furthermore, the lowest $^3\text{A}_2'$ state should retain the ideal D_{3h} structure. While the excited states of Al_3As_2^+ may distort, on the basis of our computed results on the neutral species, we expect the Jahn–Teller stabilization energy to be rather small. Removal of an electron from the $2e'$ orbital of the $^2\text{E}'(D_{3h})$ state of the neutral Al_3As_2 results in an open-shell $2e'^2$ electronic configuration. This yields three possible electronic states, namely a $^3\text{A}_2'$ state, a $^1\text{E}'$ state, and a $^1\text{A}_1'$ state. By Hund's rule, the $^3\text{A}_2'$ state should be the lowest among these in energy consistent with our MRSDCI results in Table 2. The $^1\text{E}'$ state should be the next one in the order of energy, while the higher $^1\text{A}_1'$ state would be the second root in the C_{2v} symmetry (the first root corresponding to $^1\text{A}_1$ being $^1\text{E}'$), and was thus not computed. As seen from Table 2, the $^3\text{A}_2'$ state is the ground state of Al_3As_2^+ , while the $^1\text{E}'$ state is 0.18 and 0.34 eV above the $^3\text{A}_2'$ state at the MRSDCI and MRSDCI+Q levels, respectively. Consequently, the positive ion would not distort in the ground state, but small geometrical distortions are anticipated in the excited states.

As seen from Table 2, the adiabatic ionization energy of Al_3As_2 is 6.84 eV at the MRSDCI level. The energy required to remove an electron from the close-shell $1e''$ orbital in the $^2\text{E}'(D_{3h})$ state of the neutral cluster would be larger. This process would result in two feasible electronic states with same configuration, namely $^3\text{E}''$ and $^1\text{E}''$. As seen from Table 2, these states are 1.28 and 1.90 eV above the $^3\text{A}_2'$ ground state of Al_3As_2^+ at the MRSDCI level. The $^1\text{A}_1'$ state, which arises from

the same configuration as the $^3\text{A}_2'$ ground state, is likely to be below the $^3\text{E}''$ and $^1\text{E}''$ states. Thus, there are at least four low-lying excited states for Al_3As_2^+ below 2 eV relative to the ground state.

As seen from Table 4, the $^3\text{A}_2'$ state of Al_3As_2^+ exhibits $\text{Al}(\text{s}^{1.539}\text{p}^{0.737})$ and $\text{As}(\text{s}^{1.800}\text{p}^{3.473})$ populations, compared to the $^2\text{E}'$ state of the neutral Al_3As_2 cluster whose populations are $\text{Al}(\text{s}^{1.648}\text{p}^{0.892})$ and $\text{As}(\text{s}^{1.804}\text{p}^{3.581})$. Consequently, the As(s) populations are nearly the same, while there is a significant depletion of the Al(s) population. This is fully consistent with the nature of the $2e'$ orbital of the neutral species in which the Al(s) orbital makes the principal contribution. The Al(s) population decreases from 1.648 to 1.539 and 1.487 in the $^3\text{A}_2'$ and $^1\text{E}'$ states, respectively. It can be concluded that the ionization process takes place predominantly at the Al sites. This also agrees with the lower ionization potential of Al compared to As.⁴⁰ On the other hand, both As(p) and Al(p) populations decrease when an $1e''$ electron is removed from the $^2\text{E}'$ state of Al_3As_2 . That is, as seen from Table 4, the As(p) and Al(p) populations of the $^3\text{E}''$ and $^1\text{E}''$ states (3.318–3.325 and 0.637–0.707) are smaller than those (3.581 and 0.892, respectively) of the $^2\text{E}'$ state of Al_3As_2 . This agrees with the fact that the $1e''$ orbital is predominantly made of the p orbitals of the As and Al atoms. Since both As and Al sites are involved in the ionization process, higher ionization energies are required for the $^3\text{E}''$ and $^1\text{E}''$ states.

Next we consider the anion, as there is significant interest in the anion photoelectron spectroscopy of these species. As seen from Table 2, the lowest state of the Al_3As_2^- anion is $^1\text{A}_1'$ with a regular trigonal bipyramid (D_{3h}) geometry. The closed-shell ground state of the Al_3As_2^- anion can be justified on the basis of the low-lying states of the neutral Al_3As_2 , which are $^2\text{E}'$ and $^2\text{E}''$ states. Attachment of an electron to either the open-shell $2e'$ orbital in $^2\text{E}'$ or the $1e''$ orbital in $^2\text{E}''$ results in the same closed-shell electronic configuration (see Table 3), yielding a $^1\text{A}_1'$ ground state for the Al_3As_2^- anion. Hence the anion would not undergo Jahn–Teller distortion and remains in its ideal D_{3h} geometry. A critical comparison of the Mulliken populations of the neutral cluster and the anion reveals that the electron attachment increases the charge density of the Al(s) and As(p) orbitals. As presented in Table 4, the Al(s) and As(p) Mulliken populations of the $^1\text{A}_1'$ state of Al_3As_2^- are (1.750 and 3.719) significantly larger than the corresponding values (1.648 and 3.581) of the $^2\text{E}'$ state of Al_3As_2 . This is because the $2e'$ orbital is principally π -bonding between the As atoms. Consequently, the As–As bond is strengthened in this state due to a filled $2e'$ orbital. Thus, the As–As bond length (2.616 Å) in the $^1\text{A}_1'$ state of Al_3As_2^- is contracted compared to the corresponding As–As (2.704 Å) bond length in the $^2\text{E}'$ state of Al_3As_2 at the MRSDCI level. Our computed electron affinity for Al_3As_2 is 2.33 eV at the MRSDCI level. Although it appears that there is no experimental result for the electron affinity of Al_3As_2 , Xu et al.⁷ have obtained the EA of In_3P_2 as 2.07 eV using anion photoelectron spectroscopy. We expect the EA of Al_3As_2 to be larger than In_3P_2 primarily due to significant participation of the As orbitals in the LUMO of Al_3As_2 . Thus, our calculation exhibits the correct trend consistent with the experimental result of Xu et al.⁷ on the analogous In_3P_2 .

We computed the atomization energy of Al_3As_2 in a two-step sequential process. As seen from Table 2, the dissociation energy for



is computed as 5.58 and 5.69 eV at the MRSDCI and MRSDCI+Q levels, respectively. We also computed the at-

omization energy needed to separate Al_3 into three aluminum atoms (^2P) as 3.32 and 3.58 eV at the same levels of theory. By combining the two values, the atomization energy of Al_3As_2 to form three separated Al and two As atoms is deduced as 8.90 and 9.27 eV at the MRSDCI and MRSDCI+Q levels. Because of limitations in the basis sets and electron correlation techniques, we believe that the MRSDCI+Q result of 9.27 eV should be closer to the true atomization energy of the cluster. These values confirm that the As–As and Al–As bonds play a more important role than the Al–Al bonds in the Al_3As_2 cluster.

B. Electronic States of Al_2As_3 , Al_2As_3^+ , and Al_2As_3^- . Table 2 shows the optimized geometries and energy separations for all of the doublet electronic states of Al_2As_3 with D_{3h} geometries. The locations of the atoms in the Al_2As_3 cluster are shown in Figure 1. In contrast to Al_3As_2 , it is found that the Al_2As_3 cluster has an undistorted trigonal bipyramid (D_{3h}) geometry since the ground state is a $^2\text{A}_2''(D_{3h})$ state. The first excited $^2\text{E}''(D_{3h})$ state is 1.02 eV higher than the $^2\text{A}_2''$ state at the MRSDCI level. Another doublet state, namely $^2\text{E}'(D_{3h})$, is even higher than the $^2\text{E}''(D_{3h})$ state in energy. It is expected that both $^2\text{E}''$ and $^2\text{E}'$ states would undergo Jahn–Teller distortion, although the distortion energy is anticipated to be less than 0.4 eV. The second half of Table 1 shows our calculated results for two distorted electronic states, namely $^2\text{A}_2$ and $^2\text{A}_1$ (both C_{2v}), which are Jahn–Teller components of the $^2\text{E}''$ and $^2\text{E}'(D_{3h})$ states, respectively. Although the $^2\text{A}_2(C_{2v})$ state is lower than the corresponding $^2\text{E}''(D_{3h})$ state, due to a smaller Jahn–Teller stabilization energy of ~ 0.33 eV, the $^2\text{A}_2(C_{2v})$ state is still 0.69 eV higher than the undistorted $^2\text{A}_2''(D_{3h})$ state at the MRSDCI level.

The distortion in the excited states of Al_2As_3 can be illustrated by comparing the geometries of the $^2\text{A}_2(C_{2v})$ and $^2\text{E}''(D_{3h})$ states. As seen from lower parts of Tables 1 and 2, three As atoms form an equilateral triangular base in the $^2\text{E}''(D_{3h})$ state of Al_2As_3 with equilibrium As–As bond lengths of 2.457 Å. The equilateral triangular base is distorted into an isosceles triangle (the apex angle is 55.6°) in the $^2\text{A}_2(C_{2v})$ state in which the elongated isosceles sides are $\text{As}_1\text{--As}_2$ or $\text{As}_1\text{--As}_3$ (2.485 Å) and a contracted base with an $\text{As}_2\text{--As}_3$ bond length of 2.319 Å. The average As–As bond length of the three sides in the $^2\text{A}_2(C_{2v})$ state is 2.430 Å which is comparable to the As–As bond length (2.457 Å) in the $^2\text{E}''(D_{3h})$ state. The distance between the axial Al atoms in the $^2\text{A}_2(C_{2v})$ state is 4.865 Å, which is close to the Al–Al bond (4.828 Å) in the $^2\text{E}''(D_{3h})$ state, suggesting little distortion of the axial Al atoms. The $^2\text{E}'(D_{3h})$ state of Al_2As_3 exhibits the same features in that the equatorial atoms depart from an ideal equilateral triangular configuration into an isosceles triangular configuration, while the axial atoms are not affected.

The $1\text{a}_1'$ orbital (1a_1 in C_{2v}) of Al_2As_3 is predominantly $\text{As}_1\text{--}(s) + \text{As}_2(s) + \text{As}_3(s)$, while the $2\text{a}_1'$ orbital (4a_1 in C_{2v}) is made of $\text{Al}_1(s) + \text{Al}_2(s)$. The $3\text{a}_1'$ orbital (5a_1 in C_{2v}) is composed of $[\text{As}_1(s) + \text{As}_2(s) + \text{As}_3(s)]$ and $[\text{As}_2(p_y) + \text{As}_3(p_y)]$. The $1\text{e}'$ orbital (2a_1 and 1b_2 in C_{2v}) consists of two orthogonal degenerate linear combinations, namely $2\text{As}_1(s) - [\text{As}_2(s) + \text{As}_3(s)]$ and $[\text{As}_2(s) - \text{As}_3(s)]$, while the $2\text{e}'$ orbital (3a_1 and 2b_2 in C_{2v}) is composed of $[\text{As}_2(p_z) - \text{As}_3(p_z)]$ and $[\text{As}_2(p_y) - \text{As}_3(p_y)]$. The $3\text{e}'$ orbital (6a_1 and 3b_2 in C_{2v}) is made up of $\text{As}_1(p_y) + \text{As}_2(p_y) + \text{As}_3(p_y)$ and $\text{As}_2(p_y) - \text{As}_3(p_y)$. The $1\text{e}''$ (2b_1 and 1a_2 in C_{2v}) orbital has two orthogonal linear combinations, namely $2\text{As}_1\text{--}(p_x) - [\text{As}_2(p_x) + \text{As}_3(p_x)] + [\text{Al}_1(p_y) - \text{Al}_2(p_y)]$ and $[\text{As}_2(p_x) - \text{As}_3(p_x)] + [\text{Al}_1(p_z) - \text{Al}_2(p_z)]$. The $1\text{a}_2''$ (1b_1 in C_{2v}) orbital is composed of $\text{Al}_1(s) - \text{Al}_2(s)$, while the $2\text{a}_2''$ orbital (3b_1 in

C_{2v}) is $\text{Al}_1(p_x) + \text{Al}_2(p_x)$ combined with a nonnegligible contribution from $\text{Al}_1(s) - \text{Al}_2(s)$.

Table 3 outlines the leading configurations contributing to the electronic states of Al_2As_3 . As seen from the table, all of the D_{3h} electronic states of Al_2As_3 have $(1\text{a}_1'^2 2\text{a}_1'^2 3\text{a}_1'^2 1\text{e}'^4 2\text{e}'^4 - 1\text{a}_2'^2)$ in common, while $(1\text{a}_1'^2 2\text{a}_1'^2 3\text{a}_1'^2 5\text{a}_1'^2 1\text{b}_2'^2 2\text{b}_2'^2 1\text{b}_1'^2 2\text{b}_1'^2)$ is common to the $^2\text{A}_2$ and $^2\text{A}_1$ (C_{2v}) states. As evidenced from the table, the principal distinction between the low-lying $^2\text{A}_2''$ and $^2\text{E}''(D_{3h})$ electronic states originates from different electronic occupancies for the $1\text{e}''$ and $2\text{a}_2''$ orbitals. The $1\text{e}''$ orbital exhibits a bond between the Al(p) and As(p), while the $2\text{a}_2''$ orbital is antibonding with respect to the two Al p and s orbitals along the x axis. The $1\text{e}''$ orbital is fully occupied in the $^2\text{A}_2''$ state, which has only an electron in $2\text{a}_2''$, resulting in shorter Al–As bonds (2.560 Å) in the $^2\text{A}_2''$ state compared to the corresponding Al–As bonds (2.800 Å) in the $^2\text{E}''$ state at the MRSDCI level. On the other hand, the $^2\text{E}''$ state has a filled $2\text{a}_2''$ orbital, but a partially filled $1\text{e}''$ orbital (three electrons) thus resulting in an elongated Al–Al (4.828 Å) bond in contrast to a shorter Al–Al bond (4.184 Å) in the $^2\text{A}_2''$ state. The $3\text{e}'$ orbital exhibits repulsive interactions among the three As atoms. Hence the $^2\text{E}'$ state, which is the only state with an electron in the $3\text{e}'$ orbital, has the longest As–As bond length (2.950 Å) among the three doublet states of the Al_2As_3 cluster. Likewise, the difference in the properties between the two distorted $^2\text{A}_2$ and $^2\text{A}_1$ states (C_{2v}) arises as a consequence of the occupancies of the 5a_1 and 1a_2 orbitals.

Table 4 displays the Mulliken populations on the electronic states of Al_2As_3 . Most of the previous discussions for the populations of Al_3As_2 hold for Al_2As_3 . All of the states of Al_2As_3 manifest Al^+As^- polarities of bonds. The As(p) contributions to the electronic states of Al_2As_3 are noticeably smaller than the corresponding values for Al_3As_2 . This is consistent with the fact that the charge transferred from Al to As is shared by the three As atoms, while in the case of Al_3As_2 it is shared by two As atoms. Thus, the extent of charge transfer to each As atom is smaller in the case of Al_2As_3 .

As can be inferred from Table 4, the $^2\text{A}_2''$ and $^2\text{E}''(D_{3h})$ states are composed of $\text{As}(s^{1.876} p^{3.247})$ and $\text{Al}(s^{1.537} p^{0.939})$ and $\text{As}(s^{1.878} p^{3.223})$ and $\text{Al}(s^{1.855} p^{0.671})$ populations, respectively. A striking contrast between the two states is in the population of the Al atom, which is fully consistent with the nature of the orbitals. As indicated earlier, Al(p) participation is enhanced in the $1\text{e}''$ orbital. Although this is fully occupied in the $^2\text{A}_2''$ state, it is only partially occupied in the $^2\text{E}''$ state. This leads to a larger Al(p) population (0.939) in the $^2\text{A}_2''$ state. On the other hand, $2\text{a}_2''$ has Al(s) participation and it is fully occupied in the $^2\text{E}''$ state, but half-filled in the $^2\text{A}_2''$ state leading to a noticeably higher Al(s) population (1.855) in the $^2\text{E}''$ state compared to that of the $^2\text{A}_2''$ state (1.537). Likewise, the orbital analysis for the distorted $^2\text{A}_2$ and $^2\text{A}_1$ (C_{2v}) states explains a larger Al(s) population (1.857) in the $^2\text{A}_2$ state than that of the $^2\text{A}_1$ state (1.278), but a smaller Al(p) population (0.661) than that of the $^2\text{A}_1$ state (1.137).

The dissociation energy to dissociate Al_2As_3 into As_3 and 2Al , that is



is computed as 7.59 and 7.71 eV at the MRSDCI and MRSDCI+Q levels, respectively. Combining these results with the atomization energy of As_3 to yield three $\text{As}(^4\text{S})$ atoms (5.18 eV) at the same level,³⁹ we obtain the atomization energy of Al_2As_3 as 12.77 and 13.12 eV at the MRSDCI MRSDCI+Q levels, respectively. Previous studies on As_2 ³⁷ and As_3 ³⁹ reveal

that the MRSDCI atomization energy for As₃ was considerably lower than the experimental value. Thus, we anticipate the MRSDCI calculations to underestimate the atomization energy of Al₂As₃. While the MRSDCI+Q technique would correct this to some extent, we anticipate the experimental atomization energy for Al₂As₃ to be larger than 13.5 eV, and this value should be treated as a lower bound.

Table 2 displays the energy separations of four low-lying electronic states of the Al₂As₃⁺(D_{3h}) positive ion, while Table 3 presents their leading configurations. As can be inferred from Table 2, the adiabatic ionization energy to remove an electron from the 2a₂⁺ HOMO of the ²A₂⁺(D_{3h}) ground state of the neutral Al₂As₃ cluster is 6.61 eV at the MRSDCI level and 6.87 eV at the MRSDCI+Q level. This process creates a closed-shell ¹A₁⁺ ground state for the cation of the cluster. The energy needed to remove an electron from the 3a₁⁺ orbital of the ²A₂⁺ neutral ground state is larger as expected. The removal of an electron from the 3a₁⁺ orbital creates two excited electronic states, namely the ³A₂⁺ and ¹A₂⁺ states. On the other hand, the removal of an electron from the 1e⁺ orbital of the ²A₂⁺ state leads to the ³E⁺ and ¹E⁺ excited states of which ³E⁺ would be lower. As seen from Table 2, the ³A₂⁺ and ³E⁺ states are 7.66 and 7.96 eV higher than Al₂As₃, respectively. The ¹A₂⁺ state is 8.92 eV higher at the MRSDCI level from which the ³A₂⁺ – ¹A₂⁺ energy splitting is obtained as 1.26 eV. The corresponding MRSDCI+Q result can be deduced from Table 2.

As can be seen from Table 4, there is a considerable decrease in the Al 3s and 3p populations as a result of the ionization process. This is consistent with the nature of the 2a₂⁺ HOMO, which has Al(3p) and Al(3s) as its principal components. This is anticipated in view of the smaller ionization potential of Al compared to As, and thus ionization takes place predominantly at the axial Al sites.

The Al₂As₃[−] anion has a closed-shell ground ¹A₁[−] state with a regular trigonal bipyramid D_{3h} structure. Table 2 exhibits the geometry and energy of the ¹A₁[−] state of Al₂As₃[−]. As seen from Table 2, upon electron attachment the As–As (2.495 Å) bonds are contracted, while both Al–Al (4.468 Å) and Al–As (2.658 Å) bonds are elongated in the ¹A₁[−] state of the anion compared to the corresponding bonds in the neutral ²A₂⁺ ground state. It can be inferred from Table 3 that the attached electron occupies the 2a₂[−] orbital, which is composed of the p_x orbitals of the axial Al atoms overlapping with opposite signs along the x-axis. Thus, the electron attachment to the 2a₂[−] orbital results in the elongation of the Al–Al axial bond. However, the electron attachment process is far more complicated in that after the attachment, there is considerable rearrangement of electronic density, as evidenced by the contractions of the As–As bonds at the base. This is also consistent with the Mulliken populations in Table 4. It can be inferred that the ¹A₁[−] state of the anion is composed of As(s^{1.853}p^{3.401}) and Al(s^{1.739}p^{1.034}) populations compared to the As(s^{1.876}p^{3.247}) and Al(s^{1.537}p^{0.939}) populations of the neutral ²A₂⁺ ground state. Thus, although initially the electron attachment takes place at the 2a₂[−] orbital, there is a significant rearrangement of electronic density. In the final picture, the As and Al atoms share the excess electron density due to the attachment process, although the Al atoms receive greater charge density compared to the As atoms.

The electron affinity (EA) of Al₂As₃ is calculated as 2.05 eV at the MRSDCI level, and it is smaller than the corresponding EA (2.33 eV) of Al₃As₂. However, we expect the two EAs to be close, and thus the theoretical value for Al₂As₃ is underestimated. Xu et al.⁷ obtained the EA of In₂P₃ as 2.72 eV, while Taylor et al. obtained the EA of Ga₂P₃ as 3.03 eV. The

TABLE 5: Comparison of the Geometries and Energy Separations for the Electronic States of Al₃As₂ and Ga₃As₂ with C_{2v} Structures

	Al ₃ As ₂		Ga ₃ As ₂	
	² A ₁	² B ₁	² A ₁	² B ₁
M ₂ –M ₁ –M ₃ (deg)	69.5	71.7	67.5	70.0
X ₁ –M ₁ –X ₂ (deg)	67.9	51.1	70.8	52.6
X ₁ –M ₂ –X ₂ (deg)	59.9	53.8	61.4	55.2
M ₁ –M ₂ (Å)	3.641	3.902	3.702	3.986
M ₂ –M ₃ (Å)	4.153	4.568	4.114	4.572
M ₁ –X ₁ (Å)	2.384	2.793	2.401	2.829
M ₂ –X ₁ (Å)	2.667	2.661	2.725	2.707
X ₁ –X ₂ (Å)	2.663	2.410	2.782	2.507
E (CASSCF) (eV)	0.00	0.51	0.00	0.03
E (MRSDCI) (eV)	0.00	0.56	0.00	0.02
E (MRSDCI+Q) (eV)	0.00	0.47	0.00	0.005

TABLE 6: Comparison of the Geometries and Energy Separations for the Electronic States of Al₃As₂ and Ga₃As₂ with the D_{3h} Trigonal Bipyramid Structures

system	state		MRSDCI				
			M–M (Å)	M–X (Å)	X–X (Å)	X–M–X (deg)	E (eV)
	C _{2v}	D _{3h}					
Al ₃ As ₂	² A ₁ , ² B ₂	² E'	3.748	2.552	2.704	64.0	0.27
	² A ₂ , ² B ₁	² E''	4.142	2.691	2.469	54.6	0.62
	⁴ A ₁	⁴ A ₁ ^{''}	3.205	2.499	3.360	84.5	0.73
	⁴ B ₁ , ⁴ A ₂	⁴ E''	3.193	2.517	3.427	85.8	1.49
	⁴ A ₁ , ⁴ B ₂	⁴ E'	3.549	2.611	3.236	76.6	2.31
Ga ₃ As ₂	² A ₁ , ² B ₂	² E'	3.812	2.591	2.735	63.7	0.26
	² A ₂ , ² B ₁	² E''	4.184	2.724	2.518	55.1	0.19
	⁴ B ₂	⁴ A ₂ [']	2.828	2.517	3.831	99.1	1.00
	⁴ A ₂	⁴ A ₁ ^{''}	3.274	2.538	3.387	83.7	1.10
	⁴ A ₁ , ⁴ B ₂	⁴ E'	3.637	2.685	3.347	77.1	1.91
	⁴ B ₁ , ⁴ A ₂	⁴ E''	3.093	2.646	3.905	95.1	2.10

EAs of the corresponding As clusters are expected to be smaller and thus our computed results exhibit the correct trend. The measured EAs are expected to be larger than our computed results, especially for Al₂As₃.

Although it appears that spectra of the Al₃As₂ and Al₂As₃ clusters are yet to be obtained, there are negative ion photoelectron spectroscopic studies of mixed indium phosphide clusters^{4–5,7,8} and gallium phosphide clusters.^{15,16} Mandich and co-workers⁹ have obtained the photodissociation spectra of the indium phosphide clusters ranging in sizes from 5 to 14 atoms. The photoelectron spectra of In₂P₂[−] and In₂P₃[−] obtained by Xu et al.⁷ reveal that each of the species exhibits two peaks. The In₃P₂[−] anion exhibits two peaks very close to each other and their intensities are almost same, consistent with two nearly-degenerate electronic states computed here for the isovalent Al₃As₂. The two peaks exhibited by In₂P₃[−] have different intensities and are well resolved compared to the In₃P₂[−] peaks. A possible explanation for this is that the two excited electronic states of the neutral In₂P₃ cluster, which correspond to the two peaks, are well separated in energy. This is fully consistent with the computed excited states shown in Table 7 for the isovalent Al₂As₃ and Ga₂As₃ clusters, which exhibit well-resolved excited states above their respective ground states. The photodissociation experiments⁷ suggest that the In–P bonding is the dominant chemical interaction in the indium phosphide clusters ranging in sizes 5–14. This conclusion is fully supported by our computations, which show that the M–X bonds are more important than the M–M or X–X bonds in the determination of the geometries and energy separations of the M₃X₂ and M₂X₃ species.

Taylor et al.¹⁶ have obtained the anion photoelectron spectra of Ga_xP_y[−] anions of varying stoichiometry up to 18 atoms. In a subsequent investigation, Taylor et al.¹⁵ have obtained

TABLE 7: Comparison of the Geometries and Energy Separations for the Electronic States of Al_2As_3 and Ga_2As_3 with the D_{3h} Trigonal Bipyramid Structures

state			MRSDCI				
system	C_{2v}	D_{3h}	As–As (Å)	As–Al (Å)	Al–Al (Å)	Al–As–Al (deg)	E (eV)
Al ₂ As ₃	² B ₁	² A ₂ ''	2.556	2.560	4.184	109.6	0.00
	² A ₂ , ² B ₁	² E''	2.457	2.800	4.828	119.1	1.02
	² A ₁ , ² B ₂	² E'	2.950	2.456	3.539	92.2	1.49
state			MRSDCI				
system	C_{2v}	D_{3h}	As–As (Å)	As–Ga (Å)	Ga–Ga (Å)	Ga–As–Ga (deg)	E (eV)
Ga ₂ As ₃	² B ₁	² A ₂ ''	2.563	2.589	4.249	110.3	0.00
	² A ₂ , ² B ₁	² E''	2.468	2.868	4.978	120.4	0.84
	² A ₁ , ² B ₂	² E'	2.533	2.820	4.822	117.5	1.88

TABLE 8: Mulliken Populations for the Electronic States of Al_3As_2 and Ga_3As_2

gross population														
state		total			M ₁			M ₂			X			
system	C _{2v}	D _{3h}	M ₁	M ₂	X	s	p	d	s	p	d	s	p	d
Al ₃ As ₂	² A ₁		2.547	2.623	5.605	1.233	1.209	0.105	1.822	0.731	0.070	1.815	3.615	0.175
	² B ₁		2.554	2.643	5.581	1.859	0.640	0.055	1.844	0.729	0.070	1.851	3.560	0.170
	² A ₁ , ² B ₂	² E'	2.622		5.568	1.648	0.892	0.082				1.804	3.581	0.183
	² B ₁ , ² A ₂	² E''	2.615		5.577	1.843	0.707	0.065				1.847	3.554	0.176
Ga ₃ As ₂	² A ₁		2.756	2.698	5.424	1.425	1.218	0.113	1.835	0.785	0.078	1.821	3.462	0.141
	² B ₁		2.622	2.725	5.464	1.864	0.689	0.069	1.844	0.802	0.079	1.873	3.456	0.135
	² A ₁ , ² B ₂	² E'	2.738		5.398	1.729	0.919	0.090				1.819	3.431	0.148
	² B ₁ , ² A ₂	² E''	2.688		5.468	1.850	0.762	0.076				1.803	3.473	0.192

TABLE 9: Comparison of the Mulliken Populations of the Electronic States of Al_2As_3 and Ga_2As_3

system	state		total		gross population					
	C_{2v}	D_{3h}	X	M	X			M		
					s	p	d	s	p	d
Al_2As_3	$^2\text{B}_1$	$^2\text{A}_2''$	5.277	2.586	1.876	3.247	0.154	1.537	0.939	0.110
	$^2\text{A}_2, ^2\text{B}_1$	$^2\text{E}''$	5.273	2.591	1.878	3.223	0.172	1.855	0.671	0.065
	$^2\text{A}_1, ^2\text{B}_2$	$^2\text{E}'$	5.321	2.520	1.886	3.315	0.120	1.256	1.128	0.136
Ga_2As_3	$^2\text{B}_1$	$^2\text{A}_2''$	5.184	2.724	1.872	3.160	0.152	1.602	1.012	0.110
	$^2\text{A}_2, ^2\text{B}_1$	$^2\text{E}''$	5.237	2.645	1.872	3.199	0.166	1.909	0.682	0.054
	$^2\text{A}_1, ^2\text{B}_2$	$^2\text{E}'$	5.217	2.675	1.886	3.176	0.155	1.892	0.723	0.060

vibrationally resolved anion photoelectron spectra of Ga_2P_3^- and a few three-atom clusters. The spectra of Ga_2P_3^- and Ga_3P_2^- differ in that while the spectra of the former exhibit three resolved peaks identified as X, A, and B, the latter exhibits a broad single peak, and only the ground state of the Ga_3P_2^- cluster could be assigned. The Ga_2P_3^- anion has been studied further with high-resolution vibrationally resolved spectra. The ground-state peak is centered at 3.14 eV, while the first excited state appears at 0.21 eV above this. On the basis of Franck–Condon simulations, the origin of the X peak was located at 3.004 eV.

IV. Comparison

Electronic States of Al_2As_3 and Ga_2As_3 . The electronic states of the related Ga_2As_3 cluster have been studied using matrix-isolated ESR spectroscopy by Van Zee et al.¹² and by a comparable theoretical study³⁰ as well as the density functional theory², and it would thus be enlightening to compare the two clusters. Table 7 shows the geometries and energy separations of the doublet electronic states of the two clusters with trigonal bipyramid D_{3h} geometries. As seen from the table, there are many similarities between the two clusters. Both clusters share a $^2\text{A}_2''(D_{3h})$ ground state and a $^2\text{E}''$ first excited state.

Van Zee et al.¹² have obtained the ESR spectrum of Ga_2As_3 produced by laser-heating of GaAs crystals followed by isolation in Ar and Kr matrices. The ESR spectrum revealed a $S = 1/2$ ground state for Ga_2As_3 . The hyperfine pattern was found to be consistent with a structure containing three equivalent As

atoms suggesting a regular trigonal bipyramidal structure. From the observed hyperfine pattern of Ga_2As_3 , Van Zee et al.¹² inferred that the unpaired electron resides on an orbital, which is entirely on the two axial gallium atoms. All of these features are in complete accord with our computations on the isovalent Al_2As_3 cluster, which is predicted to have a $^2\text{A}_2''$ ground state with an ideal D_{3h} structure. As discussed earlier, in the ground state of Al_2As_3 , the singly occupied $2a_2''$ HOMO is composed of $\text{Al}_1(p_x) + \text{Al}_2(p_x)$ with a nonnegligible contribution from $\text{Al}_1(s) - \text{Al}_2(s)$. For the case of Ga_2As_3 , the unpaired $2a_2''$ electron is localized on the two axial Ga atoms. Thus, our theoretical calculations fully support the experimental results of Van Zee et al.¹²

Table 7 compares the geometries and energy separations of the electronic states of the two clusters. As seen from the table, both clusters have almost the same As–As bond lengths (~ 2.56 Å) and M–As–M bond angles ($\sim 110^\circ$) in their ground states, implying that the As–As bonds are quite similar. It can be seen from Table 7 that the actual As–As bond lengths in the $^2\text{A}_2''$ ground state are 2.556 and 2.563 Å. As seen from Table 7, although the first excited states of the two clusters are similar, the second excited states differ primarily due to the differences in the characteristics of the metal–metal bonding.

Electronic States of Al_3As_2 and Ga_3As_2 . The isovalent Ga_3As_2 cluster has previously been studied theoretically,^{2,30} and thus it would be interesting to compare the properties of the two clusters. Table 5 shows the optimized geometries and energy

separations for the distorted ²A₁ and ²B₁ electronic states of these clusters with the C_{2v} geometries, while Table 6 compares the equilibrium geometries and energy separations of the undistorted D_{3h} states with trigonal bipyramid structures. As seen from the tables, all these species have the ²E' and ²E'' states as the lowest-lying states in D_{3h} symmetry; both states undergo Jahn–Teller distortion resulting in distorted states. As seen from Table 5, both clusters possess the same distorted ²A₁ ground state with C_{2v} geometries. We have already considered Jahn–Teller distortion extensively in these clusters. As inferred from Table 5, the As–As distances in the ²A₁(C_{2v}) ground state are 2.663 and 2.782 Å for Al₃As₂ and Ga₃As₂, respectively. The values are comparable to the corresponding As–As bonds in the undistorted ²E' state, viz., 2.719 and 2.762 Å, suggesting little changes to the two As atoms due to Jahn–Teller distortion. However, the three metal atoms depart from their equilateral M₃ base position in the D_{3h} states by Jahn–Teller distortion resulting in contracted M₁–M₂ (or M₁–M₃) and elongated M₂–M₃ bonds.

The As–As bond lengths in the corresponding states of Al₃As₂ and Ga₃As₂ are quite similar. For example, the shortest As–As bond distances in the distorted ²B₁ state are not too far from the diatomic As₂³⁷ distance. The metal–metal bond lengths in the ground states of M₃ are 2.521 and 2.58 Å^{38,40} for M = Al and Ga respectively, which are much shorter compared to the Al–Al (3.5–4.1 Å) and Ga–Ga (3.7–4.1 Å) bonds in the ground states of M₃As₂. Evidently, the M–M bonds in M₃As₂ are dramatically weakened by the interaction between the metal and As atoms.

As evidenced from both Tables 5 and 6, there is a significant difference between Al₃As₂ and Ga₃As₂ with regard to the ²B₁–²A₁ and ²E''–²E' energy separations. Whereas the ²B₁(²E'') and ²A₁(²E') electronic states are virtually degenerate for Ga₃As₂, this is not the case for Al₃As₂. As seen from Table 5, the ²B₁–²A₁(C_{2v}) energy separations are 0.56 and 0.47 eV at the MRSDCI and MRSDCI+Q levels, respectively, for Al₃As₂, while the corresponding values are 0.02 and 0.005 eV for Ga₃As₂ at the same levels of theory. As seen from Table 6, a similar trend is seen for the ²E''–²E' energy separations, and in fact at the MRSDCI level of theory, the ²E'' state is 0.07 eV lower than ²E' for Ga₃As₂. This requires explanation in view of the fact that Al and Ga are similar in many other ways. This apparent anomaly can be rationalized on the basis of the bonding and Mulliken populations of the two clusters. As evidenced from Table 8, while the metal and As Mulliken populations are so similar for the ²B₁ state, the corresponding populations for the ²A₁ state differ substantially for the Ga and Al clusters. The Al₁(3s) population (1.233) is substantially reduced compared to the Ga₁(4s) population of 1.425 in the ²B₁ state, and the As(4p) population in Al₃As₂ increases to 3.615 compared to 3.462 in Ga₃As₂. This suggests increased charge transfer from Al(3s) to As(4p) for the ²A₁ state of Al₃As₂ resulting in enhanced ionicity in the case of Al₃As₂ cluster compared to Ga₃As₂. Consequently, a larger charge transfer stabilizes the ²A₁ state to a greater extent for Al₃As₂ compared to Ga₃As₂.

Although all of the quartet states of M₃As₂ are much higher than the ground state due to occupied antibonding orbitals, there exists notable differences in the energy order. As seen from Table 6, the three quartet states, namely ⁴A₂'', ⁴E'', and ⁴E' of Al₃As₂ are 0.73, 1.49, and 2.31 eV higher than the ground state, respectively. But the quartet states of Ga₃As₂ are more closely spaced in that the ⁴A₂', ⁴A₁'', ⁴E', and ⁴E'' states are 1.00, 1.10, 1.91, and 2.10 above the ground state of Ga₃As₂. This is primarily due to the fact⁴¹ that the J-weighted ⁴S–²D separation

for As is 10 790 cm^{–1}, and it is lower than the corresponding separation of 11 371 cm^{–1} for P.

Acknowledgment. This research was support by the U.S. National Science Foundation under grant CHE9814056. P.Y.F. thanks Dr. Zou, the ex-director of Shanghai Metallurgy Institute, for facilitating this cooperation.

References and Notes

- O'Brien, S. C.; Liu, Y.; Zhang, Q. L.; Heath, J. R.; Tittel, F. K.; Curl, R. F.; Smalley, R. E. *J. Chem. Phys.* **1986**, *84*, 4074. Liu, Y.; Zhang, L.; Tittel, F. K.; Curl, R. F.; Smalley, R. E. *J. Chem. Phys.* **1986**, *85*, 7434.
- Wang, L.; Chibante, L. P. F.; Tittel, F. K.; Curl, R. F.; Smalley, R. E. *Chem. Phys. Lett.* **1990**, *172*, 335. Lou, L.; Wang, L.; Chibante, P. F.; Laaksonen, R. T.; Nordlander, P.; Smalley, R. E. *J. Chem. Phys.* **1991**, *94*, 8015. Lou, L.; Nordlander, P.; Smalley, R. E. *J. Chem. Phys.* **1992**, *97*, 1858.
- Jin, C.; Taylor, K.; Concicao, J.; Smalley, R. E. *Chem. Phys. Lett.* **1990**, *175*, 17.
- Arnold, C. C.; Neumark, D. M. *J. Chem. Phys.* **1994**, *99*, 3353.
- Arnold, C. C.; Neumark, D. M. *J. Chem. Phys.* **1994**, *100*, 1797. Arnold, C. C.; Neumark, D. M. *Can. J. Phys.* **1994**, *72*, 1322.
- Bernstein, E. R. *Atomic and Molecular Clusters. Stud. Phys. Theor. Chem.* **1990**, *68*, 69.
- Xu, C.; deBeer, E.; Arnold, D. W.; Neumark, D. M. *J. Chem. Phys.* **1994**, *101*, 5406.
- Burton, G. R.; Xu, C.; Arnold, C. C.; Neumark, D. M. *J. Chem. Phys.* **1996**, *104*, 2757.
- Kolenbrander, K. D.; Mandich, M. L. *J. Chem. Phys.* **1990**, *92*, 4759. Rinnen, K.-D.; Kolenbrander, K. D.; DeSantolo, A. M.; Mandich, M. L. *J. Chem. Phys.* **1992**, *96*, 4088.
- Rasanen, M.; Heimbroke, L. A.; Schwartz, G. P.; Bondybey, V. E. *J. Chem. Phys.* **1986**, *85*, 86.
- Li, S.; Van Zee, R. J.; Weltner, W. Jr. *J. Phys. Chem.* **1993**, *97*, 11393. *J. Chem. Phys.* **1994**, *100*, 7079.
- Van Zee, R. J.; Li, S.; Weltner, W. Jr. *J. Chem. Phys.* **1993**, *98*, 4335.
- Xu, C.; Burton, G. R.; Taylor, T. R.; Neumark, D. M. *J. Chem. Phys.* **1997**, *107*, 3428.
- Xu, C.; Taylor, T. R.; Burton, G. R.; Neumark, D. M. *J. Chem. Phys.* **1998**, *108*, 1395.
- Taylor, T. R.; Asmis, K. R.; Gomez, H.; Neumark, D. M. *Eur. Phys. J.*, in press. Asmis, K. R.; Taylor, T. R.; Neumark, D. M. *Chem. Phys. Lett.* **1999**, *308*, 347. Taylor, T. R.; Neumark, D. M., private communication, 1999.
- Taylor, T. R.; Asmis, K. R.; Xu, C.; Neumark, D. M. *Chem. Phys. Lett.* **1998**, *297*, 133.
- Lou, L.; Wang, L.; Chibante, L. P. F.; Laaksonen, R. T.; Nordlander, P.; Smalley, R. E. *J. Chem. Phys.* **1991**, *94*, 8015.
- Lou, L.; Nordlander, P.; Smalley, R. E. *J. Chem. Phys.* **1992**, *97*, 1858.
- Wheeler, R. G.; LaiHing, K.; Wilson, W. L.; Duncan, M. A. *J. Chem. Phys.* **1988**, *88*, 2831.
- LaiHing, K.; Chen, P. Y.; Duncan, M. A. *J. Phys. Chem.* **1987**, *91*, 6521.
- Bishop, M. B.; LaiHing, K.; Cheng, P. Y.; Peshcke, M.; Duncan, M. A. *J. Phys. Chem.* **1989**, *93*, 1566.
- Willey, K. F.; LaiHing, K.; Taylor, T. G.; Duncan, M. A. *J. Phys. Chem.* **1993**, *97*, 7435.
- Micic, O. I.; Sprague, J. R.; Curtis, C. J.; Jones, K. M.; Machol, J. L.; Nozik, A. J.; Giessen, B.; Flugel, B.; Mohs, G.; Peyghambarian, N. *J. Phys. Chem.* **1995**, *99*, 7754.
- MacDougall, J. E.; Eckert, H.; Stucky, G. D.; Herron, N.; Wang, Y.; Moller, K.; Bein, T.; Cox, D. *J. Am. Chem. Soc.* **1989**, *111*, 8006.
- Andreoni, W. *Phys. Rev. B* **1992**, *45*, 4203.
- Balasubramanian, K. *Chem. Phys. Lett.* **1988**, *159*, 71.
- Balasubramanian, K. *Chem. Rev.* **1990**, *90*, 93.
- Balasubramanian, K. *Chem. Rev.* **1989**, *89*, 1801.
- Meier, U.; Peyerimhoff, S. D.; Grien, F. *Chem. Phys.* **1991**, *150*, 331.
- Liao, M. Z.; Dai, D.; Balasubramanian, K. *Chem. Phys. Lett.* **1995**, *239*, 124.
- Feng P. Y.; Balasubramanian, K. *Chem. Phys. Lett.* **1997**, *265*, 547.
- Feng P. Y.; Balasubramanian, K. *Chem. Phys. Lett.* **1999**, *301*, 458.
- Pacios, L. F.; Christiansen, P. A. *J. Chem. Phys.* **1985**, *82*, 2664. Hurely, M. M.; Pacios, L. F.; Christiansen, P. A.; Ross, R. B.; Ermler, W. C. *J. Chem. Phys.* **1986**, *84*, 6840.

- (34) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.
- (35) Balasubramanian, K. *Chem. Phys. Lett.* **1986**, *127*, 324.
- (36) The major authors of ALHEMY II are: Liu, B.; Lengsfeld, B.; Yoshimine, M.
- (37) Balasubramanian, K. *J. Mol. Spectrosc.* **1987**, *121*, 465.
- (38) Basch, H. *Chem. Phys. Lett.* **1987**, *136*, 289.
- (39) Balasubramanian, K.; Sumathi, K.; Dingguo, D. *J. Chem. Phys.* **1991**, *95*, 3494.
- (40) Balasubramanian, K.; Feng P. Y. *Chem. Phys. Lett.* **1988**, *146*, 155.
- (41) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.
- (42) Moore, C. E. *Tables of Atomic Energy Levels*; U.S. National Institute of Standards and Technology, Circular 467, 1971; Vol. I–III.